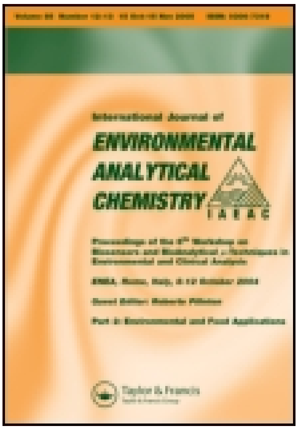

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

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To cite this article: Jameel Ahmed Baig, Tasneem Gul Kazi, Abdul Qadir Shah, Ghulam Abbas Kandhro, Hassan Imran Afridi, Sumaira Khan, Nida Fatima Kolachi & Sham Kumar Wadhwa (2012): Arsenic speciation and other parameters of surface and ground water samples of Jamshoro, Pakistan, International Journal of Environmental Analytical Chemistry, 92:1, 28-42

To link to this article: http://dx.doi.org/10.1080/03067319.2010.496053

Intern. J. Environ. Anal. Chem.
Vol. 92, No. 1, 15 January 2012, 28–42

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(*Received 14 November 2009; final version received 26 April 2010*)

This study evaluated and interpreted complex data sets of water samples collected from different sampling origins of ground water (hand pump and tube well) and surface water (municipal, river and canal). The aim was to provide information concerning the apportionment of pollution sources to obtain better information about water quality and possible distribution of As with respect to its speciation. The As (III) formed complex with ammonium pyrrolidinedithiocarbamate (APDC) and extracted by surfactant-rich phases in the non-ionic surfactant Triton X-114, while total iAs in water samples was adsorbed on titanium dioxide (TiO_2) and determined by electrothermal atomic absorption spectrometry. The accuracy of the proposed methodologies was confirmed by standard addition method. The recoveries of As (III) and total inorganic arsenic (iAs) were found to be >98%. The results revealed that the ground water of the area under study was more contaminated as compared to surface water samples. The mean concentration of As (III) and As (V) in the surface water samples was found to be 15.8 and 6.00 $\mu g\,L^{-1}$, respectively, whereas, in the case of ground water samples, the contents of As (III) and As (V) ranged from 6.20 to 51.0 and 6.40 to 53.0 $\mu g\,L^{-1}$, respectively. Principal component analysis performed on a combined (tube well and hand pump) samples data set extracted two significant factors explaining more than 60% of total variance, which suggested that the contamination sources might be natural or anthropogenic.

Keywords: cloud point; principal component analyses; arsenic species, iron; water quality parameters

1. Introduction

Arsenic (As) is of increasing concern due to its high toxicity and widespread presence in the environment. Elevated levels of As have resulted from oxidation weathering and dissolution of As-containing minerals in surface and aquifer waters [1]. It is present in drinking water as inorganic (As (III), As (V)) and organic forms (methyl and dimethyl arsenic compounds) [2,3]. Inorganic forms of As are more toxic than organic species, while As (III) is more toxic than As (V) [4,5]. As (V) can replace phosphate in several biochemical reactions, whereas As (III) may react with particular thiols in proteins

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ISSN 0306–7319 print/ISSN 1029–0397 online

http://dx.doi.org/10.1080/03067319.2010.496053
http://www.tandfonline.com

and inhibit their activities [6]. Thus, the acute and chronic poisoning of As involves the respiratory, gastro-intestinal, conjunctivitis, hyperkeratosis, hyperpigmentation and cardiovascular diseases [7]. It is recognised as a carcinogen and may cause lung, bladder, liver, renal and skin cancer [8]. Because of its toxicity and possible carcinogenicity, it is important to evaluate the different species of As in drinking water samples. Hence, the most economical and sensitive methods are required for the determination of As in environmental samples [9–11].

Analytical techniques such as electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS), can only yield a total amount of arsenic. The simultaneous determining modes are not suitable for atomic absorption spectrometry [12]. Therefore, chromatography coupled with the different instruments HPLC-AAS, HPLC-ICP-AES, HPLC-HG-AFS and HPLC-ICP- MS are suitable for speciation of As in an aqueous sample, but they cannot perform enrichment of an aqueous solution and have poor sensitivity, except for HG-AFS and ICP-MS [13–15]. Alternatively, speciation and pre-concentration methods for As species can be based on solvent extraction [16], solid phase extraction [17], co-precipitation [18], ion-exchange separation [19] and cloud point extraction [3,20]. In Pakistan, there is a need to study the status of inorganic As species in surface and ground water. Therefore, the present study was undertaken to evaluate the relationship between levels of the As species in water samples of different origins and then identify their co-relation with other physico-chemical parameters to identify their origin/source. For evaluation of the huge set of analytical data, the multivariate techniques such as principal component analysis (PCA) and cluster analysis (CA) [21] were used. Thus, As species, taken as variables are arranged into different groups/factors on the basis of contribution from probable sources. The PCA provides a basis for interpreting different clusters of the metals based on their co-variation [22].

2. Experimental

2.1 *Sampling site*

The surface and ground water samples were collected from 57 sampling sites of different origins, on alternate months in 2007, from Jamshoro (southwest edge of the Sindh Pakistan) with the help of global positioning system 'GPS' (Figure 1). Jamshoro district is situated along with right bank of Indus river and positioned between 25° 19′–26° 42′ N and 67° 12′–68° 02′ E. The province of Sindh stretches about 579 km from north to south and 442 km (extreme) or 281 km (average) from east to west. In the study area, the annual maximum and minimum average temperature is 46°C and 4°C respectively. The annual average rainfall is about 200–300 mm (SRP, 2004). 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 [23,24].

2.2 *Sampling and pretreatment*

The sampling network was designed to cover a wide range of determinates of the whole district including surface and ground water origins. From each sampling site, fresh surface water samples (canal (CS), river (RS) and municipal water (MS)) were collected from the

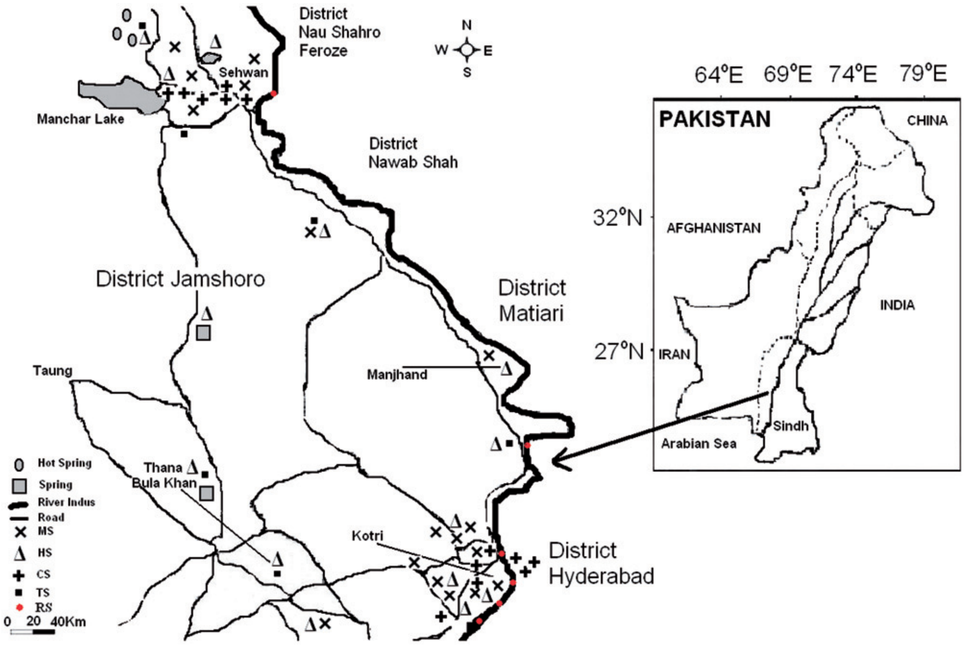

Figure 1. Sampling map of study area (Jamshoro district).

main stream of five to six different sampling points at a depth of 20–30 cm. The ground water samples of tube well 'TS' (depth > 60 m) and hand pump 'HS' (depth > 15 m) were simultaneously collected. The collections of samples was performed by using Van Dorn plastic bottles (1.5 L capacity) and were kept in well-stoppered polyethylene plastic bottles previously soaked in 10% nitric acid for 24 h and rinsed with ultrapure water. All water samples were stored in insulated coolers containing ice and delivered on the same sampling day to the laboratory and analysis of As^{3+} and iAs were accomplished on same day, to avoid risk of transformation of species, as reported elsewhere [25]. The physico-chemical parameters were determined by standard methods [26,27]. Total alkalinity was determined by acid titration using methyl-orange. Total hardness as Ca^{2+} hardness was measured by EDTA complexometric titration using Eriochrome-black-T and Calcon as indicators at pH 10 and 12, respectively with an analytical error <2% [28].

2.3 *Reagents and materials*

The ultrapure water obtained from ELGA lab water system (Marlow, UK) was used throughout the work. The extracting solutions were prepared from analytical grade reagents and were checked for possible trace metal contamination. The standard solutions of elements under study were prepared on a daily basis by diluting appropriate aliquots of a 1000 mg l^{-1} certified standard solutions (prepared with As_2O_3, NaOH and HNO_3) obtained from Fluka Kamica (Buchs, Switzerland). Ammonium pyrrolidinedithiocarbamate (APDC, Fluka) was used as the chelating agent to form the hydrophobic metal complexes. A 0.1% (w/v) of APDC solution was prepared by dissolving suitable amount of APDC in double deionised water. Titanium (IV) dioxide (Merck 99%, 0.5 µm) was used as a sorbent. The stock standard solutions of chemical modifiers of Mg $(NO_3)_2$, (2000 mg l^{-1}) was prepared from Mg $(NO_3)_2$ (Merck) and Pd (3000 mg l^{-1}), was prepared from $Pd(NO_3)_2$ Aldrich (Milwaukee, WI, USA). Working solution of modifiers was prepared by diluting 10 ml of each stock solution in 100 ml. The certified reference material SRM 1643e (water) was purchased from National Institute of standards and Technology (NIST), Giathersburg, MD, USA.

2.4 *Apparatus*

WIROWKA Laboratoryjna type WE-1, nr-6933 centrifuge (speed range 0-6000 rpm, timer 0-60 min, 220/50 Hz, Mechanika Precyzyjna, Poland) was use for the centrifugation. Mechanical shaker (Gallankamp, England) was used for shaking. The measurement of electrical conductivity (EC) and total dissolved solids (TDS) in water samples were analysed by using conductometer (InoLab Conduc. 720, Germany); pH was measured by pH meter (720-pH meter, Metrohm). A global positioning system (iFinder GPS, Lowrance, Mexico) was used for sampling locations. An ultrasonic bath with capacity 4L (Sonicor, Model SC-121TH, Sonicor Instrument Corp., Copiague, NY, USA), programmable for temperature ranging from 0°C to 90°C with intensification frequency of 35 kHz was used for heating.

The determination of As in extracts and digests was carried out by means of a double beam Perkin-Elmer atomic absorption spectrometer model 700 (Norwalk, CT, USA) equipped with the graphite furnace HGA-400, pyrocoated graphite tubes with integrated platform and an autosampler AS-800. Single element hollow cathode lamp used for As was operated at 7.5 mA with a spectral bandwidth of 0.7 nm. The graphite furnace heating program was set for different steps; drying, ashing, atomisation and cleaning as temperature range °C/time (sec) (80–120/15, 300–600/15, 2000–2100/5, and 2100–2400/2), respectively. Portions of both, standard or sample and modifier were transferred into auto-sampler cups, and 20 µl (standard or sample volume 10 µl + 10 µl modifier in each case) were injected to electrothermal graphite atomiser. Potassium, sodium and iron were determined by flame mode of atomic absorption spectrophotometer (AAnalyst 700 AAS, PerkinElmer).

2.5 *Determination of total As*

For As_T, 200 mL of surface (RS, CS, LS and MS) and ground (HS and TS) water samples were heated at 70°C on an electric hot plate to reduce the sample volume up to 25 ml, filtered, and keep at 4°C until further analysis. For accuracy, a certified reference sample of water (SRM 1643e) was treated as described in previous work [29,30].

2.6 *Determination of total inorganic arsenic*

The iAs was determined as slurry by using TiO_2 as adsorbent. The triplicate of each of the samples (100 ml) of different origin were taken in flasks and complexing agent TiO_2 (20 mg) added separately; then the pH 2 was adjusted with 0.5 M HCl. The flasks were then placed inside the ultrasonic water bath and were subjected to ultrasonic energy at 35 kHz for 10 min at room temperature. Then the sample solutions were centrifuged, to separate the precipitates and made into slurry by adding 5 ml of ultrapure water after subjected to ultrasonic bath for 2 min. Then the slurry with modifier was injected into a graphite tube by an autosampler. The same procedure was applied for blank.

2.7 *Determination of As (III)*

The triplicate of each samples (100 ml) of different origins of surface and ground water were placed in a beaker. The pH of solution was adjusted to 3.0 with 1.0 M HCl. 1.5 ml of 1% (w/v) APDC and 1.0 ml of 0.4% (w/v) $Pb(NO_3)_2$ solution was added and stirred for 15 min with mechanical shaker. Then, the sample solutions were centrifuged. The residual solid phase was dissolved in 1.0 M HNO_3 and diluted to 5.0 ml with deionised water. Then, 10 µl of sample solution with 10 µl of modifiers was injected into an electrothermal atomiser.

2.8 *Calculation of As (V)*

The concentration of As (V) could not be determined directly according to the above analytical procedure, but their concentrations were given by the difference between the iAs and As (III).

2.9 *Statistical evaluation*

All mathematical and statistical computations were made using Excel 2003 (Microsoft Office$^®$) and STATISTICA 6 (StatSoft, Inc.$^®$). Multivariate analysis of the studied water quality data set was performed through PCA and CA techniques [31]. The CA technique is an unsupervised classification procedure that involves measuring either the distance or the similarity between objects to be clustered. In hierarchical clustering, clusters are formed sequentially by starting with the most similar pair of objects and forming higher clusters step by step. Hierarchical agglomerative CA was performed on the normalised data set (mean of observations over the whole period) by means of the Ward's method using squared Euclidean distances as a measure of similarity [29,32,33].

The PCA is designed to transform the original variables into new, uncorrelated variables (axes), called the principal components (PCs), which are linear combinations of the original variables. The new axes lie along the directions of maximum variance. The PCA provides an objective way of finding indices of this type so that the variation in the data can be accounted for as concisely as possible [32]. The PCA provides information on the most meaningful parameters, which describes a whole data set with minimum loss of original information [29,33].

2.10 *Analytical performance*

The calibration and standard addition graphs were obtained for As (III) and total iAs, determined by electrothermal atomic absorption spectrometry. The linear range of the calibration graphs were obtained from the quantification limit up to 20 $\mu g\,l^{-1}$ for As (III) and total iAs. The mean and standard deviation, for $n = 6$ of the slopes of the standard calibration graph corresponding to As (III) and total iAs were 0.176 ± 0.004 and $0.236 \pm 0.006\,\mu g\,l^{-1}$, respectively. The limit of detection (LOD) was defined as

Table 1. The results for tests of addition/recovery for As^{3+} and total iAs determination in canal water samples ($n = 6$).

Species	Added conc. ($\mu g\,l^{-1}$)	Mean ± Std ($\mu g\,l^{-1}$)	^{a}% Recovery
As (III)	0.00	1.70 ± 0.50	-
	2.5	4.16 ± 0.30	99.1
	5.0	6.62 ± 0.34	98.6
	10.0	11.58 ± 0.39	98.9
Total iAs	0.00	2.90 ± 0.38	-
	2.5	5.32 ± 0.35	98.5
	5.0	7.81 ± 0.27	98.8
	10.0	12.71 ± 0.33	98.5

Element	Certified value of SRM 1643e	Found values $\bar{x} \mp ts/\sqrt{n}$	% recovery (% RSD)	$t_{\text{Experiment}}$
Validation for total As ($\mu g\,l^{-1}$) and Fe ($mg\,l^{-1}$)				
As	60.45 ± 0.72	59.3 ± 0.92	98.1 (1.60)	0.11
Fe	98.1 ± 1.40	96.9 ± 1.78	98.7 (1.83)	0.13
$t_{\text{certical}} = 2.26$ at 95% confidence limit, ($n = 6$)				

$$^{a}\%\text{Recovery} = \frac{C_{\text{after spiked}}}{C_{\text{initial}} + C_{\text{Spiked}}} \times 100.$$

$LOD = 3s\ m^{-1}$, where s is the standard deviation corresponding to 10 blank injections and m is the slope of the calibration graph. The LOD values were 0.05 and 0.22 $\mu g\,L^{-1}$ for As (III) and total iAs, respectively. The limit of quantification (LOQ), defined as $10\,s\,m^{-1}$, were 0.12 and 0.63 $\mu g\,l^{-1}$ for As (III) and total iAs, respectively. To check the accuracy of methodologies spiking was performed in six replicate at three concentration levels 2.5, 5 and 10 $\mu g\,L^{-1}$ (Table 1). The recoveries for As (III) and iAs were greater than 98.0% (Table 1). A good agreement was obtained between the added and measured analyte concentration. These results confirmed the validity of the proposed method. For total Fe and As, the accuracy was checked by using standard reference material SRM 1643e (Table 1). The paired t-test was calculated for ($n - 1 = 5$) degrees of freedom, t_{exp} (0.12) and (0.18) for total As and Fe, respectively, were less than the t_{crit} (2.57) at a confidence interval of 95% (Table 1), indicating no difference between found values and certified values.

The stability of TiO_2 slurry is affected by the pH value of the media. In this work, the slurry standard solutions were very stable at pH 2, which is consistent with reported work [20], that at pH 1> and <7 no phase separation could be observed during determination of As. In order to keep the stability, the slurry was also agitated in an ultrasonic bath before the injection. Owing to the smaller granularity of TiO_2 (<0.5 μm) used in this work, the instability resulted by the TiO_2 granularity was not obvious. In this case, R.S.D. % of the replicate slurry sample was less than 5% ($n = 5$).

Potassium, sodium and iron were determined by flame atomic absorption spectrophotometry with limit of detection (LOD), 14.0, 5.52 and 69.2 $\mu g\,l^{-1}$, respectively, whereas, chloride, nitrate, nitrite and sulphate concentrations 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 $\mu g\,l^{-1}$, respectively. For the validation of ions, ionic balances were calculated [3] and the average ion balance 2.52% with two outliers of 4.8% and −4.2% was established, for which no explanation is impending; the mean balance is 1.2%.

3. Results and discussion

In surface water, the temperature showed a very characteristic annual cycle, with higher values during the summer (28–45°C) and lower values in the winter season (18–25°C). The results of physicochemical parameters of surface (CS, RS and MS) and ground (HS and TS) water samples are given in Table 2. The analysis of the collected samples reveals some level of compliance with regulated standards (WHO) for drinking water, while the significant deviations were equally noticed. The pH of surface water was found in the range of 6.90 to 8.5 whereas it ranged from 7.1 to 8.4 in ground water samples (Table 2). All these pH values were within the WHO regulated levels. The range of TDS and EC in surface water (MS, RS and CS) were found in the range of 150 to1756 $mg\,l^{-1}$ and 0.32 to 3.72 $mS\,cm^{-1}$, respectively. The EC values in understudy CS and RS exceeded the WHO guidelines (Table 2) for drinking water, which was attributed to the high salinity and mineral contents. Our results are consistent with other studies [3,29]. The levels of TDS and EC in ground water varied from 180 to 2214 $mg\,l^{-1}$ and 0.40 to 4.50 $mS\,cm^{-1}$, respectively. Alkalinity was found in the range of 170 to 479 and 180 to 1352 $mg\,l^{-1}$ in surface and ground water samples, respectively.

In ground water, the concentration of Na^+, Ca^{2+}, Cl^- and SO_4^{2-} were observed higher than the permissible limit of the WHO, while other cations and anions were within the limit (Table 2). In surface water, Na^+ and Ca^{2+} were ranged from 191 to 540 and 6.40 to 85.1 $mg\,l^{-1}$, respectively and Cl^- concentration reached up to 386 $mg\,l^{-1}$. The levels of NO_2^-, and PO_4^{3-} were observed <10 $mg\,l^{-1}$, while the concentration of NO_3^- and SO_4^{2-} were found in the range of 5.20 to 73.75 and 107 to 984 $mg\,l^{-1}$, respectively (Table 2). In all surface water samples the F^- levels was within WHO permissible level (1.5 $mg\,l^{-1}$), whereas in HS and TS, it was reached up to 5.0 $mg\,l^{-1}$ (Table 2). The physical parameters of water (EC and TDS) are significantly correlated with cations and anions (Ca^{2+}, K^+, NO_2^-, NO_3^- and PO_4^{3-}) in ground water samples at 95% confidence level, which might be the result of ion exchange and solubilisation in the aquifer [3,34], whereas, in surface water, EC and TDS have strong correlation with cations and anions except F^-, Cl^- and SO_4^{2-} at 95% confidence level. In ground water the Fe concentration was found in the range of 0.09 to 4.30 $mg\,l^{-1}$, while it was within the WHO recommended level in surface water (Table 2).

The concentration of total As distributed in ground water samples of the district of Jamshoro (Pakistan) varied from 13 to 106 $\mu g\,l^{-1}$, while the level of As in surface water ranged from 3.0 to 50 $\mu g\,l^{-1}$ (Table 2). The average concentration of total As in surface water samples was found to be 15 $\mu g\,l^{-1}$, which is lower than the reported values for surface water [2,3]. The possible factors are frequent uses of pesticides and insecticides on agricultural lands as well as use of untreated waste water sewage sludge as agricultural fertiliser [3,29]. The average content of total As was found to be 40.0 $\mu g\,l^{-1}$ in ground water samples of the area under study, higher than the permissible limit of the WHO but lower than other countries as reported elsewhere [2,3]. As (III) is more toxic and mobile than As (V) [35]. It is because of its ability to form complex with certain co-enzymes associated with biological activity and dissolved organic water in natural water [35], so the distribution of arsenic species in drinking water is important. The studied

Table 2. Ranges of analytical data of the ground and surface water samples in the district of Khairpur Mir's, Sindh, Pakistan.

Parameter	WHO Recommended values		CS^a	RS^b	MS^c	TS^d	HS^e
			$n = 120$	$n = 36$	$n = 120$	$n = 36$ (60–120 m)	$n = 124$ (15–60 m)
pH	6.5–8.5	Min	7.1	7.1	6.9	7.9	7.1
		Max	7.8	7.5	8.5	8.1	8.4
		Mean	7.4	7.2	7.5	8	7.75
EC $mS\,cm^{-1}$	0.4	Min	0.40	0.34	0.32	0.52	0.40
		Max	2.66	0.49	3.72	1.09	4.50
		Mean	1.16	0.40	1.30	0.89	1.91
TDS $mg\,l^{-1}$	1000	Min	188	150	150	321	180
		Max	1250	450	1756	513	2214
		Mean	543	188	620	444	896
Ca^{2+} $mg\,l^{-1}$	100	Min	8.20	8.20	6.40	48.9	33.6
		Max	85.5	39.1	85.1	69.1	297
		Mean	39.8	25.9	42.0	56.4	111
Mg^{2+} $mg\,l^{-1}$	50	Min	6.80	6.80	2.70	21.1	11.1
		Max	39.5	13.1	45.2	26.8	99.7
		Mean	19.8	10.9	16	24.6	41.1
Na^+ $mg\,l^{-1}$	200	Min	216	191	135	240	190
		Max	710	225	540	396	945
		Mean	382	211	304	344	520
K^+ $mg\,l^{-1}$	12	Min	2.96	3	4.69	4.25	2.20
		Max	18.8	5.7	42.8	7.84	54.8
		Mean	8.67	4.3	14	6.39	17.4
HCO_3^- $mg\,l^{-1}$	–	Min	179	170	111.4	210	180
		Max	346	288	479	310	1352
		Mean	271	248	198	253	426
F^- $mg\,l^{-1}$	1.5	Min	0.42	0.40	0.10	0.50	0.40
		Max	1.40	1.30	3.00	1.10	5.00
		Mean	0.73	0.73	0.80	0.97	1.52
Cl^- $mg\,l^{-1}$	250	Min	119	0.47	53.0	130	164
		Max	265	0.60	386	290	720
		Mean	173	0.50	234	189	329
NO_2^- $mg\,l^{-1}$	3	Min	0.44	1.35	0.45	0.20	0.43
		Max	1.01	1.79	3.19	1.65	7.50
		Mean	0.64	1.19	1.10	0.94	2.03
NO_3^- $mg\,l^{-1}$	50	Min	6.37	5.20	0.44	6.37	1.45
		Max	18.5	8.40	73.7	18.5	48.3
		Mean	10.4	6.40	14.0	10.4	17.2
PO_4^{3-} $mg\,l^{-1}$	–	Min	0.40	0.52	0.47	0.50	0.40
		Max	0.60	0.70	0.85	0.70	5.10
		Mean	0.48	0.59	0.57	0.60	0.82
SO_4^{2-} $mg\,l^{-1}$	250	Min	108	107	103	108	113
		Max	1240	201	984	1240	1516
		Mean	532	144	334	532	740

(*Continued*)

Table 2. Continued.

Parameter	WHO Recommended values		CS[a] n = 120	RS[b] n = 36	MS[c] n = 120	TS[d] n = 36 (60–120 m)	HS[e] n = 124 (15–60 m)
Fe mg l^{-1}	0.3	Min	0.08	0.14	0.02	0.09	0.21
		Max	0.38	0.21	0.30	4.30	2.45
		Mean	0.19	0.17	0.12	0.79	0.96
AsT μg l^{-1}	10	Min	3.00	5.20	4.00	37.0	13.0
		Max	37.0	10.0	50.0	65.0	106
		Mean	14.7	6.50	9.70	49.3	40.0
Asi μg l^{-1}	–	Min	2.90	5.00	3.80	35.2	12.6
		Max	35.8	9.50	48.0	62.9	104
		Mean	14.2	6.20	9.10	47.7	38.0
As (III) μg l^{-1}	–	Min	1.70	2.90	2.30	18.9	6.20
		Max	20.7	5.40	30.5	36.4	51.0
		Mean	8.20	3.60	15.8	27.6	18.0
As (V) μg l^{-1}	–	Min	1.20	2.10	1.50	16.3	6.40
		Max	15.1	4.10	17.5	26.5	53.0
		Mean	6.00	2.60	4.20	20.1	20.0

[a]Canal water sample, [b]River water sample, [c]Municipal treated water sample, [d]Tube well sample, [e]Hand pump samples.

methods were applied successfully for the speciation of trace amounts of inorganic arsenic species in different origins of surface and ground water samples.

The iAs was analysed by the TiO_2-slurry method, and it represented about 94 to 98% of total As (Table 2), showing that the total amount of organic arsenic could be very small [36]. The concentrations of As species in five of the origins studied were obtained in increasing order as: $RS < CS < MS < TS < HS$ (Table 2). Arsenic speciation in ground water is an important factor in determining mobilisation, toxicity and general water chemistry. The redox As species are unstable in natural waters because of the transformation between As (III) and As (V), due to the organic matrices, redox potential (Eh) and pH [37]. The pH and Eh are the most important factors controlling As speciation. Under oxidising conditions, As (V), (H_2AsO^{4-}) is dominant at low pH (<pH 6.9), while at higher pH, $HAsO_4^{2-}$ becomes dominant (H_3AsO_4 and AsO_4^{3-} may be present in extremely acidic and alkaline conditions, respectively). Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species H_3AsO_3 will predominate [3]. So, all water samples were delivered on the same sampling day to the laboratory and analysis of As (III) was accomplished on same day, to avoid risk of transformation of species [25,38]. The resulting data was presented in Table 2.

The average As (III) concentrations was found to be 8.20, 3.60 and 15.8 μg l^{-1} in water samples of CS, RS and MS, respectively (Table 2). The high levels of As (III), as the most toxic arsenic species in the aquatic environment, found in canal and municipal treated water samples may cause tracheae bronchitis, rhinitis, pharyngitis, shortness of breath, nasal congestion and black foot disease [39]. A strong linear correlation coefficient was observed between the concentrations of inorganic As species with different physico chemical parameters (TDS, EC, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, NO_3^- and SO_4^{2-}) in surface water

Table 3. Linear correlation coefficient matrix for different physico chemical parameters, Fe and As species. Significant at 5% level.

	Ground water				Surface water			
	As_T	As_i	As^{3+}	As^{5+}	As_T	As_i	As^{3+}	As^{5+}
pH	0.551	0.551	0.548	0.546	0.459	0.458	0.461	0.454
EC	0.346	0.346	0.328	0.356	**0.598**	**0.596**	**0.596**	**0.595**
TDS	0.356	0.356	0.335	0.368	**0.685**	**0.683**	**0.678**	**0.688**
Ca^{2+}	**0.585**	**0.585**	**0.594**	**0.570**	**0.903**	**0.904**	**0.908**	**0.896**
Mg^{2+}	0.524	0.524	0.546	0.499	**0.851**	**0.848**	**0.850**	**0.844**
Na^{+}	0.377	0.377	0.364	0.381	**0.867**	**0.865**	**0.863**	**0.866**
K^{+}	0.171	0.171	0.185	0.157	0.510	0.510	0.506	0.513
HCO_3^-	0.253	0.253	0.222	0.273	**0.606**	**0.604**	**0.601**	**0.608**
F^-	0.222	0.222	0.263	0.186	0.548	0.546	0.541	0.552
Cl^-	0.363	0.363	0.388	0.339	**0.743**	**0.742**	**0.741**	**0.742**
NO_2^-	0.299	0.299	0.301	0.293	**0.637**	**0.633**	**0.639**	**0.624**
NO_3^-	0.370	0.370	0.406	0.336	0.571	0.567	0.576	0.553
PO_4^{3-}	−0.108	−0.108	−0.171	−0.058	−0.021	−0.020	−0.017	−0.024
SO_4^{2-}	0.499	0.499	0.496	0.494	**0.902**	**0.900**	**0.901**	**0.898**
Fe	**0.847**	**0.847**	**0.854**	**0.830**	0.194	0.193	0.196	0.189

(Table 3), indicating possible contamination caused by both natural and anthropogenic sources [29].

Mean concentration of As (III) in the TS and HS water samples were found to be 26.5 and 53.0 $\mu g\,l^{-1}$, respectively. It was observed that most of the ground water (TS and HS) samples were contaminated with a higher proportion of As (V) than surface waters (Table 2). It is reported in the literature that the elevated level of As(V) in ground waters under oxidising condition are characterised by elevated contents of SO_4^{2-} and pH, that is responsible for the release of As in oxidising quaternary sedimentary aquifers [2]. The concentrations of As^{3+} and As^{5+} in ground water were strongly correlated to Fe concentrations (Table 3). It is reported in the literature that As (V) is relatively immobile in the subsurface because it tends to sorb onto positively charged particles, such as iron hydroxides. Changes in redox conditions, such as reduction of metal oxides, may enhance the mobility of arsenic [1,2].

The concentrations of As (III) and As (V) in ground water were strongly correlated to Ca^{2+} and Fe concentrations (Table 3), which proved the above-mentioned facts. Recently toxicity order of arsenic species has been reported as inorganic As (III) > organic As (III) > organic As (V) > inorganic As (V) [40]. It is reviewed by Smedley and Kinniburgh [41] that this can provide an explanation for both the oxidising and reducing high-As environments. An abundant source of Fe oxides with its surface-bound and co-precipitated As provides a ready source of As that may be released given an appropriate change in geo-chemical conditions [2]. Thus, the elevated concentrations of As (III) and As (V) were more likely to be found in domestic HS with short screens set in proximity to the upper confine aquifer as compared to deep ground water (Table 2). Our results for As_T, iAs, As (III) and As (V) were comparable to those reported in the literature for ground water while high value of all As species was observed in surface water samples, but the difference in results was not significant ($p > 0.05$) [42–44].

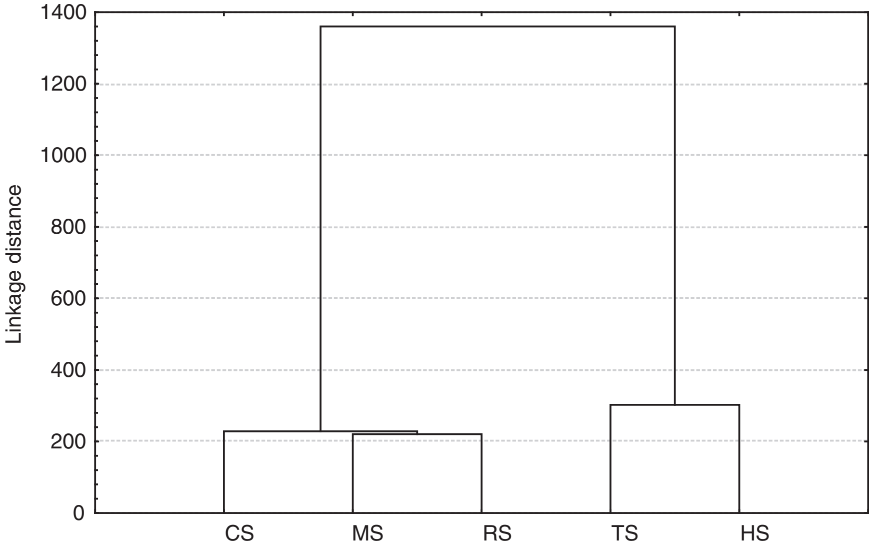

Figure 2. Dendrogram showing clustering of different origins of surface and ground water according to distribution of As species.

All this provides evidence that the anthropogenic and geological environment plays a key role in the distribution of studied inorganic As species in water bodies of the areas under study [45] and makes a significant contribution to the total intake of inorganic arsenic. In the district of Jamshoro, most of the population of the rural area depends on ground water. The consumption of drinking water is approximately 4 L containing $>50\,\mu g\,l^{-1}$. Therefore, total consumption of iAs is over 200 μg compared to an estimated daily intake of 12–14 μg iAs from diets of the North American population [46]. Therefore, chronic exposure to iAs may give rise to several health effects including gastrointestinal and respiratory tract disorders, damage to skin, liver, the cardiovascular system, the hematopoietic system, the nervous system, etc. in the areas under study. The earliest reports date back to the latter part of the nineteenth century when the onset of skin effects (including pigmentation changes, hyperkerotosis and skin cancers) were linked to the consumption of As through medicines and drinking water [29,47].

Cluster analysis was applied on surface and ground water quality data, to detect spatial similarity and dissimilarity for grouping of different ecosystems under study (spatial variability). The resulted dendogram (Figure 2) grouped all the five sampling eco-systems into three statistically significant clusters, as surface water eco-systems (MS) and (RS and CS) have low mutual dissimilarities as compared to ground water ecosystems (HS and TS), which have 18% of total dissimilarity.

Due to high concentration of arsenic species in ground water samples of the area under study, principal component analysis was performed on the analytical data set (19 variables) separately for ground water samples (HS and TS), in order to identify a reduced set of factors that could capture the variance of data set. Following the criteria of PCA reported in the literature, PCs with eigenvalue >1 were retained [32,33,38]. The first component (PC1) accounted for over 42.03% of the total variance in the data set of the ground water – in other words, the physical parameters, major cations, anions,

Table 4. Loadings of experimental variables (19) on significant principal components for ground water of Jamshoro district.

Variables	PC1	PC2	PC3
pH	0.759	−0.082	−0.254
EC	0.763	−0.275	−0.443
TDS	0.743	−0.251	−0.460
Ca^{2+}	0.774	−0.138	0.432
Mg^{2+}	0.628	−0.216	0.007
Na^+	0.776	−0.477	0.320
K^+	0.556	−0.430	0.241
HCO_3^-	0.246	−0.344	0.278
F^-	0.640	0.205	−0.432
Cl^-	0.925	−0.151	0.243
NO_2^-	0.647	−0.059	0.118
NO_3^-	0.839	−0.242	−0.313
PO_4^{3-}	0.191	0.427	0.652
SO_4^{2-}	0.574	−0.457	0.230
Fe	0.548	0.365	0.125
AsT	0.508	0.598	0.067
Asi	0.574	0.770	−0.020
As^{III}	0.617	0.740	−0.038
As^{V}	0.538	0.787	−0.006
Eigenvalue	7.99	3.51	1.75
%Total variance	42.03	18.47	9.23
Cumulative %	42.03	60.49	69.72

Fe and As species in the solution demonstrates similar behaviour in the ground water samples (Table 4). From a macroscopic point of view, all the physico-chemical parameters behave similarly, i.e. high concentration of major elements as well as As species in main body of whole ground water, except in few cases where the variation in pollution loading has some temporal effects. The strong positive loading on pH, EC, TDS, Ca^{2+}, Na^+, Cl^- and NO_3^- were observed, whereas a low loading on PO_4^{3-} was observed. The anthropogenic pollution is mainly due to the discharge of fertiliser and pesticides, as a regular source, throughout the year. However, there is no available data on the use of arsenical pesticides or industrial chemicals in the area under study. However, it is reported that about 5.6 million tonnes of fertiliser and 70 thousand tonnes of pesticides are consumed in the country every year [38]. These are pesticides, mostly insecticides, sprayed on the crops or mixed with the irrigation water, which leaches through the soil and enters ground water aquifers [38]. The trend obtained was also supported by the analysis of the results on the raw data set. The second component (PC2), explaining 18.5% of the total variance, has strong positive loadings for Fe and As species, and thus basically represents the elements of the pollution group. The third component (PC3) of PCA shows only 9.23% of the total variation and has positive loading of PO_4^{3-}. The high values of Fe, As and major cations and anions in underground water samples are above the permissible limit of WHO values for drinking water [48].

The above observation is clearer to follow in Figure 3, which shows the characteristics of samples and helps one to understand their spatial distribution. It is evident that samples distributed in the upper right quadrant are more enriched with pH, EC, TDS, K^+, F^-, NO_3^-, Fe and As species, while the lower right quadrant is more enriched with TDS, Na^+,

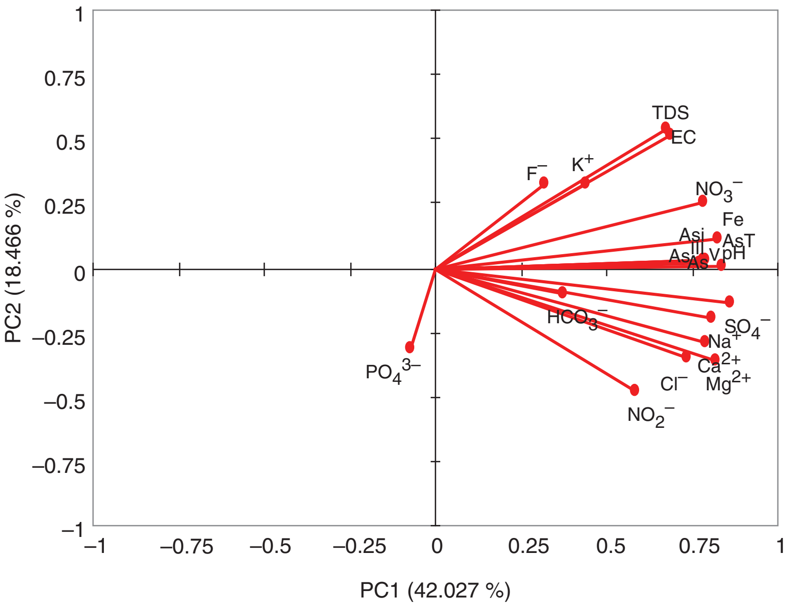

Figure 3. Plots of PCA scores for combined data set of ground water samples for distribution of Fe, As species and water quality parameters in the district of Jamshoro.

Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, NO_2^- and SO_4^{2-}, as shown in Figure 3. The sample distributed in the lower left quadrant is PO_4^{3-} to a lesser extent. All these facts revealed that the high level of As species in water is due to the dissolution of As compounds coming from Himalaya through the Indus river and settling down from year to year and then being introduced into ground water by geothermal, geo-hydrological and bio-geo chemical factors as reported elsewhere [3,38].

4. Conclusions

The speciation analysis provided more information about toxicity, bioavailability and mobility of different As species in surface and ground water samples. Therefore, evaluation of arsenic species of ground water (160 samples) as well as of surface water (276 samples) in the 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 the strong linear correlation coefficient was observed between the concentrations of inorganic As species with different physico-chemical parameters (TDS, EC, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, NO_3^- and SO_4^{2-}) in surface water but in ground water they were strongly correlated with Ca^{2+}, SO_4^{2-} and Fe. The concentrations of As species in five studied origins were obtained in increasing order as: RS < CS < MS < TS < HS. Cluster analysis grouped five sampling ecosystems into three clusters of similar surface and ground water quality characteristics and As species. Based on obtained information, it is possible to design a future, optimal sampling strategy, which could reduce the number of sampling sites and associated cost. The PCA performed on combined (TS and HS) data set extracted two significant factors explaining more than 60% of total variance. Thus, this study illustrates the usefulness of multivariate statistical techniques for analysis and elucidation of complex data sets of ground water quality evaluation and identification of possible pollution sources.

Acknowledgements

This work was supported by Higher Education Commission (HEC), Islamabad (Grant 20-1246/R&D/9). We are grateful to Dr. Akhtar Mehmood Baig, president of Young Welfare Society Mughalabad (YWSM) for sampling assistance. The authors thank anonymous reviewers for their help in reviewing and helpful advice on the structure of the research article.

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