



## Evaluation of arsenic and other physico-chemical parameters of surface and ground water of Jamshoro, Pakistan

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### ABSTRACT

Arsenic contamination in water has caused severe health problems around the world. The purpose of this study was to evaluate the geological and anthropogenic aspects of As pollution in surface and groundwater resources of Jamshoro Sindh, Pakistan. Hydride generator atomic absorption spectrophotometry (HG-AAS) is employed for the determination of arsenic in water samples, with detection limit of  $0.02 \mu\text{g l}^{-1}$ . Arsenic concentrations in surface and underground water range from 3.0 to 50.0, and 13 to  $106 \mu\text{g l}^{-1}$ , respectively. In most of the water samples As levels exceeded the WHO provisional guideline values  $10 \mu\text{g l}^{-1}$ . The high level of As in under study area may be due to widespread water logging from Indus river irrigation system which causes high saturation of salts in this semi-arid region and lead to enrichment of As in shallow groundwater. Among the physico-chemical parameters, electrical conductivity,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{SO}_4^{2-}$  were found to be higher in surface and ground water, while elevated levels of  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  were detected only in ground water than WHO permissible limit. The high level of iron was observed in ground water, which is a possible source of As enrichment in the study area. The multivariate technique (cluster analysis) was used for the elucidation of high, medium and low As contaminated areas. It may be concluded that As originate from coal combustion at brick factories and power generation plants, and it was mobilized promotionally by the alkaline nature of the understudy groundwater samples.

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### 1. Introduction

Drinking water, in general, is derived from a variety of sources, depending on availability of surface water (rivers, lakes, reservoirs and ponds) and ground water (aquifers). The arsenic (As) is a toxic metalloid and the 20th most abundant element in the earth's crust. Arsenic is predominantly present in inorganic form ( $\text{As}^{3+}$  and  $\text{As}^{5+}$ ) in aquatic system with a minor amount of methyl and dimethyl arsenic compounds. Arsenic in the water is a serious natural calamity and a public health hazard, which originates from natural systems including, anthropogenic as well as geological sources [1–8].

The literature studies show that the arsenic in water poses the health hazards to humans, creates non-cancer effects such as hyper-

and hypo-pigmentation, keratosis, black foot disease, hypertension, cardiovascular diseases and diabetes, and also typical skin, lung and bladder cancers [9–15]. Inorganic arsenicals belong to group I carcinogens [16,17]. It is reported that about 60–100 million people in India and Bangladesh are currently at risk, due to arsenic-contaminated drinking waters [18–20].

High concentration of As was observed in the surface water and shallow zones of ground water of many countries like Bangladesh, India, Argentina, Mexico, Mongolia, Germany, Thailand, China, Chile, USA, Canada, Hungary, Romania and Vietnam [21–24]. In some regions of Bangladesh, its concentration is as high as  $1000 \mu\text{g l}^{-1}$  [25]. The surface water resources (river, canal and lake) are less contaminated by As, while relatively higher contents of naturally occurring As may occur in ground water ( $10\text{--}70 \text{mg l}^{-1}$ ), as a result of its input from geothermal sources (e.g. western USA and New Zealand) [26]. The Manchar Lake in Sindh, the largest freshwater lake in Pakistan is the main source of water for domestic and agricultural purposes. Water of lake as well as groundwater, in this vicinity is saline and has high As contamination [27,28].

Like India, Bangladesh and other neighboring countries, Pakistan is also facing serious public health disasters due to arsenic contaminated water and has acknowledged the need of appraising drinking water quality and As problem. Different areas of our country have

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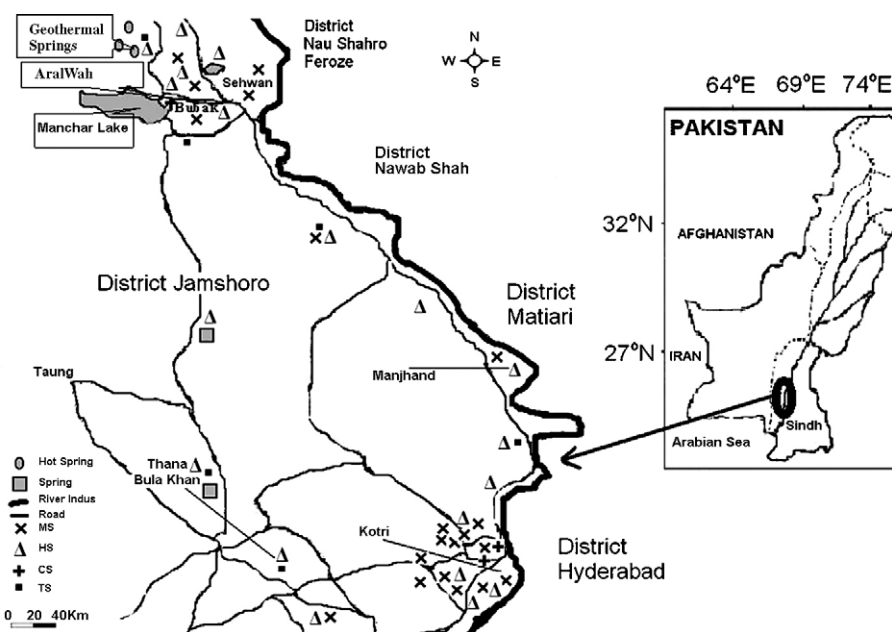


Fig. 1. Sampling map of study area (Jamshoro district).

high As concentration in drinking water (ground and surface water) [29]. On the basis of groundwater quality monitoring program, Pakistan Council of Research in Water Resources (PCRWR) and UNICEF reported that As contaminated groundwater ( $10\text{--}200\ \mu\text{g l}^{-1}$ ) was observed in some areas of Punjab province. In Sindh, 16–36% people are exposed to high arsenic ( $10\text{--}50\ \mu\text{g l}^{-1}$ ) in groundwater [30].

In study area, the analysis of As concentration in drinking water was not carried out so far, by any government organization or other national laboratories. Thus, the evaluation of arsenic in surface and underground water and its correlation with other physico-chemical parameters in understudy area was the need of the hour. Therefore, the aim of current study was to determine the As contamination in surface and ground water of District Jamshoro, Sindh (Pakistan) and to evaluate the possible contamination sources by characterizing the geochemical data. The water quality parameters (temperature, pH, total dissolved salt, electrical conductivity, sodium, potassium, calcium, magnesium, chloride, bicarbonate, nitrate, nitrite, sulphate, and iron) were also determined. The multivariate technique, cluster analysis (CA) was used, in view to find out the information about similarities and dissimilarities among the different sampling sites, according to As contamination levels.

## 2. Materials and methods

### 2.1. Description of study area

The area under study, Jamshoro district is located in south-west edge of the Sindh Pakistan, along with right bank of the river Indus and positioned between  $25^{\circ}19'\text{--}26^{\circ}42'\ \text{N}$  and  $67^{\circ}12'\text{--}68^{\circ}02'\ \text{E}$  (Fig. 1). The study area has a semi-arid and subtropical continental climate, the temperature ranged from 4 to  $46\ ^{\circ}\text{C}$  with  $<200\ \text{mm}$  average rainfall [31]. Jamshoro is composed of quaternary alluvial-deltaic sediments derived from Himalayan rocks while most of its area is situated at offshoots of the Kirthar range with quaternary and tertiary volcanic rocks having thermal springs [32,33].

Most of the villages are located on fertile agricultural land in the flood plain of the Indus River. It is observed that, the agricultural/industrial pollution is a possible source of As in surface and underground water [27,34,35].

### 2.2. Sampling and pretreatment

About 309 surface and ground water samples were collected from 48 sampling points of Jamshoro, Pakistan with the help of Global positioning system (GPS) in 2007 (Fig. 1). Out of total collected samples, 153 groundwater samples were collected from  $>15\ \text{m}$  depth and 156 were surface water samples (canals and municipal water supply). The canal water samples were collected from main stream of five to six different sampling points at a depth of 20–30 cm due to the low-flow conditions [36]. The collection of samples was performed by using Van Dorn plastic bottles (1.5 l capacity) and was kept in well stoppered polyethylene plastic bottles previously soaked in 10% nitric acid for 24 h and rinsed with ultrapure water. In the field, we measured water temperature, pH, electrical conductivity (EC) and total dissolved solids (TDS) by thermometer, pH meter (781-pH meter, Metrohm) and conductivity meter (InoLab conduc. 720, Germany), respectively.

### 2.3. Water analysis

The collected water samples were stored in an ice box, and delivered on the same day to the laboratory. Five to six water samples from each site were mixed into a washed plastic bucket to make a composite sample and filtered through  $0.45\ \mu\text{m}$  filter paper with the help of vacuum pump and stored at  $4\ ^{\circ}\text{C}$  until processing and analysis.

Standard solutions of understudy elements were prepared by dilution of  $1000\ \text{mg l}^{-1}$  certified standard solutions obtained from Fluka Kamica (Buchs, Switzerland) of corresponding metal ions. To prevent the sample contamination, all the glassware and plastic containers were treated with 5M  $\text{HNO}_3$  and rinsed with distilled water and finally with ultrapure water. The physico-chemical parameters were determined by standard methods [37,38]. Total alkalinity was determined by acid titration using methyl-orange. Total hardness as Ca hardness was measured by EDTA complexometry titration using Erichrome-black-T and Calcon as an indicators at pH 10 and 12, respectively with an analytical error  $<2\%$  [39]. For As and other metal analyses, water samples were pre-concentrated as reported elsewhere [27,40]. To estimate the equilibrium condition of the minerals possibly controlling the soluble chemical

species, saturation indices were calculated using speciation modeling PHREEQC (USGS, 2007).

#### 2.4. Analytical figure of merit

For quality assurance and quality control (QA/QC), data was treated according to the reported method [41]. Potassium, sodium and iron were determined by flame atomic absorption spectrophotometer FAAS (AAAnalyst 700 AAS, PerkinElmer) with limit of detection (LOD) of 14.0, 5.52 and 69.2  $\mu\text{g l}^{-1}$ , respectively while total As was measured by using hydride generation atomic absorption spectrophotometer HG AAS (MHS 15 system) with 0.02  $\mu\text{g l}^{-1}$  LOD. Chloride, nitrate, nitrite and sulphate concentration were determined by ion chromatography (Metrohm 838 Advanced Sample Processor with chemical suppression) with LOD of 1.3, 1.5, 1.4 and 2.8  $\mu\text{g l}^{-1}$ , respectively. For the validation of ions, ionic balances was calculated [42] as

$$\text{Ion balance percent} = \left\{ \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \right\} \times 100$$

The average ion balance 1.17% with two outliers of 1.8% and -3.2% was established, for which no explanation is impending; the mean balance is 0.5% (Table 1).

### 3. Results

For convenience in description, groundwater samples were grouped into two categories according to depth: hand pump samples (HS,  $n = 117$ ) from 15 to 30 m depth and tube well samples (TS,  $n = 36$ ) from 60 to 120 m depth (Table 1a). The surface water samples were also divided into two groups, canal water sample (CS,  $n = 36$ ) and municipal treated water sample (MS,  $n = 120$ , Table 1b). The descriptive statistical results of physico-chemical analyses in ground and surface water samples have been shown in Table 2.

#### 3.1. Physico-chemical parameters

The temperature of TS was higher than that of HS (Tables 1 and 2). Since water temperature is one of the conservative properties in the water cycle, the difference in temperature ranges for the shallow and middle depth groundwater is indicative of the presence of two separate confined aquifers. The pH values for underground water samples, HS and TS were observed in the ranges of 7.1–8.4 and 7.9–8.1, respectively. The EC values in HS and TS were in the ranges of 0.40–4.51  $\text{mS cm}^{-1}$  and 0.52–1.10  $\text{mS cm}^{-1}$ , respectively. The TDS were determined in the ranges of 188–2214 and 321–513  $\text{mg l}^{-1}$  in HS and TS, respectively. Alkalinity was found in the range of 181–1350  $\text{mg l}^{-1}$  for both groundwater samples.

In case of surface water samples, the pH for CS and MS were found in the ranges of 7.1–7.8 and 6.9–8.5, respectively (Tables 1 and 2). There was no significant difference in temperature values of CS and MS ( $p < 0.05$ ). There was no significant difference for the values of EC and TDS in CS and MS ( $p < 0.05$ ). Alkalinity was found in the range of 111–479  $\text{mg l}^{-1}$  for both types of surface water.

The pH of surface and groundwater samples was within the permissible level of WHO. Higher values of EC, TDS and alkalinity were found for ground water as compared with those of surface water ( $p > 0.05$ ).

#### 3.2. Major ions in water samples

The concentrations of major cations and anions in surface and ground water have been shown in Tables 1 and 2. Sulphate was one of the principal anions, with a concentration range of 113–1516  $\text{mg l}^{-1}$ ,  $\text{Cl}^-$  (131–721  $\text{mg l}^{-1}$ ), while  $\text{Na}^+$ , the most governing cation was found in the range of 191–945  $\text{mg l}^{-1}$ . Calcium

**Table 1a**  
The mean values of physico-chemical parameters and arsenic concentration in ground water from district Jamshoro Sindh, Pakistan.

Sample ID	T (°C)	pH	EC ( $\text{mS cm}^{-1}$ )	As ( $\mu\text{g l}^{-1}$ )	TDS ( $\text{mg l}^{-1}$ )	$\text{Ca}^{2+}$ ( $\text{mg l}^{-1}$ )	$\text{Mg}^{2+}$ ( $\text{mg l}^{-1}$ )	$\text{Na}^+$ ( $\text{mg l}^{-1}$ )	$\text{K}^+$ ( $\text{mg l}^{-1}$ )	$\text{HCO}_3^{2-}$ ( $\text{mg l}^{-1}$ )	$\text{Cl}^-$ ( $\text{mg l}^{-1}$ )	$\text{NO}_2^-$ ( $\text{mg l}^{-1}$ )	$\text{NO}_3^-$ ( $\text{mg l}^{-1}$ )	$\text{SO}_4^{2-}$ ( $\text{mg l}^{-1}$ )	Fe ( $\text{mg l}^{-1}$ )	Balance
HS1	29	8.1	2.41	83.2	1138	216	49.1	754	42.9	1352	233	2.44	24.8	1013	3.89	-1.8
HS2	27.9	7.8	1.69	15.1	796	165	26.9	652	8.9	972	266	1.36	12.4	708	0.25	0.6
HS3	28.3	8.4	4.14	106	1948	297	99.7	799	18.7	358	647	4.21	48.3	1516	4.28	1.1
HS4	26.6	7.8	3.93	13.1	1836	79.1	35.9	525	54.9	211	415	2.35	41.6	722	0.21	-0.1
HS5	27.9	8.2	2.98	58.3	1386	105	63.5	945	52.8	538	721	3.46	27.1	1050	1.21	1.1
HS6	29	7.7	1.90	29.0	896	87.3	42.7	520	17.2	218	347	1.05	12.6	829	0.52	-0.2
HS7	26.6	7.2	0.83	13.3	387	33.6	39.4	368	14.2	271	237	0.91	5.3	462	0.09	0.8
HS8	28.6	7.4	1.56	20.0	734	36.9	11.1	238	6.0	181	180	0.92	12.5	246	0.11	-0.9
HS9	26.4	7.2	0.57	57.0	270	38.2	26.8	191	4.4	269	199	1.39	1.4	113	0.69	0.2
HS10	27.5	8.2	2.14	20.3	869	110	67.0	736	9.9	520	521	7.50	25.1	903	0.25	0.6
HS11	31	8	4.51	54.1	2214	50.0	21.0	548	7.6	359	217	1.76	12.6	787	0.59	-0.9
HS12	30	7.8	1.11	27.0	524	89.1	25.9	597	17.1	330	295	1.21	12.6	877	0.19	0.9
HS13	30.4	7.9	1.06	55.0	499	54.5	21.5	293	13.0	280	205	2.55	9.7	418	0.49	-2.6
HS14	29.4	7.9	0.90	46.1	421	34.5	17.5	316	17.7	290	205	2.21	13.1	334	0.39	-1.6
HS15	28.4	8.2	2.52	42.0	1185	227	81.7	627	13.3	510	516	2.21	25.7	1107	0.48	-1.1
HS16	28.3	7.6	0.40	58.3	188	244	65.9	548	2.2	310	458	2.78	5.9	1121	0.51	-0.1
HS17	27.6	7.7	2.72	29.0	1280	124	46.5	486	10.9	285	236	0.43	24.9	979	0.38	-1.5
HS18	27.9	7.2	0.41	13.3	193	43.6	15.4	330	8.1	420	164	0.60	6.2	322	0.12	-1.1
HS19	31.8	7.1	0.57	20.0	266	77.7	24.3	419	11.9	420	230	0.50	6.3	562	0.32	-1.8
TS1	32.6	7.9	1.10	37.0	513	69.1	25.9	395	7.8	310	291	0.98	6.2	473	0.21	-0.8
TS2	29.6	8.1	0.52	65.0	321	48.9	21.1	241	7.1	240	130	0.20	0.9	366	2.45	-1.6
TS3	35.4	8	1.06	46.0	499	51.2	26.8	396	4.3	210	145	1.65	12.8	729	0.21	-2.2
TS4	28.2	8	1.08	39.0	524	79.0	26.0	395	7.80	310	291	0.98	7.2	473	0.31	0.2
TS5	25	7.9	1.14	45.0	612	59.0	21.0	241	7.10	240	130	0.20	0.9	366	0.48	0.1
TS6	32.5	7.8	1.07	36.0	674	41.2	27.0	396	4.30	210	195	1.65	12.8	629	0.34	-1.9

HS, hand pump sample; TS, tube well sample.

**Table 1b**  
The mean values of physico-chemical parameters and arsenic concentration in surface water from district Jamshoro Sindh, Pakistan.

Sample I.D.	T (°C)	pH	EC (mScm <sup>-1</sup> )	As (µg l <sup>-1</sup> )	TDS (mg l <sup>-1</sup> )	Ca <sup>2+</sup> (mg l <sup>-1</sup> )	Mg <sup>2+</sup> (mg l <sup>-1</sup> )	Na <sup>+</sup> (mg l <sup>-1</sup> )	K <sup>+</sup> (mg l <sup>-1</sup> )	HCO <sub>3</sub> <sup>2-</sup> (mg l <sup>-1</sup> )	Cl <sup>-</sup> (mg l <sup>-1</sup> )	NO <sub>2</sub> <sup>-</sup> (mg l <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg l <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg l <sup>-1</sup> )	Fe (mg l <sup>-1</sup> )	Balance
CS1	22.5	7.1	0.41	3.00	190	25.9	13.1	221	4.3	179	136	0.44	6.4	248	0.08	-0.1
CS2	23.8	7.2	0.40	4.0	180	4.0	6.8	216	3.0	289	119	0.50	6.4	108	0.11	-0.4
CS3	24.2	7.8	2.66	37.0	250	85.5	39.5	710	18.8	346	265	1.01	18.5	1240	0.38	-0.8
MS1	22.5	7.2	0.42	5.3	188	39.1	14.9	241	5.7	249	180	0.52	6.4	195	0.12	1.6
MS2	21.8	6.9	0.40	5.1	255	11.4	7.6	182	6.5	269	86	0.55	5.8	116	0.09	-0.7
MS3	23.5	8.4	1.85	16.0	265	51.6	20.4	461	17.2	229	271	1.58	15.7	613	0.10	0.3
MS4	22.6	7.1	0.45	6.3	210	15.5	5.5	246	7.3	208	172	0.55	6.2	187	0.14	-1.0
MS5	23.6	7.8	1.68	50.0	193	224	37.5	481	15.7	268	359	1.11	13.5	984	0.11	0.3
MS6	25.4	7.1	0.47	4.0	221	12.7	9.3	209	5.1	209	174	0.51	6.3	103	0.09	-0.4
MS7	22.5	7.9	3.61	6.0	196	21.8	12.2	229	11.9	190	173	0.98	14.3	208	0.12	-1.4
MS8	23.8	7.1	0.42	5.0	198	6.4	23.6	270	34.9	202	322	0.45	4.9	126	0.09	-0.9
MS9	24.2	7.1	0.50	4.2	212	24.5	17.5	242	4.7	194	224	0.55	5.2	181	0.09	-0.5
MS10	22.8	7.1	0.49	10.2	208	47.7	18.3	212	14.9	187	206	0.62	6.1	214	0.02	-0.2
MS11	24.5	7.3	0.52	7.0	228	23.6	11.4	359	42.8	479	243	0.72	4.9	236	0.10	-2.4
MS12	23.4	7.2	0.41	17.0	194	86.4	33.6	404	7.2	172	282	2.38	73.8	597	0.14	-0.2
MS13	22.5	7.1	0.49	6.0	233	21.8	3.2	332	14.2	164	245	1.50	12.0	325	0.12	-1.5
MS14	21.8	7.8	3.72	6.0	256	20.0	12.0	240	26.0	157	235	1.12	0.4	206	0.30	-1.7
MS15	23.5	7.1	0.54	5.2	214	17.3	2.7	251	14.4	149	196	0.60	0.5	215	0.10	-0.5
MS16	22.6	7.8	3.50	11.1	246	71.8	45.2	540	9.9	141	316	3.19	48.6	891	0.02	0.0
MS17	23.6	7.8	1.42	11.2	169	81.8	25.2	438	7.1	134	325	1.28	12.5	622	0.27	1.5
MS18	25.4	8.1	3.25	8.1	124	15.3	10.7	328	24.3	126	386	1.60	14.3	205	0.14	-3.2
MS19	22.5	8.5	0.93	4.2	245	24.5	10.5	136	9.3	119	53	0.88	2.3	234	0.12	-1.1
MS20	23.8	7.4	0.32	6.0	150	15.8	8.2	286	6.0	111	230	0.49	32.2	226	0.14	1.0

CS, canal water sample; MS, municipal water supply sample.

**Table 2**  
Ranges of analytical data of the ground and surface water samples in district Jamshoro, Sindh, Pakistan.

Parameter	Recommended values WHO (2004) [53]	Water type											
		Ground water						Surface water					
		Hand pump water, n = 117 <sup>a</sup>			Tube Well water, n = 36 <sup>a</sup>			Canal water, n = 36 <sup>a</sup>			Water supply, n = 120 <sup>a</sup>		
		Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
T (°C)	-	26.4	31.8	28.5	29.6	35.4	32.5	22.5	24.2	23.5	21.8	25.4	23.3
pH	6.5–8.5	7.1	8.4	7.76	7.9	8.1	8.0	7.1	7.8	7.4	6.9	8.5	7.5
EC (mScm <sup>-1</sup> )	0.40	0.40	4.51	1.91	0.52	1.10	0.89	0.40	2.70	1.16	0.32	3.72	1.3
TDS (mg l <sup>-1</sup> )	1000	188	2214	896	321	513	444	180	250	210	124	265	204
Ca <sup>2+</sup> (mg l <sup>-1</sup> )	100	33.6	297	111	48.9	69.1	56.4	8.2	85.5	39.9	6.4	224.5	42
Mg <sup>2+</sup> (mg l <sup>-1</sup> )	50	11.1	99.7	41.1	21.1	26.8	24.6	6.8	39.5	19.8	2.7	45.2	16
Na <sup>+</sup> (mg l <sup>-1</sup> )	200	191	945	520	240	396	344	216	710	382	136	540	304
K <sup>+</sup> (mg l <sup>-1</sup> )	12	2.20	54.9	17.4	4.25	7.84	6.39	2.96	18.8	8.67	4.69	42.8	14
HCO <sub>3</sub> <sup>-</sup> (mg l <sup>-1</sup> )	-	180	1352	426	210	310	253	179	346	271	111	479	198
Cl <sup>-</sup> (mg l <sup>-1</sup> )	250	164	721	330	131	291	189	119	265	173	53.0	386	234
NO <sub>2</sub> <sup>-</sup> (mg l <sup>-1</sup> )	3	0.43	7.50	2.03	0.20	1.65	0.94	0.44	1.01	0.65	0.45	3.18	1.1
NO <sub>3</sub> <sup>-</sup> (mg l <sup>-1</sup> )	50	1.45	48.3	17.3	0.90	12.8	6.64	6.37	18.5	10.4	0.44	73.7	14
SO <sub>4</sub> <sup>2-</sup> (mg l <sup>-1</sup> )	250	113	1516	740	366	729	523	108	1240	532	103	984	334
As (µg l <sup>-1</sup> )	10	13.0	106	40.0	37.0	65.0	49.0	3.00	37.0	15.0	4.00	50.0	10.0
Fe (mg l <sup>-1</sup> )	0.3	0.09	4.28	0.79	0.21	2.45	0.96	0.08	0.38	0.19	0.02	0.30	0.12

<sup>a</sup> No. of samples.

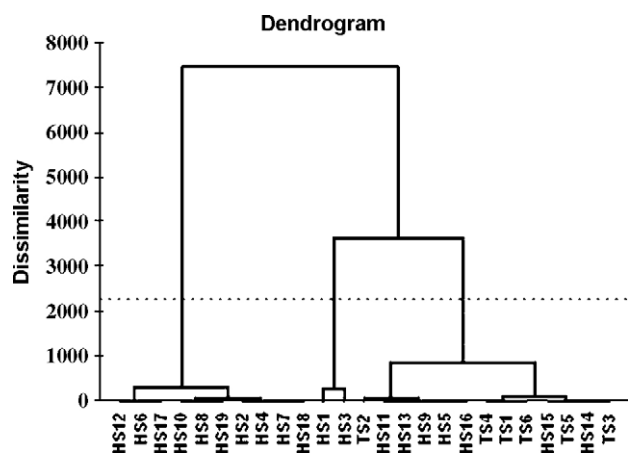


Fig. 2. Dendrogram showing sampling side clusters on Jamshoro (ground water).

concentrations ranged between 33.6 and 297 mg l<sup>-1</sup>. The highest NO<sub>3</sub><sup>-</sup> concentration was observed in hand pump samples at sampling spots 5–6 (Table 1a), probably, due to the use of fertilizers for different crops in this area. The pH for TS was observed in between 7.9 and 8.1. The alkalinity was ranging from 210 to 310 mg l<sup>-1</sup> and SO<sub>4</sub><sup>2-</sup> was found up to 766 mg l<sup>-1</sup>. The concentration of Na<sup>+</sup> reached up to 396 mg l<sup>-1</sup> while the concentration of Ca<sup>2+</sup> and Cl<sup>-</sup> were slightly higher than WHO permissible limits. Both of the groundwater samples (HS and TS) were found to have NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> concentrations within the WHO permissible limit (Table 2).

The surface water samples were less contaminated or polluted than the groundwater samples, except two sampling points, i.e., CS3 (Aral wah) and MS5 of Bubak, near Manchar lake. The major ion composition of municipal treated water group was similar to that of the canal surface water except sampling site CS16 (Table 1b).

### 3.3. Iron and arsenic

In ground water, the Fe was found in the range of 0.09–4.28 mg l<sup>-1</sup>, while, in surface water, it was within the range of WHO recommended level except the sampling point CS3 (Tables 1 and 2). The concentration of As distributed in groundwater samples of Jamshoro varied from 13.0 to 106 µg l<sup>-1</sup>, while in surface water it was found in the range of (3.00–50.0 µg l<sup>-1</sup>) (Table 2).

### 3.4. Cluster analysis (CA)

Cluster analysis was applied to identify spatial resemblance for grouping of sampling sites. It provided 2 dendrograms (Figs. 2 and 3), grouping 25 sites for ground water and 23 locations for surface water, shows 3 statistically significant clusters for each one.

The dendrogram (Fig. 2) showed the abnormality of groundwater sampling sites. The sampling sites HS1 and HS3 made one group as cluster 1, which contains >60 µg l<sup>-1</sup> As, while due to mutual dissimilarity, composed of cluster 2 (involved 10 site) and cluster 3, contains 13 sites, corresponding to relatively higher, lower and moderate As and Fe concentration, respectively. Similarly, the dendrogram (Fig. 3) classified the dissimilarities of the surface water sampling sites, cluster 1, involved MS5 and CS3 have >30 µg l<sup>-1</sup> As concentration as compared with other sampling sites of surface water, which may be due to non-point sources, i.e., agricultural, industrial and domestic activities. Besides cluster 1, the mutual dissimilarity among other sites was made as cluster 2, which is further divided into two classes, class 1 (involved 16 site) having As <10 µg l<sup>-1</sup> and class 2 (sites MS10, MS12, MS16 and MS17) containing >10 µg l<sup>-1</sup> As.

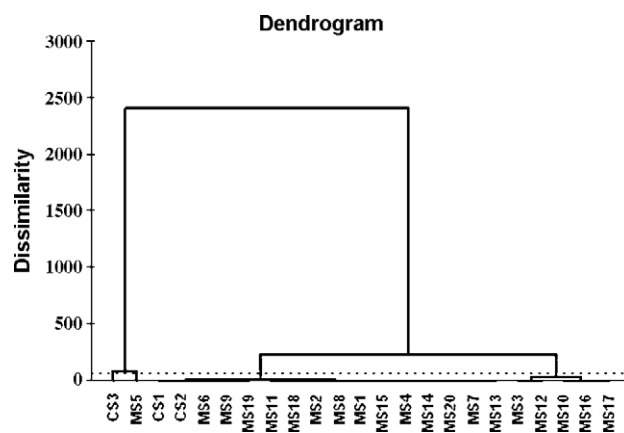


Fig. 3. Dendrogram showing sampling side clusters on the Jamshoro (surface water).

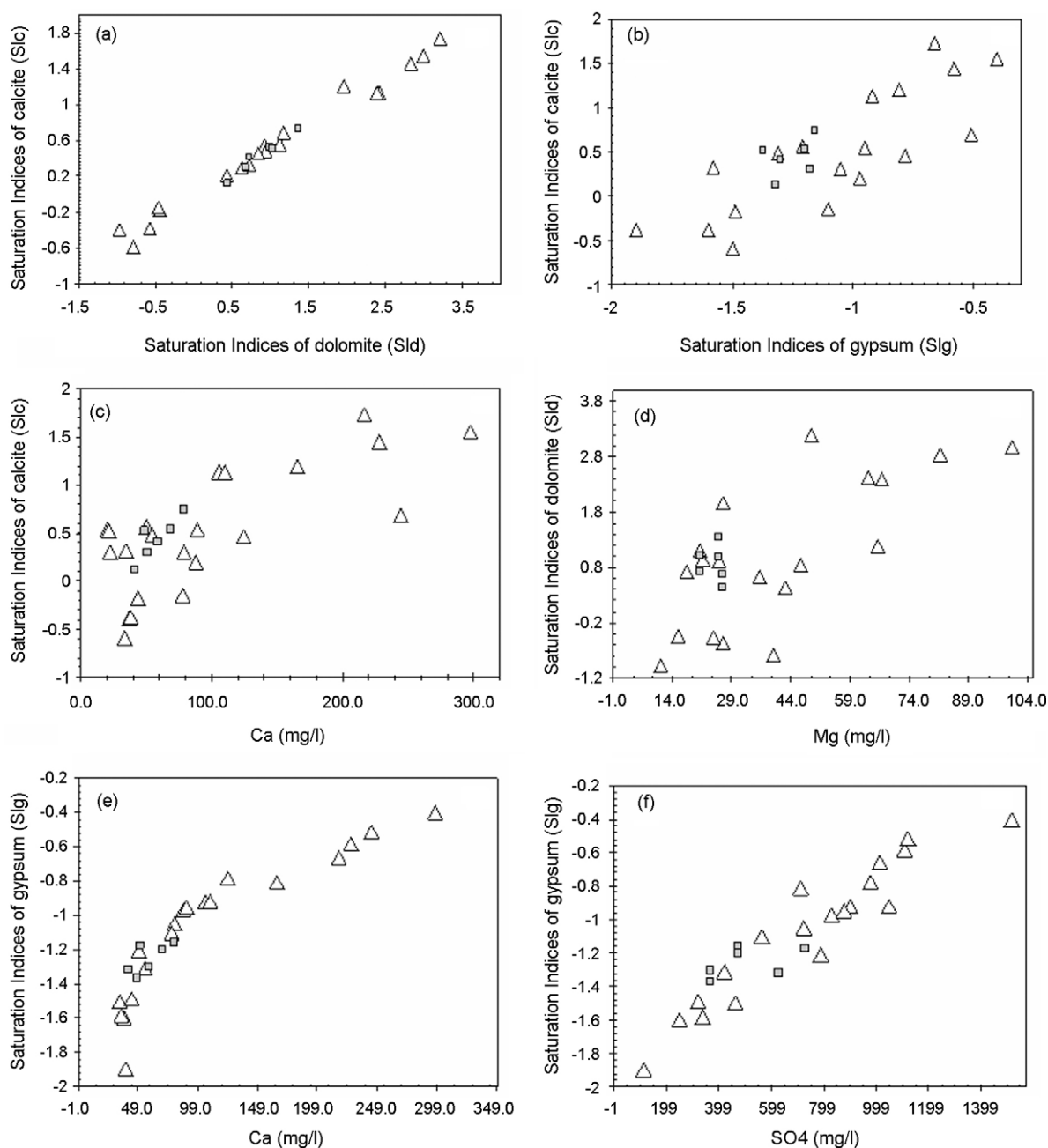
## 4. Discussion

The surface (CS and MS) and groundwater samples (HS and TS) have been used as the sole source of drinking water, cooking and personal hygiene in understudy area of Pakistan. In fact, As is known as the most serious inorganic contaminant in drinking water. Our study revealed elevated levels of As in ground and surface water samples (Table 1).

The physico-chemical parameters of surface and groundwater samples are presented (Tables 1 and 2). The pH is the most important parameter for test of water quality and useful tool for interpretation of water chemistry. The pH of both types of water samples were found from neutral to slightly alkaline, but it was within the WHO recommended values (Tables 1 and 2). Mostly, the EC values of surface and groundwater samples were found to be higher than WHO permissible level (0.4 ms cm<sup>-1</sup>), whereas, the TDS of all samples were within the limit (1000 mg l<sup>-1</sup>), except in HS (Tables 1 and 2). The annual rainfall in this basin is <200 mm, which have no effect on values of EC in the rainy season. High EC in dry season represents water with high electrolyte concentration, may be due to high rate of evaporation. It might be contributed to the high salinity, mineral contents and lower water table. A significant positive correlation was found between Ca and total hardness ( $r=0.64$ – $0.99$ ), while low correlation was observed between TDS and hardness ( $r=0.37$ – $0.40$ ) which may be due to high level of sodium and chlorides in understudy water samples. These dominant ions might be the result of ion exchange and solubilization in the aquifer [43]. The studied ground waters are usually basic in nature, have high EC due to elevated levels of TDS, reflecting moderate mineral dissolution. The intensity of soluble minerals is expressed as saturation index. In understudy groundwater samples, the saturation index (SI) of calcite has shown significant correlation with that of SI of dolomite and gypsum (Fig. 4a and b). The positive correlation of SI of calcite with Ca<sup>2+</sup>, SI of dolomite with Mg<sup>2+</sup>, while Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> corresponds with SI of gypsum (Fig. 4c–f), indicated that, these minerals are in a state of under saturation in ground water. The SI results may be attributed to extensive water logging of study area and is promoting contamination of As in the studied groundwater [44]. Expected high As contamination in ground waters might be caused by oxidizing environments due to elevated concentrations of Ca<sup>2+</sup> (>100 mg l<sup>-1</sup>), SO<sub>4</sub><sup>2-</sup> (>250 mg l<sup>-1</sup>) and pH > 7.5 [2].

Arsenic elution from organic matter (in soil) may be due to elevated alkalinity of soil [45,46]. Therefore, desorption of arsenic can either be promoted by an increase in pH or by the concentration of competing ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>). The pH was significantly correlated with As ( $r=0.55$ ,  $n=153$ ). The weak correlation was observed between As and Cl<sup>-</sup> concentrations ( $r=0.30$ ,  $n=153$ ),





**Fig. 4.** Relationships between various chemical components of analyzed in groundwater samples. (a) Dolomite saturation index (Sid) and calcite saturation index (Sic); (b) dolomite saturation index (Sid) and gypsum saturation index (Sig); (c) calcite saturation index (Sic) and Ca<sup>2+</sup>; (d) dolomite saturation index (Sid) with Mg<sup>2+</sup>; (e) gypsum saturation index (Sig) and Ca<sup>2+</sup>; (f) gypsum saturation index (Sig) and SO<sub>4</sub><sup>2-</sup> (Square icon for TS and triangle for HS).

however, chloride showed a significant correlation with Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> ( $r=0.64, 0.85, 0.81$  and  $0.74$ , respectively,  $n=153$ ), whereas HCO<sub>3</sub><sup>-</sup> was not significantly correlated with Cl<sup>-</sup> ( $r=0.15$ ,  $n=153$ ).

The mean As concentration in surface water samples is  $15.0 \mu\text{g l}^{-1}$ , with a range of  $3.00\text{--}50.0 \mu\text{g l}^{-1}$ , which is lower than the reported values of other areas [47]. In the present study, most of the collected samples have As contents within the recommended values of WHO, except in surface water samples of Manchar lake and its canal (Aral wah), i.e., sampling point CS3 and the municipal water supply samples (MS5). This might be due to natural processes, i.e., extensive evaporation of water due to high temperature and low rate of rain falls, which enhance the amount of salts, trace and toxic elements and other pollutants. The possible anthropogenic sources in study area include wastewater of agricultural lands, industrial

effluent and domestic wastes of urban areas, as described in previous study [27]. The average concentration of As in groundwater samples was found to be  $41.0 \mu\text{g l}^{-1}$ , which was less as compared to other countries like Bangladesh, India, Taiwan, China, Hungary, USA, Finland, Thailand, Argentina, Taiwan, Chile, Japan and Vietnam [12,48].

Concentrations of naturally occurring arsenic in ground water are varied due to the geological and climatic changes [2]. The study area exhibited elevated As concentrations in ground water, as it is situated in a zone of normal and hot spring (Fig. 1) with great thickness of sediments, and depth of burial which has produced very high geothermal temperatures. The literature counts various examples, which showed that trace elements including arsenic are more readily mobilized and transported by warm or hot water in the geothermal areas, like Jamshoro [49].

The significant correlation of As with Fe ( $r=0.83$ ) in ground water indicated that the elevated concentration of As in study area might be due to the presence of Fe containing ores [50]. In this connection, three mechanisms may explain the As discharge from sediment deposits to groundwater, the reduction of iron hydroxides, release of sorbed As from the sediments following the oxidation of As-rich pyrite in the sediments and the anion exchange of sorbed As with phosphate from fertilizers [51]. Korte and Fernando hypothesized that desorption of As from Fe oxides could occur at reducing condition in alluvial sediments, which could lead to high-As in ground waters [2]. According to our findings, the iron concentrations in groundwater samples of different sampling sites were found to be higher than those of the WHO recommended level (Tables 1 and 2).

Fertilizers such as di ammonium phosphate and urea are extensively used, which may seep down to underground water table, hence, altering its composition. A thermal power station, many brick and chemical factories are located here. In thermal power station coal burning for energy production is the main causative of air and terrestrial pollution, as, burning mineral coal is known to emit toxic elements such as As [52]. The high usage of arsenical pesticides for protecting crops and industrial effluents from chemical and sugar industries are also polluting aquatic system in the region. Keeping in view of the above said facts, these sources of pollution are main source of As contaminations in water bodies of understudy areas.

## 5. Conclusion

The evaluation of total arsenic contents in groundwater (153 samples) as well as in surface water (156 samples) of Jamshoro district, Sindh, Pakistan, was carried out in order to have an insight about the extent of arsenic toxicity in the study area. It was concluded that arsenic concentration in most of HS and TS samples was higher than the permissible limits proposed by WHO. The multivariate technique, cluster analysis of understudy sites clearly showed the high, medium and less polluted sites for surface and underground water. In general, the groundwater arsenic level was considerably higher than that of surface water, possibly due to some geothermal and anthropogenic factors, which enhanced pH level, and concentration of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and Fe. However, a more detailed understanding of local sources of arsenic and mechanisms of arsenic release is required. More extensive studies will be required for building practical guidance on avoiding and reducing arsenic contamination especially in ground water, and also control this threat to local residence, its flora and fauna.

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