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Hydrochemical and geophysical appraisal for effects of Gadoon Amazai Industrial Estate on water resources, Swabi District, Pakistan

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ABSTRACT

Pakistan is facing the serious threat of reduced availability of clean drinking water due to its growing population, industrialization and urbanization. National water demand is stressing subsurface aquifers. The present study integrated hydrochemical and geophysical tools to identify contamination associated with industrial effluents from Gadoon Amazai Industrial Estate into local water resources. Seventy water samples were taken from surface and subsurface water resources, and forty Vertical Electrical Soundings were acquired using Schlumberger electrode configuration. The results of hydrochemical tests revealed values for Ca^{2+}, K^{1+}, Mg^{2+}, Na^{1+} remained within WHO limits. As^{3+} (31%), Cd^{2+} (58%), Fe^{2+} (57%), Pb^{2+} (41%), Hg^{2+} (95%) and Zn^{2+} (2.8%) were exceeding the WHO permissible limits. pH indicated the nature an acidic nature for both surface and groundwater. 84.29% samples have values less than 7.7. Electrical conductivity, turbidity and total dissolved solids also exceed the permissible limits. Statistics of microbial analysis revealed that 61% of the samples of groundwater contain coliform. VES points correlated with boreholes revealed four discrete subsurface layers namely intermixed clay with gravels, massive clay, boulders and dry boulders. Aquifer thickness map at depth of 30m shows that the unconfined aquifer is thick in the northwest and southeast. These maps further reveal that in the north eastern part of the study area there is a thick layer of clay, while in the west there is a clay starved zone, having gravels and boulders near the surface, which may cause infiltration of industrial contaminants into groundwater. Results of the hydrochemical analysis and vertical electrical soundings reveal that the unconfined aquifer as well as surface water is contaminated and hazardous for drinking and agricultural uses. The present study will be important for the local community and government as it highlights the surface as well as surface contamination in the vicinity of Gadoon Amazai Industrial Estate.

Keywords: Coliforms; Gadoon Amazai Industrial Estate; Heavy metals; Industrial effluents; Unconfined aquifers; Vertical electrical sounding

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1. Introduction

Fresh, clean water is an indispensable natural resource for sustainable development of humans and the maintenance of ecological systems. Rising populations globally, especially in the vicinity of economic zones, are deteriorating the quality of water resources, and leading to water scarcity challenges [1]. The past four decades have seen an increase in global industrialization, with increasing effluents discharged into the aquatic systems [2]. High quantities of dissolved and suspended particles, alongside toxic trace elements, from industrial effluents, are having disastrous effects on freshwater and associated vegetation [3,4].

Anthropogenic and geologic sources are both contributing to freshwater contaminations; anthropogenic activities are playing a dominant role, with evidence found through trace elements concentration, which are above the permissible maximum limits established by the World Health Organization. Industries are engines of socio-economic development for increasing populations, but without regulations and treatment, their effluent discharge is hazardous to freshwater resources [5].

Trace elements from industrial processes introduce chronic toxicity into ecosystems that humans depend on for food and water [6,7]. Ingestion of toxic and heavy metals from freshwater sources by humans and animal life leads to several common diseases, that is, diarrhoea, anaemia, nausea, kidney damage, abdominal pain, salivation and anorexia [8,9]. Toxic heavy metals from freshwater sources also present high carcinogenic potential, with continuous exposure being dubbed a front-runner fatal health hazard [10,11].

In Pakistan, effluents are released into the surrounding areas without proper treatment damaging human and animal life [7]. About 20% of the country's population has access to quality drinking water, whereas the remaining 80% of the population is consuming unsafe drinking water due to the lack of safe and healthy freshwater resources [3]. Close to half the country's population suffers from diarrheal cases each year. National statistics from healthcare units showed more than eighty thousand cases related to waterborne diseases only in Rawalpindi, one of Pakistan's major secondary cities. Between 20% and 40% hospitals in Pakistan are filled with people suffering from waterborne illnesses [11], with diseases such as cholera, typhoid, dysentery, hepatitis, giardiasis, and cryptosporidiosis, and guinea worm infections being responsible for 33% of national deaths [12].

Subsurface water quality also provides relevant information on several fronts, namely: the geologic history of rocks, identification of sources of groundwater recharge, subsurface movement of water, its contaminants, and their storage and freshwater use potential [13]. The hydrology and geochemistry of waters have been discussed in the previous work [14–16]. Specifically, hydrochemical analysis of groundwater helps establish the suitability of freshwater for various economic and ecosystem purposes [5,6].

The main groundwater reservoirs of Khyber Pakhtunkhwa province of Pakistan are the alluvial plains and valleys in intermountain basins of tectonic origin. Unconsolidated alluvial deposits have filled the basins, which have the coarse-grained stratigraphy. Most of these unconfined aquifers represent coarse-grained formations. The vulnerability of the aquifers is affected by hydraulic characteristics of the water-bearing layers, that is, transmissivity, specific yield, or storage coefficient, which directly depend on the nature or type of aquifer. The discharge from the aquifer is also related to hydraulic characteristics of the aquifer. The number of wells that can be used to extract water from these aquifers depends on recharge and discharge conditions. Ultimately, the hydrochemistry of the surface and subsurface water determines their suitability for domestic, agricultural and industrial use [6,16].

Geophysical resistivity methods, especially electrical resistivity methods, are appropriately used to calculate the thickness and electrical nature of these formations; these methods provide useful information on groundwater potential [17–21]. Vertical electrical sounding (VES) is the most widely used electrical resistivity method to decode subsurface geoelectrical units for various geotechnical purposes, such as groundwater exploration, which is done by citing a borehole site, determining depth to bedrock, aquifer system, suitable site of a landfill, to determine the extent of leachate contamination at the landfill site, estimating hydraulic conductivity and natural recharge [15,17,18]. The objective of VES is to infer the variation of resistivity with depth below a given point and to correlate it with available geological information, thereby inferring groundwater depth.

The present study assesses the effect of Gadoon Amazai Industrial Estate (GAIE) on groundwater and surrounding environment. The population in the area is suffering from various waterborne diseases. The study investigates the aquifer thickness, type, quality of the water inside GAIE and its surrounding areas. This is achieved by integration of borehole geology, resistivity and hydrochemical analysis. The geophysical study involved the generation of subsurface cross-sections, aquifer thickness maps and aquifer vulnerability assessment. Whereas hydrochemical studies make use of trace elements, physicochemical and microbial analyses to estimate the contribution of GAIE in contaminating local water systems, both for surface and subsurface water systems. The present study gives new insights into the growing deterioration in quantity and quality of groundwater in the area, highlighting the need for more stringent monitoring and regulation.

2. Methodology

2.1. Study area

The area of study lies between latitudes 72°24′30″ N to 72°43′30″ and longitude 33°56′30″ E to 34°18′00″ E (Fig. 1). The study area comprises a mountainous area in the North and an alluvium Gadoon plain in the south. The plain covers an area of about 48 km^2 and is part of District Swabi. The catchment area covers 155 km^2. The Gadoon plain is bordered by Peshawar Vale in the south, and by Totali area in the west. Its catchment area stretches to the catchment of Chamla River in the north, and a mountain range separates it from Tarbela reservoir in the east (Fig. 2) [22].

The Gadoon plain is filled with alluvium consisting of flood deposits over most of the plain, with alluvial fans in the foothills of the mountains. The topography is moderate to steep. The main streams of the area include Sargari

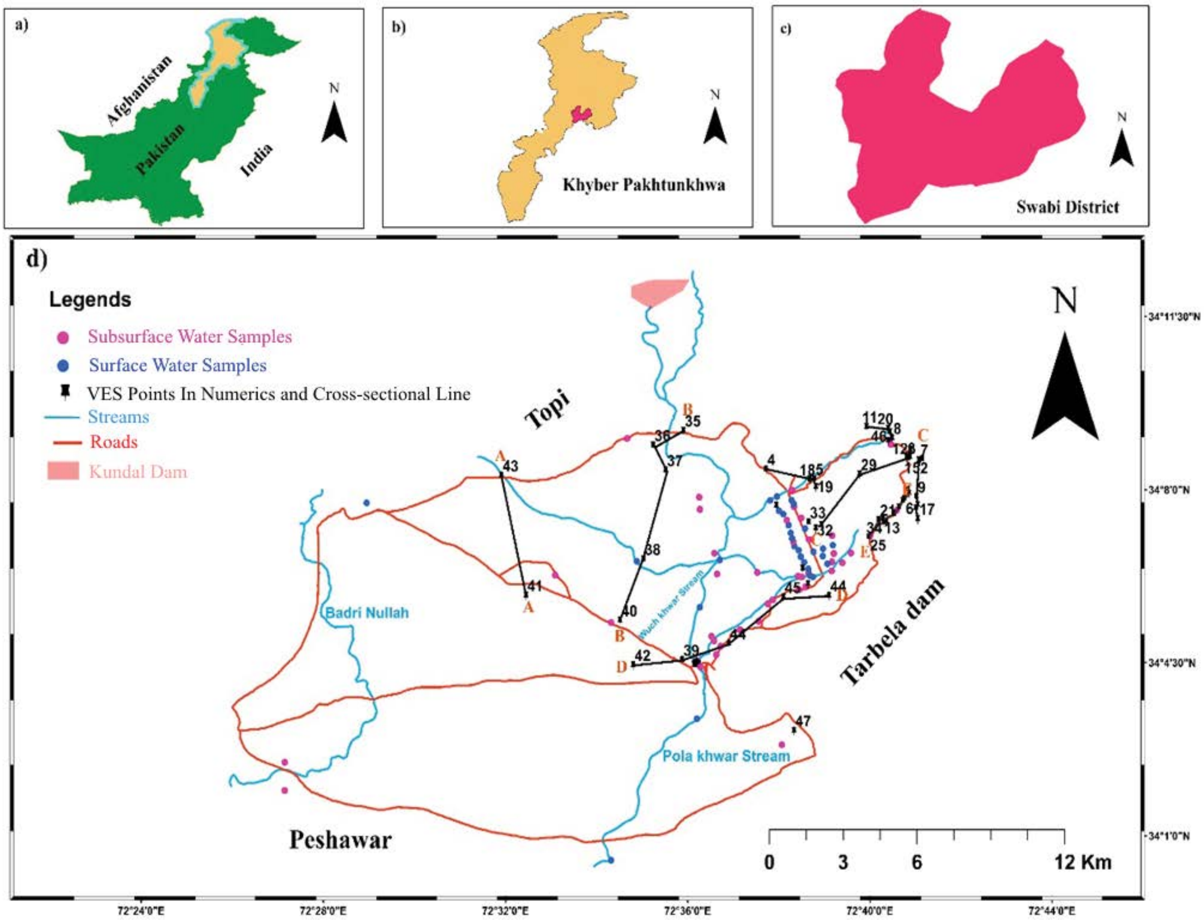

Fig. 1. GIS base map of the area water sample locations, VES points, dam and roads.

Khwar, Badgai Khwar, Gajai Khwar, Jammu Khwar, Wuch Khwar, and Polah Khwar. All the streams join and leave the area as one river, the Kundal Khwar, which eventually discharges into the Indus. The Gadoon plain is underlain by quaternary alluvial deposits of clay, silt, gravel, and boulders in the foreland area. The deposits are fan-shaped and consist of angular to sub-angular coarse material intermixed with clay [22]. The plain consists dominantly of the industrial zone, with untreated wastes discharged into the Polah Khwar and Wuch Khwar.

The study area climate is described as sub-humid subtropical continental lowland type. The average annual rainfall in Tarbela is 868 mm; maximum precipitation is in the summer period. The precipitation in winter is of long duration and low intensity, whereas the precipitation in summers comes in short showers with high intensity, highlighting their monsoon characteristics. It is assumed that the rainfall in the catchment area is 20% higher, that is, 1,040 mm. The mean monthly temperature varies from 12.2°C in January to 34.8°C in June [22].

2.2. Hydrochemical data

Sampling was done randomly at seventy stations (Fig. 1). Thirty-four samples were collected directly from effluent flow at industrial outlets. Thirty-six groundwater samples taken from tube wells, hand pumps, industrial and residential bores. Two samples from each station were taken for physiochemical and microbiological analyses. Both samples were preserved in 250 mL capacity bottles. For the study purposes, polystyrene bottles were used. Bottles were washed and rinsed with distilled water and filled with surface/subsurface water. The water samples were stored in ice and were immediately brought to the laboratory for physiochemical and microbiological analyses [23].

Hydrochemical characteristics included general physicochemical properties, such as pH, electrical conductivity (EC), total dissolved solids (TDS) and total hardness, and microbiological parameters included coliforms testing, which were quantified using standards. Cations like Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, As^+, Zn^+, Pb^+, Hg^+ and Cd^+ were determined with the help of atomic absorption spectrometry at the Instrumental Lab, COMSATS University Islamabad, Abbottabad Campus. All analyses were preceded keeping in view the standard procedure.

2.3. Vertical electrical sounding

1D Resistivity survey was carried out using depth sounding method, that is, VES. Forty VES soundings were

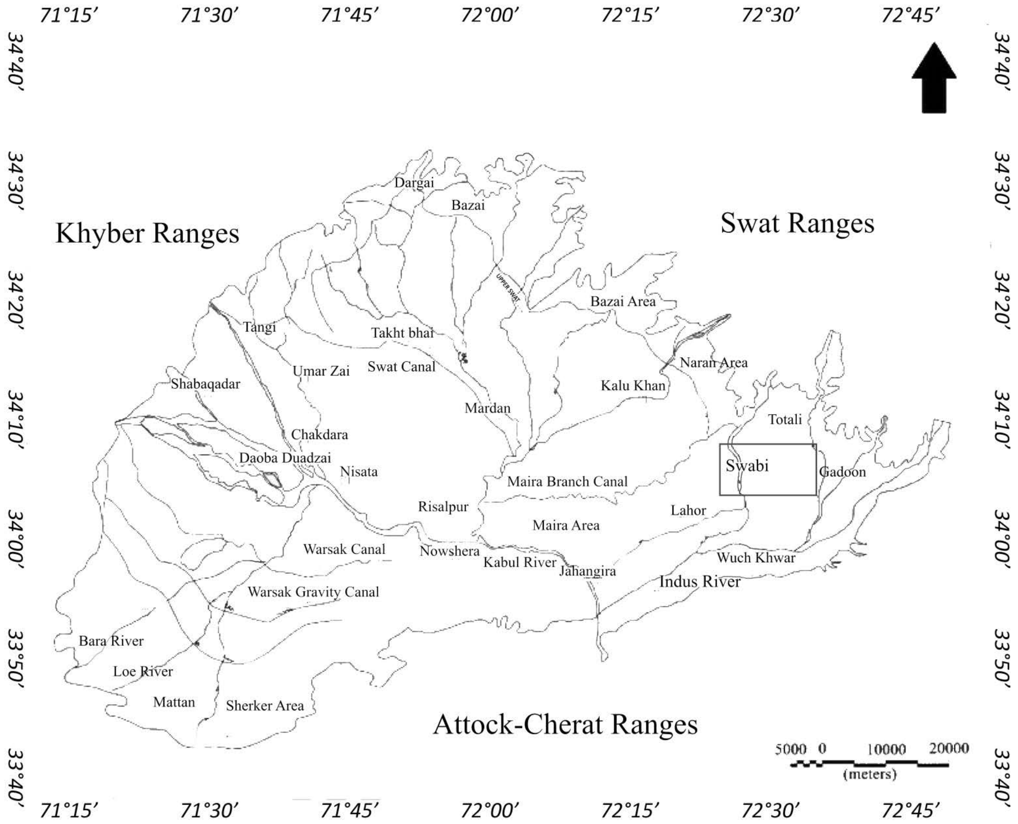

Fig. 2. Physiography of the study area [18,19].

carried out using Schlumberger electrode configuration, as Schlumberger configuration is economical, takes less time to deploy and give better resolution than other configurations. The instrument used for the acquisition of VES was a DDC-8 Resistivity 1D meter. The principle of Schlumberger configuration is to keep the distance between potential electrodes constant and increase the distance between current electrodes. The data acquisition was performed with different AB/2 spacing ranging from 10 to 400 m, according to change in resistivity values in the subsurface. Greater the distance between the current electrodes, the deeper is the investigation [24–26]. VES determines the resistivity distribution as a proxy of the subsurface setup. The resistivity depends on lithology as well as the water content in the aquifer [25,26]. The measured apparent resistivity data is digitized and inversion is done using IPI2WIN software [27] to determine the depth and thickness of the subsurface layers.

2.4. Microbiological analysis of subsurface water samples

The subsurface water samples were tested for coliforms. For the microbiological analysis, samples were transferred to the lab immediately after collection, and were kept in ice until the analysis started [10]. Bacteria were identified by using membrane filtration (MF) technique. The bacterial count was analysed using Eosin Methylene Blue (EMB) Agar nutrient as a medium. EMB agar is selective media for growth of Gram-Negative bacteria and is differential for fecal coliform (*E. coli*) bacteria. The total coliforms and *E. coli* were determined simultaneously using selective media. The petri-dishes were incubated at 37°C for 24 h in a bacteriological incubator and counted for bacterial colonies. The obtained results were compared with World Health Organization [11] drinking water standards.

3. Results and discussion

3.1. Heavy metal analysis

3.1.1. Potassium (K)

K for surface water ranges between 3.07–31.65 mg/L (Table 1). K for groundwater ranges between 0.969–11.96 mg/L (Table 2). The K-content of all the surface and subsurface samples in the study are lower than the permissible limit of 100 mg/L defined by [11]. The primary reason for this is geogenic, as the clay content is less. Previous studies have concluded that soils that have the maximum ability to retain K are distributed in granitic areas [28]. In the study area, granite is not found.

3.1.2. Sodium (Na)

Na for surface water samples ranges between 4.754–53.55 mg/L (Table 1). Na for groundwater samples ranges between 3.97–41.25 mg/L (Table 2). The Na content of all the above samples in the study is lower than the permissible limit of 200 mg/L defined by [11].

Table 1
Results of hydrochemical tests heavy metals of surface water (SW) samples from GAIE, District Swabi, Pakistan

Sample ID	As	K	Na	Ca	Mg	Fe	Zn	Cd	Pb	Hg
1	10.8	15.2	24.0	37.0	21.7	12.9	1.3	0.5	0.0	9.1
2	12.4	9.7	12.1	55.5	22.1	7.3	0.7	0.1	0.0	3.3
3	10.3	10.4	13.7	46.5	21.7	5.1	0.6	0.1	0.0	1.9
4	10.3	13.1	22.1	43.7	21.8	8.4	0.5	0.1	0.0	0.7
5	6.5	8.6	30.9	1.8	9.7	11.0	0.5	0.0	0.0	0.4
6	8.5	4.7	10.3	60.1	19.4	19.4	0.3	0.0	0.0	0.0
7	5.5	10.1	13.7	52.3	22.9	6.7	0.5	0.0	0.0	1.2
8	0.0	9.8	14.9	44.2	20.4	5.8	0.4	0.0	0.0	1.4
9	35.1	11.2	24.1	13.6	13.0	6.3	0.4	0.0	0.0	1.8
10	0.0	6.8	11.8	47.2	20.1	0.0	0.3	0.0	0.0	0.0
11	0.0	13.3	12.6	46.9	24.7	1.3	0.5	0.0	0.0	1.0
12	0.0	12.7	12.7	46.2	24.2	1.2	0.4	0.0	0.0	1.6
13	0.0	9.2	11.8	47.8	23.3	5.8	0.3	0.0	0.0	1.0
14	0.0	10.9	28.5	53.5	28.5	7.5	0.5	0.0	0.0	0.0
15	0.0	10.8	14.0	51.9	28.2	2.9	0.4	0.0	0.0	1.4
16	0.0	3.5	12.3	89.5	34.9	3.6	0.4	0.0	0.0	0.4
17	0.0	4.3	14.0	94.6	44.6	4.1	0.4	0.0	0.0	1.0
18	0.0	7.4	13.6	65.0	36.5	5.0	0.4	0.0	0.0	2.4
19	0.0	5.2	10.2	46.6	22.4	3.1	0.4	0.0	0.0	0.6
20	0.0	11.1	26.2	31.3	18.1	0.0	0.3	0.0	0.0	3.1
21	0.0	4.7	12.4	66.8	26.4	0.0	0.2	0.0	0.0	2.2
22	0.0	6.1	8.2	59.3	27.7	3.3	0.2	0.0	0.0	1.4
23	0.0	3.8	16.8	34.8	9.7	0.2	0.7	0.2	0.8	3.1
24	0.0	3.2	15.1	35.7	0.1	0.2	0.9	0.2	0.8	2.2
25	0.0	3.1	15.5	48.6	9.3	0.2	0.7	0.2	0.7	3.6
26	0.0	3.4	15.1	56.8	9.3	0.2	0.6	0.2	0.9	2.3
27	0.0	3.8	5.2	42.0	6.9	0.3	0.6	0.2	0.9	2.2
28	0.0	3.7	4.8	47.4	7.0	0.2	0.7	0.2	1.0	2.2
29	2.9	31.7	44.1	80.6	15.5	0.1	1.0	0.2	1.0	2.5
30	0.0	30.1	5.1	59.1	7.7	0.4	1.4	0.4	3.4	1.3
31	0.0	12.1	51.6	30.2	8.8	0.6	1.1	0.2	0.7	1.1
32	2.4	15.7	25.8	39.1	11.7	0.3	1.0	0.2	0.3	1.0
33	0.0	31.7	53.6	52.1	12.9	1.0	1.2	0.5	0.7	1.2
34	0.0	30.5	15.3	94.0	9.6	0.1	0.8	0.2	1.0	0.8
Min.	0.0	3.1	4.8	1.8	0.1	0.0	0.2	0.0	0.0	0.0
Max.	35.1	31.7	53.6	94.6	44.6	19.4	1.4	0.5	3.4	9.1
Mean	0.0	10.9	18.3	50.6	18.9	3.7	0.6	0.1	0.4	1.7
Std	6.9	8.3	11.9	19.5	9.7	4.4	0.3	0.2	0.7	1.6
WHO standard	0.01	100	200	100	50	0.3	3.	0.005	0.01	0.006

All units are in (mg/L).

3.1.3. Arsenic (As)

As in surface water samples ranges between 0–35 mg/L (Table 1). As in groundwater samples range between 0–9.10 mg/L (Table 2). The As content in samples is exceeding the permissible limit 0–0.1 mg/L defined by [11]. Free form of As can be chemically generated by reduction of arsenic trioxide As_2O_3 with charcoal. As_2O_3 is produced as a by-product of metal smelting operations associated with many steel mills in the study area; hence the most probable cause of As in groundwater is the industrial zone. In addition, geothermal intrusions also increase As in groundwater, but these conditions are usually localized [10,12,29].

3.1.4. Calcium (Ca)

Ca for surface water samples ranges between 1.84–94.64 mg/L (Table 1). Ca for groundwater samples ranges between 0–347.56 mg/L (Table 2). The Ca content of

Table 2
Results of hydrochemical tests heavy metals of subsurface water (SSW) samples from GAIE, District Swabi, Pakistan

Sample ID	As	K	Na	Ca	Mg	Fe	Zn	Cd	Pb	Hg
1	9.102	2.86	9.475	64.89	18.06	21.59	0.42	0.04	0	2.10
2	7.2	2.72	10.8	81.65	23.37	11.06	3.79	0.02	0	2.08
3	5.67	2.86	10.67	90.45	24.17	33.2	0.71	0.02	0	1.46
4	2.3	3.38	10.57	48.83	19.63	2.313	0.28	0	0	1.37
5	0	2.96	9.84	0	19.25	2.101	0.36	0	0	0.95
6	0	3.08	9.86	56.57	18.85	6.185	0.24	0	0	0
7	0	3.13	10.09	54.77	18.78	9.138	0.21	0.01	0	0.75
8	0	3.13	12.26	62.89	28.58	3.279	0.31	0.01	0	0.17
9	0	2.04	9.423	61.62	22.52	10.68	0.51	0	0	1.09
10	0	10.05	13.55	54.29	27.53	1.457	0.37	0	0	1.81
11	0	11.96	18.61	23.96	25.66	2.955	0.41	0	0	0.61
12	0	2.431	11.29	64.66	28.37	4.821	0.35	0	0	1.99
13	0	0.969	3.975	17.3	3.99	1.489	0.35	0	0	1.01
14	0	3.194	9.5	53.77	19.44	0	0.22	0	0	1.78
15	0	3.132	9.047	66.11	18.54	0	0.29	0	0	1.46
16	6.24	2.464	11.29	53.66	17.88	0	0.20	0	0	1.71
17	0	2.028	10.3	57.18	16.31	0	0.27	0	0	1.53
18	0	1.026	7.244	31.99	5.144	0	0.20	0	0	1.68
19	5.91	2.215	24.94	73.17	13.11	0.041	7.76	0.76	1.37	13.5
20	3.69	1.319	20.49	38.98	10.06	0.171	1.34	0.52	0.77	3.96
21	4.5	6.62	23.3	49.02	12.83	0.153	1.16	0.27	0.74	4.54
22	0	2.898	11.54	28.05	8.04	0.141	0.61	0.2	0.78	3.33
23	1.45	3.162	9.782	40.01	7.65	0.167	0.49	0.22	0.52	2.07
24	5.9	3.178	13.23	37.86	9.46	0.148	0.87	0.24	0.55	3.7
25	1.51	3.212	10.69	40.53	8.44	0.095	0.90	0.23	0.55	3.05
26	0	3.49	41.25	42.36	12.04	0.234	0.67	0.25	0.55	1.94
27	2.13	3.878	10.37	31.69	6.97	0.249	0.77	0.20	0.72	1.99
28	0.19	3.599	15.45	50.47	9.41	0.089	1.82	0.18	0.6	2.2
29	0	2.896	18.74	58.84	2.34	0.122	1.07	0.22	0.60	1.31
30	0	2.334	11.23	347.56	6.99	0.212	1.05	0.22	0.83	3.27
31	0	2.994	24.69	43.49	11.44	0.232	0.61	0.19	0.73	2.75
32	0	2.062	13.25	37.68	10.06	0.171	0.75	0.18	1.00	2.88
33	0	2.987	18.84	38.58	12.8	0.157	0.65	0.20	0.99	2.47
34	0	2.53	23.18	90.93	11.46	0.094	0.8	0.19	1.19	3.71
35	0	6.055	13.65	47.54	12.47	0.201	0.78	0.24	1.32	3.13
36	0	1.909	13.896	86.9	11.16	0.264	1.07	0.23	0.98	4.24
Min.	0	0.969	3.975	0	2.345	0	0.20	0	0	0
Max.	9.1	12.0	41.3	347.6	28.6	33.2	7.8	0.8	1.4	13.6
Mean	1.5	3.4	14.1	59.1	14.8	3.1	0.9	0.1	0.4	2.4
Std	2.6	2.2	6.9	53.2	7.2	6.8	1.3	0.2	0.5	2.2
WHO standard	0.01	100	200	100	50	0.3	3	0.005	0.01	0.006

All units are in (mg/L).

groundwater samples are less than the permissible limit 100 mg/L defined by [11] in majority samples.

3.1.5. Magnesium (Mg)

Mg for surface water samples ranges between 0.133–44.6 mg/L (Table 1). Mg for groundwater samples ranges between 2.345–28.58 mg/L (Table 2). The Mg content of all the surface and groundwater samples is less than the permissible limit 50 mg/L defined by [11].

3.1.6. Iron (Fe)

Fe for surface water samples ranges between 0–19.37 mg/L (Table 1). Fe for groundwater samples ranges between 0–33.2 mg/L (Table 2). The Fe content of both surface and groundwater samples is higher than the permissible limit 0.3 mg/L defined by [11]. The high content of Fe may also be due to its nature, as it is easily absorbed in clays. Another contributory factor may be the presence of waste of steel mills waste.

3.1.7. Zinc (Zn)

Zn for surface water samples ranges between 0.17–4.696 mg/L (Table 1). Zn for groundwater water samples ranges between 0.205–3.0 mg/L (Table 2). The Zn content of 2.8% samples in the study is higher than the permissible limit 3 mg/L defined by [11].

3.1.8. Lead (Pb)

Pb for surface water samples ranges between 0–3.431 mg/L. Pb for groundwater samples ranges between 0–13.72 mg/L. The Pb content of all samples is higher than the permissible limit 0.001 mg/L defined by [11]. The sources of lead can be gasoline, paints, pigments from the paint industry and smelting of ores [12].

3.1.9. Cadmium (Cd)

Cd for surface water samples ranges between 0–0.541 mg/L. Cd for groundwater samples ranges between 0–0.769 mg/L. The Cd content of all samples in the study area is higher than the permissible limit 0.005 mg/L defined by [11]. Cd is found naturally in rocks and soils; and contributes to the water after its contact with groundwater/surface water. It is introduced by paints, pigments, plastic stabilizers, mining and smelting operations and other industrial operations, such as electroplating, fossil fuel, fertilizer, and sewage sludge disposal. Similar results are found in a previous study, confirming the environmental impact of GAIE [30].

3.1.10. Mercury (Hg)

Hg for surface water samples ranges between 0–9.116 mg/L. Hg for groundwater samples ranges between 0–13.59 mg/L. The Hg content of the acquired samples in the study area is higher than the permissible limit 0.006 mg/L defined by [11]. The results are comparable to previous studies in the same area, that is, 68.4% of samples exceed the guidelines for Hg [31]. The sources of Hg in groundwater samples include anthropogenic activities such as agriculture, municipal wastewater, mining, and discharges of industrial wastewater [32]. Long-term association of rock with water and presence of cinnabar HgS, gangue and clay minerals add Hg to water [33,34].

Exceeded limits of trace or heavy metals are due to the effluents of the industry including the paint industry, pharmaceuticals, plastic industry, and steel mills. The increased values of heavy metals can also be related to sediments and their weathering, which through recharge help the contaminants reach groundwater. Minor trace elements generally tend to be more concentrated in shales than in sandstones and carbonate rocks [35]. Alkaline effluent in an industrial zone is generated from the coating of paint to wheels; this effluent contains calcium chloride and heavy metals, while acidic effluent contains heavy metals like chromium, nickel, cadmium, lead, cadmium, etc., and high TDS [36,37].

3.2. Physicochemical analysis

3.2.1. pH

One of the most important water quality parameters is pH. Measurement of pH relates to the acidity or alkalinity of the water. In this study, the pH value for the surface water samples ranges between 4.739 and 9.523 (Table 3). The pH value for the groundwater samples ranges between 6.144 and 8.23 (Table 4). The drinking water analysis shows that the water is alkaline as most of the groundwater samples have values trending towards alkalinity and results are close to previous studies [31,33,34]. The surface water samples near the industrial zone are acidic.

3.2.2. Electrical conductivity

EC value for the surface water samples ranges between 4,106 and 4,000 us/cm (Table 3). EC value for the groundwater samples ranges between 925 and 313.13 us/cm (Table 4). The EC value for surface water samples exceeds the permissible limit; for groundwater the EC value is within the permissible limit. EC depends on TDS, known as ion concentration, which determines water quality. The highest EC value was found in the samples collected from GAIE; effluents containing soluble salts from local industries likely increased this concentration, resulting in the highest EC, as in a previous study [30]. The TDS is also exceeding permissible limits, highlighting that there are inorganic pollutants that entered into the surface water resources through industrial effluents [38].

3.2.3. Total dissolved solids

The TDS value for the surface water samples ranges between 31–2,000 mg/L (Table 3). The TDS value for the groundwater samples ranges between 35–1,020 mg/L (Table 4). The value of TDS for surface water samples exceeds the permissible limit (1,000 mg/L by WHO). These results closely correlate with the earlier reports on TDS values of the industrial discharge from different areas of Pakistan [16,30,39]. In comparison to groundwater samples, surface water samples have higher TDS values, indicating the mixing of industrial and residential water. This may cause a change in taste of water and lead to gastrointestinal irritation and physiological reactions. Effluents with high TDS values may also cause salinity problems, if discharged to irrigation water. [40]

3.2.4. Hardness

The hardness for surface water samples ranges between 35 and 75.94 mg/L (Table 3). The hardness for groundwater samples ranges between 33.54 and 354.30 mg/L (Table 4). The hardness for surface and groundwater samples exceeds the permissible limit (50 mg/L) [11].

Table 3
Results of physicochemical tests of surface water samples from GAIE, District Swabi, Pakistan

Sample ID	pH	EC (µS/cm)	TDS (mg/L)	Hardness (mg/L)	Turbidity (NTU)
1.0	6.6	127.0	31.0	125.0	57.1
2.0	6.6	106.0	56.0	145.2	14.2
3.0	6.6	186.0	91.0	134.7	2.1
4.0	6.8	187.0	92.0	132.4	20.2
5.0	9.5	234.0	66.0	41.4	28.3
6.0	6.6	126.0	83.0	138.7	1.7
7.0	6.8	164.0	91.0	145.5	2.7
8.0	7.5	166.0	108.0	127.0	8.9
9.0	8.8	229.0	78.0	66.6	21.2
10.0	6.7	151.0	81.0	129.0	3.0
11.0	6.7	157.0	78.0	147.4	0.9
12.0	6.7	159.0	63.0	144.7	3.4
13.0	6.6	146.0	65.0	142.6	0.8
14.0	6.7	229.0	95.0	169.4	0.4
15.0	6.5	174.0	90.0	166.4	1.2
16.0	7.2	157.0	96.0	231.5	0.0
17.0	7.1	172.0	89.0	275.9	0.0
18.0	6.7	173.0	72.0	213.5	0.1
19.0	7.8	124.0	64.0	137.7	0.3
20.0	4.7	204.0	68.0	104.9	117.0
21.0	7.2	148.0	72.0	174.0	0.8
22.0	8.0	136.0	87.0	172.0	0.5
23.0	7.1	445.0	218.0	44.2	0.1
24.0	7.3	459.0	230.0	35.6	0.7
25.0	7.6	461.0	232.0	57.6	0.3
26.0	7.9	376.0	180.0	65.9	0.8
27.0	7.6	221.0	107.0	48.7	17.3
28.0	7.2	272.0	136.0	54.1	5.1
29.0	7.5	2,154.0	120.0	95.9	0.8
30.0	7.2	265.0	135.0	66.6	5.4
31.0	6.9	3,436.0	122.0	38.8	18.5
32.0	7.5	1,255.0	630.0	50.5	11.2
33.0	6.7	4,000.0	113.0	64.7	44.1
34.0	7.6	443.0	221.0	103.4	0.6
Min.	4.7	106.0	31.0	35.6	0.0
Max.	9.5	4,000.0	630.0	275.9	117.0
Mean	7.1	513.0	122.4	117.4	11.5
Std	0.8	902.1	103.5	59.4	22.8
WHO standard	6.5–8.5	1,000.0	1,000.0	50.0 up	5 NTU

3.2.5. Turbidity

The concentration of turbidity for the surface water samples varies between 0.03 to 27.6 NTU (Table 3). The turbidity value for the groundwater samples ranges between 0 to 354.30 NTU (Table 4). The turbidity for surface and groundwater samples exceeds the permissible limit (5 NTU by WHO). Turbid water is more vulnerable to microbiological contamination as pathogens attach themselves to the suspended particles in turbid drinking water. These suspended particles then shield pathogens from disinfectants and interfere with the disinfection process. Higher temperature influences pH, conductivity, dissolved gases, and alkalinity; this can lead to poor water quality [40].

The comparison of analysis of water resources for drinking purposes showed that the physical parameters of sampling sites, such as bore-wells and hand pumps were not according to the recommendations of Pakistan Environment Protection Act, 1997 and WHO. Turbidity was above permissible limits in the samples collected from hand

Table 4
Results of physicochemical and microbiological tests of subsurface water groundwater samples from GAIE, District Swabi, Pakistan

Sample ID	pH	EC (μS/cm)	TDS (mg/L)	Hardness (mg/L)	Microbial CFU/100 mL		Turbidity (NTU)
					TPC (Total plate count)	Coliforms	
1	7.218	136	76	138	5	0	0.1
2	6.974	126	66	176	23	0	0.5
3	7.222	128	149	188	3	0	0.1
4	7.583	120	67	128	75	0	0.03
5	7.219	121	62	77	170	27	0.03
6	7.438	119	60	133	681	1	0.05
7	7.435	118	73	131	340	60	1.41
8	7.408	136	72	179	490	285	0.1
9	7.192	119	114	153	18	1	0.04
10	6.144	177	82	166	155	28	8.48
11	7.112	194	91	128	0	0	1.6
12	7.365	133	35	179	416	175	1.36
13	6.965	68	63	33	235	60	15.48
14	7.295	117	65	132	100	580	2
15	7.532	120	100	141	210	10	0.03
16	6.465	129	63	126	300	0	0.05
17	6.864	123	42	123	70	10	0.1
18	6.951	80	77	52	3	1	0.12
19	7.42	925	470	86	0	0	1
20	7.73	505	258	48	3	26	0.18
21	7.79	762	375	61	0	0	0.45
22	8.23	283	138	35	0	0	0
23	7.41	270	140	47	0	172	0
24	7.89	407	201	47	0	141	1.01
25	7.42	351	176	48	6	0	1.18
26	7.89	835	411	54	25	80	0.01
27	7.64	250	127	38	0	26	27.6
28	7.58	540	265	59	0	0	1.19
29	7.28	459	230	60	0	28	0
30	7.55	461	232	354	1	1	2.1
31	7.57	221	107	54	0	0	2.38
32	7.24	445	136	47	0	2	0
33	7.54	550	1,020	51	0	53	0.25
34	7.58	572	221	102	0	1	0.18
35	7.5	684	341	59	0	79	0
36	7.42	489	244	97	0	164	0.79
Min.	6.144	68	35	33	0	0	0
Max.	8.2	925.0	1,020.0	354.0	681.0	580.0	27.6
Mean	7.4	313.1	179.1	103.6	92.5	55.9	1.9
Std	0.4	236.6	181.6	65.2	164.7	112.0	5.2
WHO standard	6.5–8.5	1,000	1,000	50	0	0	5 NTU

pumps, bore wells, and dug well. The EC and contents of total solids, TDS, and total suspended solids were above the WHO recommendations in the samples collected from hand pumps, bore wells, and dug wells. Factors including pH, conductivity, dissolved gases, and low alkalinity are affecting the quality of drinking water [11,40,41].

3.3. Microbiological analysis

There are four main indicators of microbial safety of drinking water. Heterotrophic plate counts (HPC), total coliform (TC), fecal coliform (FC) and *Escherichia coli* (*E.coli*). The heterotrophic group of bacteria encompasses a broad range of bacteria that uses organic carbon sources to grow.

Colony counts of HPC provides an indication of the general load of aerobic and facultative anaerobic bacteria of a water sample. This indicator is also known as standard plate count (SPC), aerobic plate count (APC) and total plate count (TPC). The total coliform group is a large collection of bacteria that are mostly found in the environment. The fecal coliform group is a subset of the total coliform group that principally exists in feces, while *E. coli* belongs to the fecal coliform group and is the only member that is specific to the intestinal tract of warm-blooded animals [42].

The results of microbiological analysis of subsurface water samples show that most of the samples have microbial content far more than the permissible limits (0 CFU) for drinking water, according to WHO standards. Drinking water should be free from TC and FC. Table 4 shows a maximum value is 580 CFU from the study samples. The groundwater samples near industrial zones have more coliforms. The presence of microbial content is associated with residential areas in GAIE and its vicinity. The drainage from residential areas is mixing with the industrial effluents, which are then used for agriculture. This is a significant regulatory negligence, and may cause damage to crops and human health. In general, low pH values obtained in the analysed samples are due to the high level of CO_2 in the water, which may consequently affect the bacterial count [43–47].

3.4. Vertical electrical sounding

Forty soundings (Fig. 1) have been interpreted using inversion technique. The comparison of apparent resistivity curves obtained from the field shows that the maximum parts of study area relate to H-type curves (§1 > §2 < §3) (Figs. 3 and 4). The identified lithology is divided into four electrical units; clay with gravels and boulders, gravel, boulders, dry boulders. The shallowest layer contains clay with gravel and boulders causing the upper part of the aquifer to be permeable thus allowing the infiltration of

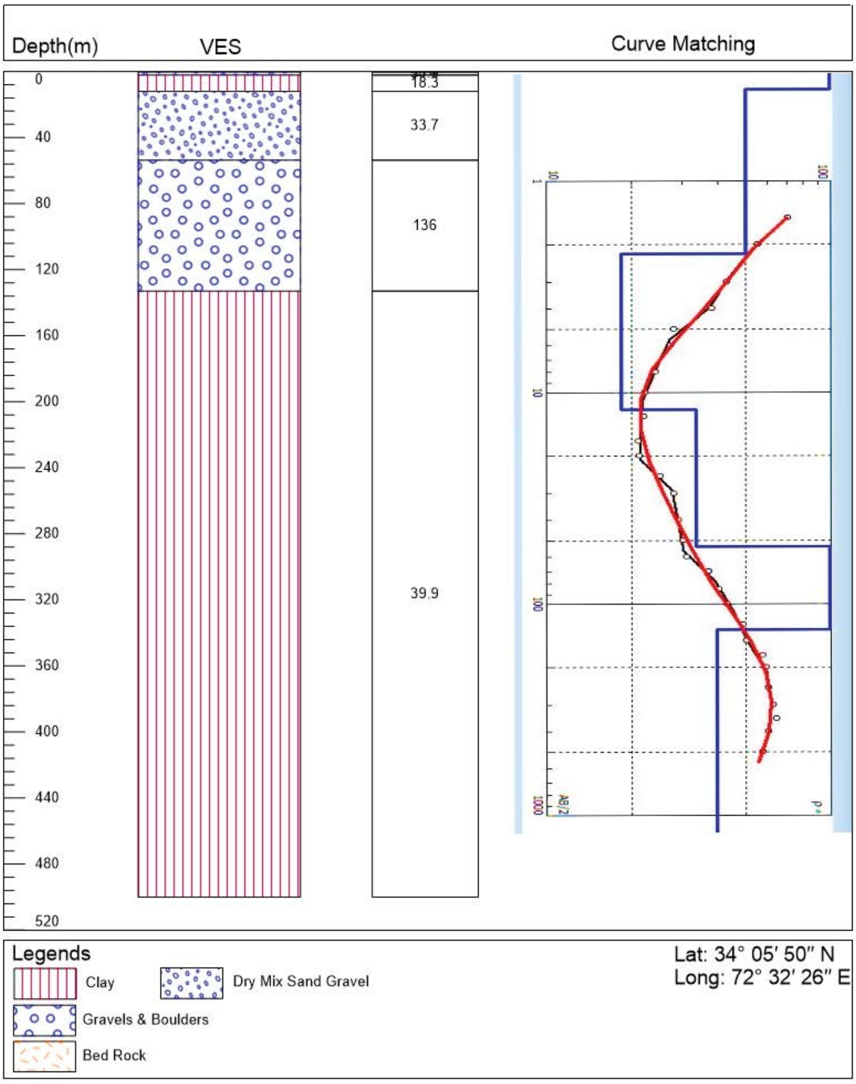

Fig. 3. Inversion of VES data at point 33 showing H-Type curve.

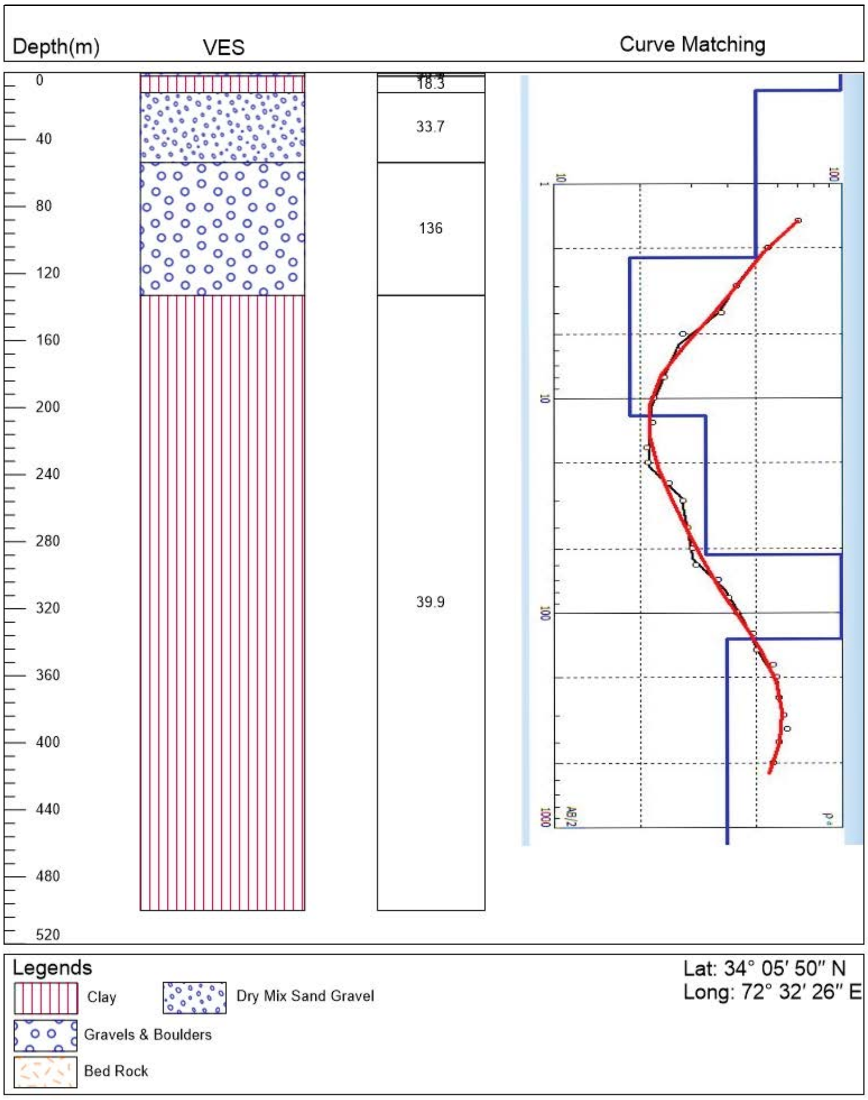

Fig. 4. Inversion of VES Data at point 45 shows the H-Type curve.

industrial effluents. VES data is converted to electrical units attributed to lithologies. Each litholog is then correlated to generate the cross-sections oriented in North-South and East-West directions. These cross-sections are used to determine the aquifer thickness and the nature of the aquifer.

The cross-section AA′ (Fig. 5) shows the thickening of gravel and boulder layers towards the south. Some clay patches are found, which can act as aquitard in some places, to retard the infiltration of surficial effluents [23]. Cross-section BB′ (Fig. 6) shows the thickening of the aquifer in the east. Thick clay patches (Fig. 5) of approximately 100 m thickness are also found. These clay patches are found, as a clay mound, which is visible in some cross-sections. The clay mound is also shown in a previous study, carried out further west of the current study area [48]. The clay layer above the aquifer is very thin; in VES interpretation, it is revealed as mixed lithology, that is, clay and dry boulders, which increases the vulnerability of shallow aquifers, due to permeability. Hydrochemical analysis revealed more contamination in shallow aquifers. In shallow aquifers, groundwater occurs in unconfined conditions [49,50].

3.5. Integration of VES and hydrochemical analysis

The VES dataset provides indirect measurements of the subsurface anomalies [9]. The availability of other datasets such as borehole logs, pumping data, and hydrochemical data can place strong constraints on the results of the VES dataset. In this study, the forty VES and four borehole datasets are correlated with hydrochemical analysis of the water samples collected from surface and subsurface water sources. The VES data interpretation, using Master curves, shows the shallow unconfined aquifers in the area. The low values identified by the resistivity data attribute to the dissolved impurities in identified aquifer system. These impurities infiltrate from surficial polluted channels into shallow aquifer system, which is unconfined in nature (Figs. 3 and 4).

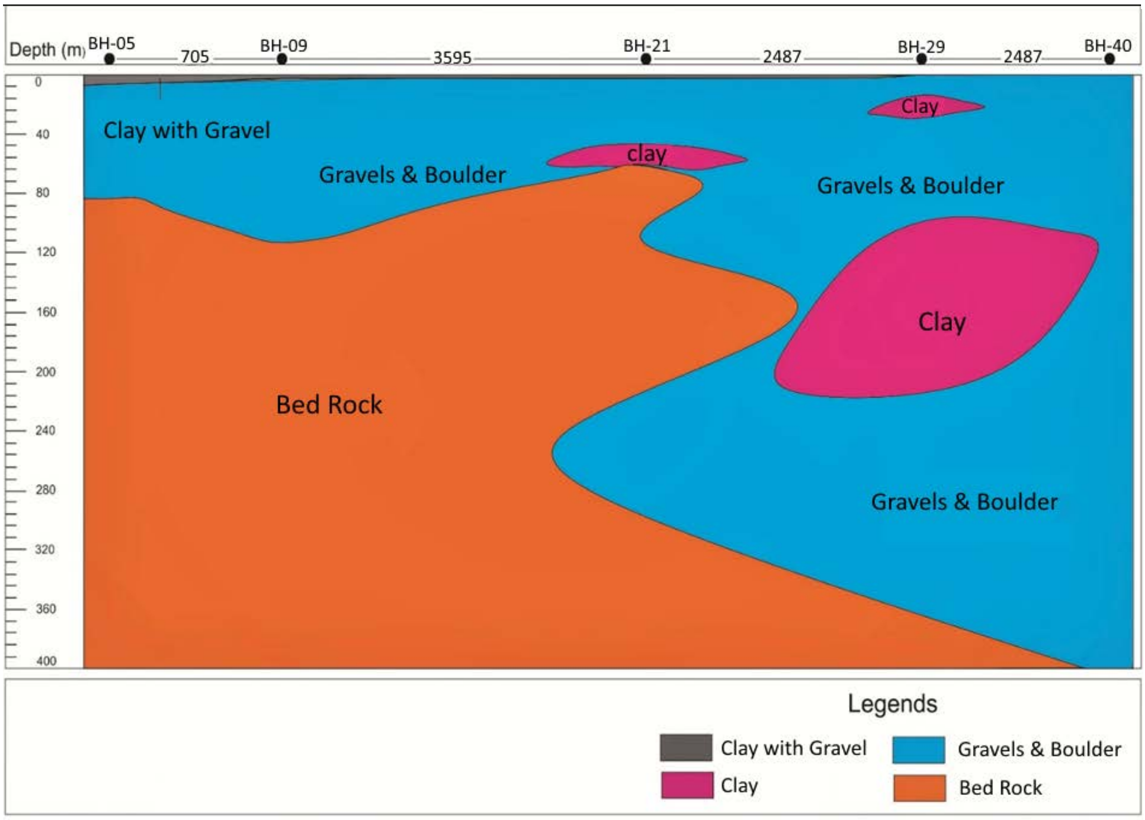

Fig. 5. Cross-section AA' from north to the south, using VES data.

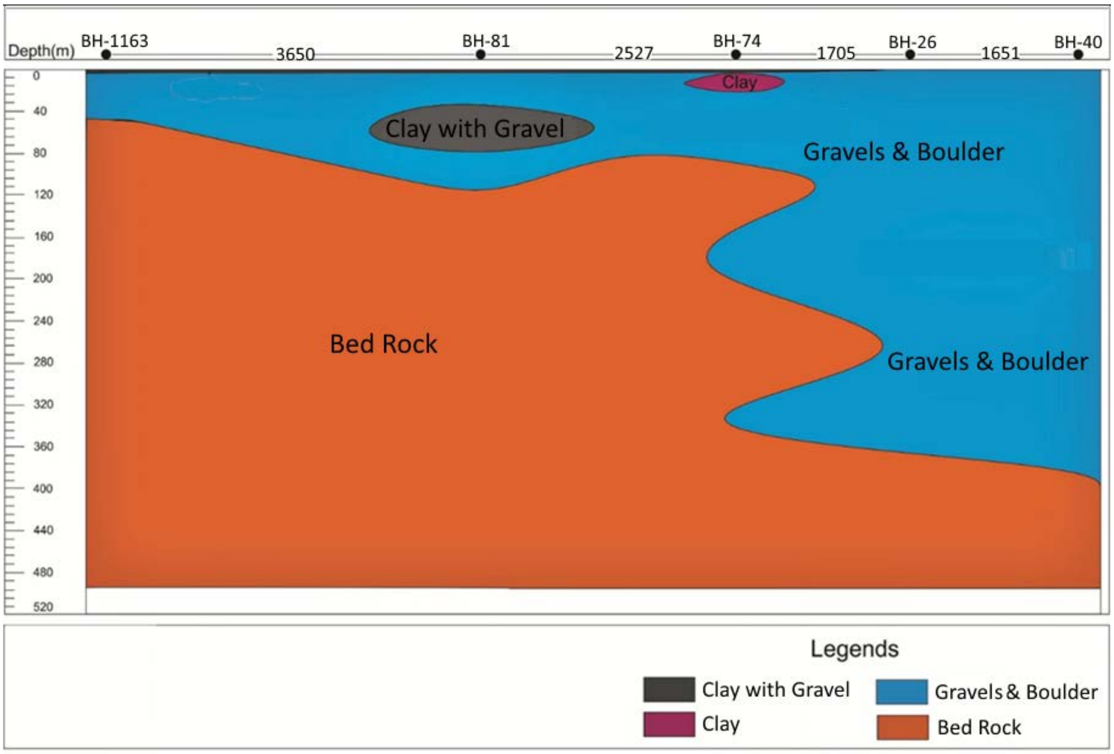

Fig. 6. Cross-section BB', from west to east of the area using VES data.

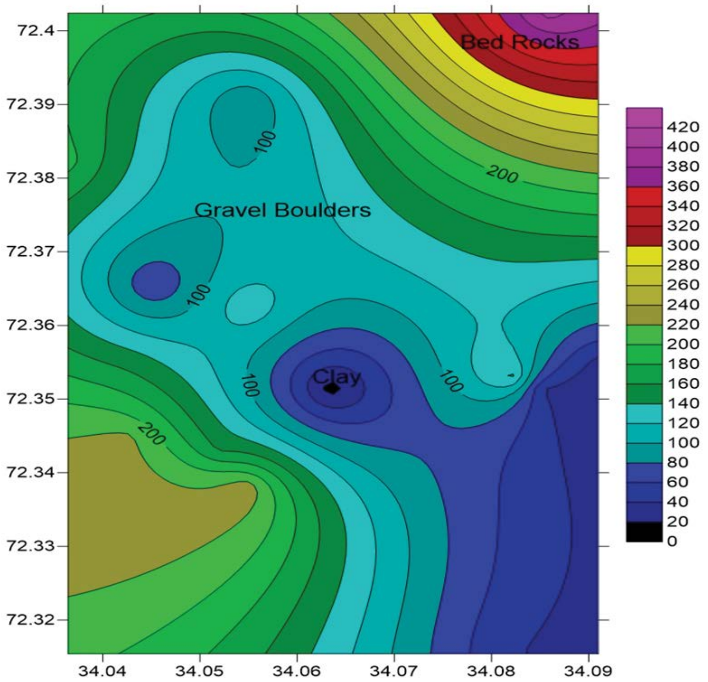

Fig. 7. Thickness map at 30 m depth.

The hydrochemical results show higher ECs are associated with impurities present in the water, due to their increased conductivity. The thickness map (Fig. 7) indicates clay starved zones towards the northwest and the southeast. The starved zones are defined as the zones that are dominated by coarser lithology with high permeability, which can transmit the surficial contaminants to the shallow subsurface aquifer. The hydrochemical analysis of water samples in these parts of the area also reveals higher EC and turbidity, as well as certain heavy metals (Hg, Cd, As, Ca, Fe, Zn, and Pb) for surface and groundwater samples. Additionally, Tables 1 and 2 are indicative of low water quality [23,51,52]. The data is analysed carefully and also constrained with the previous study in the western part of the area [43].

4. Conclusion

The integration of hydrochemical and geophysical data sets during the current study proved to be very useful. The chemical analysis of both surface and subsurface water samples revealed higher concentrations of Cd, Hg, Pb, Fe, As and Zn. The higher concentrations of these heavy metals were attributed to factories, specifically textile mills, paint industries and pharmaceuticals in GAIE. The physicochemical parameters revealed that concentrations of heavy metals in surface and subsurface water samples have decreased the pH. Furthermore, coliforms identified in the vicinity of industrial zones were mostly associated with the residential areas of the GAIE. The presence of *E. coli* in drinking water samples usually indicates recent faecal contamination, which means there is a greater risk that pathogens are present.

The geophysical studies identified the shallow unconfined aquifers that mostly comprised of gravel and boulders and were mostly located below 30 m depth. The low resistivity in VES (H-type curve) confirms the presence of heavy metals and TDS. It was further revealed that the protective clay cover thins out towards the southeast. The aquifer thickness increases towards the southwest of the area and these areas are vulnerable to surficial contamination.

The study revealed that the population inside and in the vicinity of GAIE is under serious threat due to the industrial effluents. It is recommended to treat the wastewater before dumping it into surrounding areas as this water is also used for agricultural purposes and is finding its way into the human food chain.

This study helped to analyse the results of hydrochemical analysis integrated with the geophysical studies, which has enhanced the accuracy of results that anthropogenic activities are degrading the groundwater resources in the area.

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Supplementary information

Table S1
Statistical analysis of physicochemical parameters from subsurface water and surface water samples

Parameters	WHO standard	SSW				SW			
		Min.	Max.	Mean	Std	Min.	Max.	Mean	Std
As (mg/L)	0.01	0	9.01	4.55	117	0	35.09	0	49.99
K (mg/L)	100	0.96	11.96	3.35	2.18	3.07	3,088	1,805.47	7,291.53
Na (mg/L)	200	3.97	41.25	14.06	6.89	4.75	53.55	18.27	11.86
Ca (mg/L)	100	0	347.56	59.09	53.27	1.84	94.64	50.63	19.54
Mg (mg/L)	50	2.34	28.58	14.80	7.16	0.13	44.6	18.85	9.73
Fe (mg/L)	0.3	0	33.2	2.84	7.00	0	19.37	3.41	4.75
Zn (mg/L)	3	0.20	30,847	857.7	5141	0.17	1.442	0.59	0.32
Cd (mg/L)	0.005	0	0.769	0.12	0.174	0	0.541	0.10	0.15
Pb (mg/L)	0.01	0	1.372	0.68	1.49	0	3.431	0	1.57
Hg (mg/L)	0.006	0	13.59	2.43	6.97	0	9.116	1.71	1.65
pH	6.5–8.5	6.14	8.23	7.36	0.38	4.73	9.523	7.12	0.78
EC (µS/cm)	1,000	68	925	313.1	236.59	106	4,000	513	902.14
TDS (mg/L)	1,000	35	1,020	179.1	181.55	31	2,000	250.44	446.68
Hardness (mg/L)	50	33.54	354.30	104	65.13	35.59	275.94	117.39	59.39
Turbidity (NTU)	5 NTU	0	27.6	1.94	5.24	0.03	117	11.46	22.84