Evaluates the physicochemical characteristics and change in the concentration of arsenic species in groundwater, release from 2nd aquifer of coal mining area, its drain outlet and different sites of reservoir: Application of multivariate techniques

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Original Research

Keywords: Aquifer ground water, coal mining, reservoir, drain outlet, toxic elements, multivariate technique

DOI: https://doi.org/10.21203/rs.3.rs-196845/v1

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Abstract

For energy production activity the ground water of 2nd aquifer (AQ2) of block 2 of Thar coal field is drained out in a reservoir/Gorano dam. In present study the physico-chemical and toxic elemental levels in ground water samples of 2nd aquifer (AQ2) of Thar coalfield at the depth of 100–120 m was carried out. The further sampling of water was carried out from drain outlet (DW) and four sampling sites of reservoir (S1, S2, S3 and S4). The sediment samples of water reservoir were collected from four sites and analyzed for toxic elements. The large data set of water quality of AQ2, DW and four samples sites at different spots of reservoir, carried out during 2019 for 17 parameters in triplicate of each composite samples were further analyzed by multivariate statistical techniques involving cluster (CA) and principal component analysis (PCA). The all water samples were analyzed for physicochemical parameters including cations and anions. The resulted data of cations (sodium, potassium, calcium, magnesium, cadmium, lead, total arsenic and iron), anions (chloride, fluoride, nitrate, sulphate and bicarbonate) and physicochemical parameters were descript in terms of basic statistical parameters, PCA and CA. The chemical correlations among different parameters were observed by PCA, which were employed to categorize the water samples by CA. The positive correlation of fluoride (F⁻) and total arsenic with sodium and bicarbonate indicated that the GW (AQ2), DW and water samples of reservoir with high conductivity and salinity stabilized the toxic elements in the water samples of different origin. Results showed that all collected water samples have high values of sodium absorption ratio. The water quality assessment indicated that the high levels of physicochemical parameters and toxic elements in ground and reservoir water have concern in and make it unsuitable for drinking and domestic purposes.

1. Introduction

The maximum content of lignite coal is originated in district Tharparkar, Sindh, Pakistan. At the present time different national and international agencies are working on power plans (Ali et al. 2015; Imran et al. 2014). In ground water of mining areas, numbers of pollutants such as organic and inorganic minerals are dissolved in water and there by adversely distressing its quality and utility (Singh et al. 2012; Kurwadkar, 2019). In adding, water can liquefy lot of the chemicals from soil and rock. The refuse masses containing sulphides (pyrite) be able to rise the acid mine drainage problems in the environment. Departure of huge quantity of water for diverse requirement through mining processes frequently causes considerable changes in its physico-chemical characteristics as well as regularly creates depression of groundwater in the region which may result in its shortage (Ali et al., 2015).

The feature of groundwater based on different factors and their contents, which are generally resulting from the geological information of the mining area. Arsenic (As) in the water is a severe natural misfortune for living and non-livings, which instigate from geological and anthropogenic resources (Smedley et al., 2002; Anawar et al., 2003; Ayoob and Gupta, 2006; Rafique et al., 2009). Ground water, surface water, soil and different foods are to be regard as main resources of inorganic Arsenic (Tuzen et al., 2010). The consumption of contaminated water with arsenic in the different regions of the world is the main task for scientists in different region of world (Smedley et al., 2002; (Baig et al., 2009a; Brahman
et al., 2013; Farooqi et al., 2007. In the inorganic form arsenic can be get from four sources such as arsenate \((\text{H}_2\text{AsO}_4)\), arsenite \((\text{H}_2\text{AsO}_3)\) and organic forms \((\text{methyl arsenic acid [CH}_3\text{AsO(OH)}_2\text{]}\) and di-methyl arsenic acid \([\text{(CH}_3\text{)}_2\text{AsO(OH)}]\). Different researcher consider that As is a group I carcinogens and causes cancer of different organs such as skin lungs, bladder and different severe physiological disorders in human being (Morales et al., 2000; Yoshida et al., 2004; Kazi et al., 2009).

Generally the organic As compounds are less toxic than inorganic (As compounds). For the determining of inorganic arsenic in water the very sensitive methods was developed (Marahel et al., 2011). Cadmium is also dangerous to living beings, it can cause of injures of organs living things such as kidney, Lungs and Liver (Bernard, 2008; Satarug et al., 2011). Intake of cadmium for long time creates more problems for metabolism of calcium in the life system which initiates the damage of cell and its death (Chakraborty et al., 2013). Cadmium also discourages the function of essential elements such as zinc assisted enzymes by exchange. It also causes cancer and dermatogens include radiation, maternal infections, chemicals, and drugs. (Barrera et al., 1997).

Lead is more in quantity in atmosphere, its cause of contamination in water and air and also other things. It is hazards metal which gradually increases and causes such diseases damage of brain, anemia, kidney disorder and hematological disorder (Shah et al., 2010). Livings beings are affected by lead (Pb) from anthropogenic as well as natural example contaminated beverages, food, drinking water, industrial emissions, soil. To analyze the environmental and biological samples numbers of techniques was comprehensively used including: atomic absorption spectrometry (Detcheva and Grobecker, 2008), inductively coupled plasma optical emission spectrometry (Zhu and Alexandratos, 2007) and others.

For coal mining purposes the elimination of water of aquifer (ground water), its removal devoid of drain system can be expensive. The open cut withdrawal system needs the proficient elimination of overload and inter-burden stratum in order to access coal seams. The dewatering of the surface mine is carried out by use of an pumping-out via a borehole (entirely piercing the whole depth of the aquifer), then the water of aquifer of coal mining is forced out at a regular ejection rate to reduce the piezometric level of the ground water beneath the coal mining horizon at the pit boundary (Liang et al., 2017).

The current study has been is in connection with Thar coalfield, where the coal mining and power generation plants by Sindh Engro Coal Mining Company is carried out. Initially the ground water of 2nd aquifer of block 2 of Thar coal field, had started releasing into the reservoir, locally called Gorano dam, to diminish the amount of groundwater that lies underneath of the 2nd aquifer. This study was served during 2019 for determination of trace and toxic elements (As, Cd and Pb) and other parameters such as \((\text{pH, EC, TDS, salinity, Na}^+\text{, K}^+, \text{Ca}^{2+}\text{, Mg}^{2+}\text{, Cl}^-, \text{SO}_4^{2-}\text{, HCO}_3^-\text{, Fe}^{3+}\text{, NO}_3^-\text{, and F}^-\) in ground water (2nd aquifer of block-2) of coal mining area of Thar coal, drain out let of it and from four sites of reservoir at equal distance (500m). The sediment of four sites of reservoir/gorano dam were analysed for toxic elements. The accuracy of the methodologies was determined by simultaneously analyzed matrices matched certified sample of water (Table 2).
Table 2
The physicochemical parameters, cation and anions concentration in ground water of aquifer AQ2, drain out let (DW) and sampling sites (S1, S2, S3 and S4) of Gorano reservoir

| Parameters / Units | WHO Limits | Aquifer 2 | DW   | S1    | S2    | S3   | S4   |
|--------------------|------------|-----------|------|-------|-------|------|------|
| pH                 | 6.5–8.5    | 8.0 ± 0.16| 7.75 ± 0.24| 7.6 ± 0.24| 7.4 ± 0.18| 7.3 ± 0.21| 7.0 ± 0.20|
| EC                 | 0.25       | 10.8 ± 1.44| 10.4 ± 1.10| 9.44 ± 1.12| 8.24 ± 1.20| 7.34 ± 0.85| 6.24 ± 0.88|
| a TDS              | 1000       | 9350 ± 202| 9290 ± 147| 9190 ± 298| 7280 ± 435| 5650 ± 368| 4930 ± 312|
| aSal               | -          | 9.85 ± 5.80| 9.71 ± 0.78| 9.2 ± 1.92| 7.3 ± 1.55| 5.7 ± 1.18| 5.1 ± 1.52|
| aF                 | 1.5        | 40.0 ± 8.1| 38.8 ± 7.2| 36.4 ± 6.42| 34.7 ± 5.42| 32 ± 4.46| 27.5 ± 4.26|
| aCl                | 250        | 1360 ± 44.4| 1340 ± 58.7| 1330 ± 86.8| 1220 ± 84.2| 1110 ± 71.1| 920 ± 47.5|
| aNo3               | 50         | 65.2 ± 5.3| 63.8 ± 7.2| 48.5 ± 3.97| 42.8 ± 3.5| 38.6 ± 3.4| 32.5 ± 2.9|
| aSO4^-2            | 500        | 597 ± 71.9| 565 ± 70.3| 535 ± 117| 481.5 ± 106| 401 ± 88| 339 ± 74|
| HCO3^-             | -          | 432 ± 23.2| 419.7 ± 22| 397 ± 55.4| 359 ± 49.3| 299 ± 41.2| 249 ± 34.5|
| Na^+               | 200        | 1670 ± 37.4| 1649 ± 72.1| 1590 ± 134| 1380 ± 141| 1300 ± 150| 1090 ± 140|
| K^+                | 12         | 25 ± 2.24| 24.2 ± 2.17| 20.6 ± 2.45| 19.7 ± 2.4| 17.5 ± 2.32| 14.8 ± 1.8|
| Ca^2+              | 100        | 378 ± 15.2| 369 ± 14.4| 358 ± 16| 331 ± 14.7| 298 ± 13.6| 254 ± 11.4|
| Mg^2+              | 50         | 183 ± 4.8| 173 ± 4.1| 169 ± 6.4| 164 ± 5.85| 141 ± 5.24| 132 ± 4.12|
| Fe                 | 0.2        | 1.25 ± 0.19| 1.20 ± 0.19| 1.0 ± 0.05| 0.82 ± 0.04| 0.78 ± 0.06| 0.58 ± 0.038|
| As                 | 10         | 47.3 ± 7.6| 46.2 ± 6.25| 44 ± 5.58| 41 ± 5.23| 37 ± 4.87| 31 ± 3.76|
| Cd                 | 3          | 45.8 ± 4.82| 44.4 ± 4.32| 38.2 ± 3.89| 27.2 ± 5.54| 20.8 ± 3.4| 15.8 ± 3.9|

Key = a mg/L; b µg/L
The huge data set obtained was calculated successfully with multivariate techniques, principal component (PCA) and cluster analysis (CA) to estimate the information concerning the similarities/dissimilarities between the diverse sampling sites, to recognize the water quality variables. These methods have been used to assess the effectiveness of water quality monitoring networks of aquifer 2 and drain outlet in reservoir, plans to increase the number of examining sites and select the basic parameters of water quality. Along these lines, it is conceivable to identify and evacuate sites of reservoir as well as repetitive parameters to reduce the economic cost of monitoring plan without sacrificing fluctuation in water quality data. The analytical precision for the estimations of cations and anions indicates by anions/cations balance error/ionic balance error, calculated based on the concentration of all ions in meq/L. To verify the appropriateness of drained ground water of 2nd aquifer of coal mining area in a reservoir for irrigation purpose, the sodium absorption ratio of each site were also calculated.

### 2. Material And Methods

#### 2.1. Study area

The huge reservoir of natural coal Thar in district Tharparkar, Sindh, Pakistan, detail is reported in our previous work (Ali et al., 2017). Different power generation projects are carried out by different national and international agencies (Ali J et al. 2015; Imran et al. 2014). The discharge of the water of 2nd aquifer of block 2 of Thar coal mining field in Gorano reservoir, which are at the depth of 120 m. Gorano reservoir is newly developed reservoir in 2017 spread in 1,500 acres. This site completely reserved for dewatering discharge by a pipe which is 27 Km away from coal mine site. The Gorano dam/reservoir is geographically located at the southern part of Pakistan. The water sampling was carried out from drain outlet and from four sites of reservoir as mention in Fig. 1.

#### 2.2 Chemical reagents and glassware

Ultrapure water which was used throughout procedure system was taken from ELGA lab water system (Bucks, UK). The acids and oxidizing reagents obtained from Merck (Darmstadt, Germany) analytical reagents were rated for purpose determination of trace and toxic elements in studied samples. The standard solution of As, Cd and Pb were prepared from certified standard solution (1000 ppm) obtained from Fluka Kamika (Buchs, Switzerland) and made upto volume with. 0.1 M HNO$_3$. Before analysis all the glassware was kept in 5M HNO$_3$ for 24 hours and then rinsed with deionized water.

#### 2.3. Instrumentation
The pH meter (720-pH meter, Metrohm) was applied for the determination of pH, of water samples of
different origin. Inductively coupled plasma optical emission spectroscopy (ICP-OES) The Thermo
Scientific™ iCAP™ 7000 Series ICP-OES, A atomic absorption spectrometer Model 700, Perkin Elmer
(Norwalk, CT, USA), equipped with hollow cathode lamps with addition of an air–acetylene burner has
been used. For the physico-chemical parameters such as, Electrical conductivity (EC), and Total dissolved
solids (TDS) conductometer (Ino Lab conduc. 720, Germany) was used.

2.4. Sampling and pretreatment

Samples of water were collected in summer of 2019 in the month of May and June. The groundwater
was sampled directly from second aquifer with the legal permission and assistance of Sindh coal
authority. The high power compressor was operated for withdrawing ground water of second aquifer
during construction of power plant. Then further sampling was carried out from the drain outlet of
groundwater of second aquifer of block-2 in a gorano dam/reservoir. Then water samples were also
collected from reservoir of four sites at equal distance of 500 m (length of dam is 2.0 km), with the help
of water grab sampler (1.5 L capacity), equipped with a simple pull-ring that allowed for sampling of
water at surface and depths of 20–30 cm, from 10 to 20 spots of each sites (S1, S2, S3 and S4) at
random and held in well stopper polyethylene plastic bottles, formerly washed with 10% nitric acid and
rinsed with ultrapure water obtained from ELGA Lab water system. Then collected water (AQ2 and DW)
and from four sampling sites was made five composite samples (surface and lower levels of same site).
Then filtered through 0.45 microspore size membrane for the removal of suspended particular materials
to laboratory carefully and labeled. Finally samples of water were stored at 4°C in refrigerator before
analysis. The sampling of sediment was carried out simultaneously with water from 5 to 7 spots of each
site, SD1, SD2, SD3 and SD4 (except AQ2 and DW sites) by means of an Ekman dredge which was
designed as SD1, SD2, SD3 and SD4. The samples were kept tightly closed in polyethylene bags. At the
same day the water and sediment samples were transported in the laboratory.

In laboratory sediment samples were dried in an electric oven at 70°C for 24 h. Then crushed and passing
through a sieve (200 µm). For the preparation of sediment sample, triplicate of each samples (0.5g) were
taken in crucibles and added 3.0 to 5.0 mL of mixture of nitric acid and hydrogen peroxide at 2:1 ratio.
After 10 to 15 minutes the crucibles placed on hot plate at 70°C temperature for digestion purpose then
add 10 mL of 0.2 M solution of nitric acid (HNO₃). Finally filter solution in 100mL sample bottles by using
whatman filter paper and samples were prepared for run on instrument.

2.6. Analytical procedures

The analysis of water samples of different origin for different physico chemical parameters in water
samples of AQ2, DW, S1, S2, S3 and S4, were carried out in triplicate of each composite samples by
standard methods (APH Association 2005; Organization WHO 2006; Jamshed et al., 2015). Initially 50 mL
of each water samples were taken in 100 ml of beakers and with the help of pH-meter and
conductometer, different physico-chemical parameters such as pH, TDS, EC and salinity were measured
respectively (Table 1S). The TDS were not measured in water samples directly due to its high values, and
for that purposes the each composite samples (n = 10) were 10 times diluted with deionized water then conductometer was applied to measure TDS. An ion chromatograph was used for the estimation of anions levels in water samples of different origin using peak area of each with an error < 2% (Brahman et al., 2013; Ali et al., 2015). The other experimental steps was indicated in our previous work (Brahman et al., 2013), to determined the anions a mixed standards of each F⁻, Cl⁻, NO₃⁻, and SO₄²⁻ was made at different concentration range (0.5–10 mg L⁻¹) from certified stock standard solutions. The major cations, Ca²⁺, Na⁺, K⁺ and Mg²⁺ were analysed in 20-time diluted acid-treated water samples with ultrapure water, FAAS. Whereas iron was estimated by FAAS without dilution. The As, Cd and Pb were determined in the triplicate of each composite samples, which were diluted 2 times and subjected to inductively couple plasma optical emission spectrometer. For accuracy in determination of different cations in real water samples, a certified sample (SRM 1643e) of water was simultaneously analyzed (Kazi et al., 2009). The major cation Na⁺ is scientifically also termed as alkali hazard is estimated by the total and comparative levels of cations and is stated as sodium absorption ratio (SAR). The method for calculating the SAR is also accounted in previous work (Brahman et al., 2013).

### 2.7. Statistical evaluation

To analysed the resulted data obtained from huge number of real water samples, obtained from different origin were calculated using statistical computations with Excel 2003 (Microsoft Offices) and STATISTICA 6 (Stat Soft, Inc.s). Multivariate statistical techniques for categorization, representations and elucidation of huge datasets from ecological checking plans permit the diminution of the wideness of the data and the drawing out the information to facilitate the evaluation of water quality (Liu et al., 2003; Kazi et al. 2009; Brahman et al., 2013). Basic statistics and correlation calculations were conducted in order to give preliminary information concerning the water quality data of six sites (AQ2, DW, S1, S2, S3 and S4).

### 2.8. Application of multivariate technique

Basic statistics was carried out in order to give initial information about the change of water quality of different origin (ground water/reservoir). The multivariate techniques, CA and PCA were applied to evaluate the quality of water samples at different origin (AQ2, DW, S1, S2, S3 and S4) (Kazi et al. 2009, Arain et al., 2014 Brahman et al., 2013). The CA Involves in calculating either distance or the resemblance among objects to come mutually. In this technique the clusters are based on the similarity of the data among different groups. The technique is based on the normalized data set (average values of observations of all over water samples of different origin) using of the Ward’s method with squared Euclidean distances (Arain et al. 2014; Sarbu and Pop 2005). The both multivariate techniques were applied on the resulted data of eighteen thousand, three hundred sixty values (17 factors) determined in five composite samples of each origin such as 6 sampling sites in twice (sampling in two month) and analysis in triplicate (17×6×30×2×3 = 18360).

### 2.9. Analytical figure of merit

The calibration of standards were prepared for Na, K, Ca, Mg, Fe, As, Cd and Pb at required concentration range, using FAAS and ICP-OES. The limits of detection (LOD) was estimated according to (LOD = x ×
where “s” is the standard deviation of 10 determinations of the blank and “m” is the slope of the calibration graph attained, the LODs; 5.52, 14.0, 164.3, 2.46, 69.2, mg/L for Na, K, Ca, Mg and Fe, respectively. The calibration graphs of As, Cd and Pb were prepared their solution starting from the limit of quantification up to 20 µg/L using ICP-OES. The LOD were found as 0.02, 0.13 and 0.05 µg/L, respectively. The precision of methods was carried out by analysis of matrices matched certified sample of water (SRM 1643e) and sediment (SRM 1944) as shown in Table 1. The prominence of the analytical resulted data was maintained throughout with cautious standardization, measurement of procedural blanks and all the time average resulted data obtained by triplicate analysis of each composite sample. For justification of the resulted data of cations and anions in water samples of each (AQ2, DW, S1, S2, S3 and S4) were within the ± 5%, the ionic balances was calculated by equation as revealed in our earlier work (Kazi et al., 2009; Arain et al., 2014) was observed as ± 5%.
Table 1
Analytical results of standard reference material of water, SRM 1643e samples.

| parameters | SRM 1643e (µg/L) | SRM Sediment 1944 (mg/Kg) |
|------------|------------------|----------------------------|
|            | Certified values | Measured values            | Certified values | Measured values |
| Na         | 20,740 ± 260     | 20,500 ± 284<sup>a</sup>  | (98.9)          |                 |
| K          | 2034 ± 29        | 2010 ± 43.5               | (98.9%)        |                 |
| Ca         | 32,300 ± 1100    | 32000 ± 1110              | (98.8)         |                 |
| Mg         | 8040 ± 98        | 7950 ± 99.0               | (98.9%)        |                 |
| Fe         | 98.1 ± 1.4       | 96.2 ± 1.5                | (98.1%)        |                 |
| tAs        | 60.45 ± 0.72     | 59.4 ± 0.81               | 18.9 ± 2.8     | 18.6 ± 2.9     | (98.3%)        | (98.4)       |
| Cd         | 6.6 ± 0.07       | 6.5 ± 0.06                | 8.8 ± 1.4      | 8.7 ± 1.3      | (98.4%)        | (98.8)       |
| Pb         | 19.6 ± 1.21      | 19.2 ± 1.25               | 330 ± 48.0     | 325 ± 49.0     | (98.3%)        | (98.5)       |

<sup>a</sup>mean±s  
<sup>b</sup>Values in the parenthesis ( ) indicates %Recovery

3. Results And Discussion

The mean with standard deviation (n = 30) of physicochemical parameters of groundwater samples (AQ2), drain outlet and four sites of reservoir (Gorano dam) are given in Table 2. To estimate the correlations using Pearson correlation coefficients (r) among the data of variables, were estimated. The obtained resulted values of different variables/parameters of all collected water samples of different origin, groundwater samples (AQ2), drain outlet (DW) and from different four sites of reservoir (S1, S2, S3 and S4) were extensively deviate from the recommended standard values of WHO, for drinking water.
However, the values of pH and $\text{SO}_4^{2-}$ in all water samples except ground water of AQ2 are in agreement with recommended standards of WHO for drinking water. The pH of AQ2, DW, S1, S2, S3 and S4 of was found in the range of 7.75 – 8.5, 7.6–7.92, 7.5–7.75, 7.2–7.64, 7.0–7.4 and 6.7–7.2 respectively, are consisted with WHO regulated levels. This confirms that it is slightly alkaline in nature, which is attributable to the concentration of $\text{HCO}_3^-$ ion, which is relatively high in all sites of reservoir, ranged as 249 to 397 mg L$^{-1}$. However, the pH values of water samples of reservoir were diminished with the distance. This reducing in pH is taking placed owing to the decline in dissolved minerals (Tripathy 2002).

The mean values with standard deviation of TDS and EC of water samples of different origin, AQ2, DW, S1, S2, S3 and S4 were given in Table 2. The TDS values in Aq2, DW, S1, S2, S3 and S4 were found in the range of 8940–9710, 8680–9440, 8680–9240, 6980–7840, 5280–5870, 4650–5210 mg/L, respectively. The EC were found in the range of 9.8 – 11.5, 9.46–11.0, 8.86–10.5, 7.68–9.54, 6.75–8.12, 5.89–7.45 mS/cm, respectively. The total dissolved and electrical conductivity enhanced up to five times than WHO suggested allowable limit for drinking water (Table 3), which may be owing to the elevated salinity and mineral substances in the selected groundwater of 2nd aquifer (AQ2) of coal mining area (Block 2), drain water at initial and different distance of reservoir (S1, S2, S3 and S4, corresponding to average 500 m among each site), these data are consisted with literature reported study ((Brahman et al., 2014; Nag and Saha 2014).

Table 3  Factor loadings Eigen values for physicochemical parameters, cations, anions and toxic elements of water samples of different origin

| Variables/parameters | F1   | F2   | F3   | F4   |
|----------------------|------|------|------|------|
| pH                   | 0.610| 0.758| 0.218| -0.031|
| EC                   | 0.872| -0.477| 0.002| 0.111|
| TDS                  | 0.368| 0.915| 0.155| 0.038|
| Sal                  | 0.658| 0.283| -0.697| 0.000|
| $\text{F}^-$         | 0.433| 0.891| -0.087| 0.099|
| $\text{Cl}^-$        | 0.300| 0.950| -0.087| 0.001|
| $\text{NO}_3^-$      | 0.988| -0.100| -0.085| -0.070|
| $\text{SO}_4^{2-}$   | 0.450| 0.891| 0.017| -0.046|
| $\text{HCO}_3^-$     | 0.880| -0.274| 0.067| 0.383|
| $\text{Na}^+$        | 0.692| 0.150| 0.703| -0.058|
| $\text{K}^+$         | 0.985| -0.122| -0.097| -0.075|
| $\text{Ca}^{2+}$     | 0.896| -0.422| -0.113| -0.074|
| $\text{Mg}^{2+}$     | 0.842| -0.517| -0.078| -0.065|
| $\text{Fe}^{3+}$     | 0.978| -0.159| -0.008| -0.136|
| $\text{Cd}^{2+}$     | 0.961| -0.268| 0.058| 0.006|
| $\text{Pb}^{2+}$     | 0.853| -0.504| 0.131| -0.022|
| tAs                  | 0.411| 0.907| -0.088| -0.006|

| Eigenvalue | 9.67 | 5.95 | 1.14 | 0.216 |
| Variability % | 56.9 | 35.0 | 6.67 | 1.27 |
| Cumulative % | 56.9 | 91.9 | 98.6 | 99.8 |
It was observed that the EC of initial drained water (DW) have higher values than four sites, decreasing from (6.34 to 37.7% in S1 to S4). The total dissolved salts at S4 were about 47% reduced than initial values of DW. The EC of groundwater (AQ2) samples was found to be 24 to 40 time elevated than WHO guidelines for drinking water (Table 2). It was observed that the change in EC is almost the same as TDS. The value of Na\(^+\) were observed in the range of 1610 – 1720, 1588–1703, 1210–2000, 1117–1847, 1016–1680, and 859–1420 mg/L. The value of K\(^+\) were observed in the range of 21.9 – 28.2, 20.1–25.5, 17–22, 15–21, 14–19 and 12–16 mg/ L. The levels of Ca\(^{2+}\) were observed in the range of 345–410, 333–391, 339–382, 313–353, 282–318 and 241–271 mg/L. It was detected that the groundwater samples (AQ2) and DW have elevated concentrations of Na\(^+\), which might be indicates that either due to the solubilization of lithogenic Na\(^+\) and swap over the soluble Ca\(^{2+}\) with Na\(^+\) via minerals origin in clay in ground water of coal mining area (block 2). Guo and Wang, 2007 et al., have also supported the hypothesis further, that due to high ratio of Na\(^+\)/Ca\(^{2+}\) (4.42), which demonstrate the ion substitute amongst Na\(^+\) on the shell of clay minerals and elevated levels of Ca\(^{2+}\) in the groundwater.

The values of Mg\(^{2+}\) were observed in the range of 176 – 190, 164–169, 159–207, 146–190, 134–174 and 118–153 mg/l in AQ2, DW, S1, S2, S3, S4, respectively. The levels of Fe were observed in the range of 0.85 – 1.7, 0.81 – 1.6, 0.78–1.3, 0.75-1.0, 0.1–0.2 and 0.45–0.82 mg/L. The levels of Fe was 3 to 5 folds higher in water samples of AQ2, whereas in sample S4 the concentration of it was reduced but still higher than recommended levels of it (0.3mg/L). Whereas The value of F\(^-\) and Cl\(^-\) were observed in the range of (31.4 – 52, 30-50.2, 24–44, 22–40, 20–38, 17–31) and (1304 – 1519, 1240 1501, 1140–1639, 1053–1514, 961–1382, 809–1164) mg/l, respectively in AQ2, DW, S1, S2, S3 and S4. The concentrations of NO\(_3^-\) were observed to be elevated than acceptable limit of WHO for water used for drinking purposes especially for children, while the levels of SO\(_4^{2-}\) in water samples of all origin was inside the permissible limit (Table 2). The levels of HCO\(_3^-\) were found in the range of 411 – 494, 399–483, 300–480, 271–434, 226–362 and 188–301 mg/l in AQ2, DW, S1, S2, S3 and S4, respectively.

The resulted values of toxic elements (tAs, Cd and Pb) in groundwater of second aquifer of Thar coal mining area, its drain outlet and four sampling sites of reservoir have high concentration. The obtained results indicated that ground water (AQ2), DW, S1, S2, S3 and S4 were contaminated with larger concentration of As, Cd and Pb, higher than the suggested WHO limit for drinking water (10 \(\mu\)g L\(^{-1}\)). The total contents of As in AQ2 was found in ranged as 39.2 – 59.5 \(\mu\)g/L, whereas the drain water (discharge out let) have As concentration slightly lower than AQ2, the difference was not significant (p < 0.05). The concentration of As in water samples of reservoir at different sites (S1, S2, S3 and S4), were found to be decreasing, observed in the range of 35–57, 32–53, 30–48 and 25.5–40.0 \(\mu\)g/L. The total Cd in water samples 2nd aquifer of Block 2 of coal mining area and it drain out let was observed in the range of 35–58 \(\mu\)g L\(^{-1}\) and 34–51 \(\mu\)g L\(^{-1}\), respectively indicates insignificant difference, The Cd levels in water samples of reservoir were found in the range of 33–44, 19–36, 16–25 and 11.5–20.4 \(\mu\)g L\(^{-1}\) for S1, S2, S3 and S4, respectively. The resulted data indicate two to four folds higher levels of Cd in all water samples than limit for drinking purposes. The levels of Pb in AQ2, DW, S1, S2, S3 and S4 were found in
the range of \(51.4–74.6, 43.6–69.4, 54.5−56.4, 36.4–55.5, 28.6–49.5\) and \(22.4–35.2\) µg L\(^{-1}\), respectively, these all values were three to six fold higher than those values of water recommended by WHO. The all toxic elements were found in decreasing order based on sequence of sampling sites as AQ2 ≤ DW < S1 < S2 < S3 and < S4 as shown in Table 2.

### 3.1. Sodium absorption ratio (SAR)

On the basis of these results sodium adsorption ratio was calculated for the selected water samples by the equation given below and also indicated in previously published work (Brahman et al., 2013; Arain et al., 2014).

\[
\text{SAR} = \frac{[\text{Na}^+]}{\sqrt{\left\{\left[\text{Ca}^{2+}\right] + \left[\text{Mg}^{2+}\right]\right\}/2}}
\]

Where Na\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\) are sodium, calcium, and magnesium concentrations in milli-equivalents per liter. The exposure of Na\(^+\) is stated as sodium absorption ratio (SAR). The calculated SAR values of groundwater of AQ2, DW, S1, S2, S3 and S4 based on minimum to maximum values of each variables was observed in the range of 19.2–30.9, 18.9–30.6, 14.4–30.24, 13.3–29.6, 12.1–28.4 and 10.8–25.6 with a mean value of 24.5, 22.3, 21.5, 20.3, 18.2 and 14.7, respectively, which designated the elevated levels of Na\(^+\) and lower concentrations of Ca\(^{2+}\) in AQ2 and other collected water sample designated that the cation-exchange complex might be develop into saturated with sodium. As the salinity values was higher the SAR index become also elevated, results in to cause infiltration problems in soil. To applying the saline water for agricultural purpose, which causes adverse impacts on the crops created due to excess of Na can creates transitory saturation of the surface soil, high pH and enhanced the potential for diseases, weeds, soil erosion, lack of oxygen and inadequate availability of nutrient. It was reported by Van Voast, 2003, that water samples from the coal beds typically high in sodium and low in calcium and magnesium, resulting in a high SAR values (Cannon et al., 2007) [37]

### 3.2. Multivariate statistical analysis

Cluster analysis (CA) was also applied for qualitatively analyze the difference and similarity among the water samples of ground water of aquifer 2, its drain outlets and at different sites of reservoir. The statistical technique, cluster analysis of water samples obtained from different origin was performed on all selected physico-chemical variables (physico-chemical parameters and toxic elements), and to evaluated the dissimilarity/similarity on the resulted data of all variable in water samples of six sampling sites (Kazi et al., 2009).

The dendrogram indicates the grouping of all six sampling sites, based on resulted data of all variables, into two statistically important clusters (Fig. 2). The results of all physico chemical parameters of water samples of all selected origin after their scaling by z-transformation, to measures the % of similarity and to construction of a dendrogram (Chen et al. 2007). A percent similarity level at 100%, two clusters was formed that is further divided into two groups: from the left, the first cluster (cluster A) is composed of two groups, one comprises of site-3 and 4. Whereas in second group, and site-2 was found. The second
cluster (B) on the right side is further divided into two groups. One comprised of AQ2 and DW (where no significant difference was observed in levels of different toxic elements, cations, anions and physico-chemical parameters. Whereas the second group is involved in sight (S1), that is located at 500 meter distance from drain outlet, where the levels of all physico-chemical data including toxic elements were considerably decreased from AQ2 and DW, though the dissimilarity was not significant (p > 0.05).

The Principal component analysis (PCA) is intended to change the original data of variables into new, unassociated variables (axes), designated as principal components (PCs), which are linear arrangements of the original data of the variables. The novel affiliation lies beside the paths of highest variance. The PCA provide an objective way of finding manifestations of difference in the resulted data be accomplished for description as probable summarizing (Sarbu and Pop 2005). The spatial correlation matrix of the water quality parameters is obtained by PCA. The PCA was carried out on the resulted data set (17 parameters/variables) independently for water samples of different origin (DW, AQ2, S1, S2, S3, and S4), to regulate/identify the compact set of variables that might be capture the variance of data set. The primary/first principal component (PC1) indicated more than 56.88% of the whole discrepancy in the set of resulted data of water samples obtained from different origin is shown in Table 3. The most important point of view, the resulted data of all variables perform correspondingly, such as elevated levels of cations and anions, and different toxic elements in whole network of water sampling. The Fig. 2 indicates high loading data for \( \text{Cl}^- \), \( \text{tAs} \), \( \text{F}^- \), \( \text{SO}_4^{2-} \), TDS, PH, \( \text{Na}^+ \) and Sal especially in AQ2 and DW. The positive loading in 2nd component was observed for, \( \text{NO}_3^- \), K, Fe, Cd, \( \text{HCO}_3^- \), Ca EC, Mg, and Pb in the second factor, which is of 35.02% of the whole variance. The 3rd components corresponding to 6.67% of variance was designated with good loading of Na, which is confirmed with high values of salinity in water samples of whole network.

### 3.4. Correlation among different variables

The Pearson correlation among physicochemical factors of water samples obtained from AQ2 collected from 2nd aquifer of coal field, DW and four sites have equal distance of reservoir are indicates in Table 2S. The water samples collected from AQ2 and other sites, have good correlation/connection of physical parameters among all anions and cations (p < 0.05), which designated that all the determined cations and anions are causative for enhanced values of pH, EC, and TDS of groundwater (AQ2). The pH of groundwater and reservoir water samples have positive correlation among all anions and cations (p < 0.05), except for \( \text{HCO}_3^- \) and \( \text{Mg}^{2+} \). This capacity is might be due to the less accessibility of gypsum and carbonated rocks (Brahman et al. 2013). The Pearson correlation between physico-chemical parameter, anions, cations and toxic elements groundwater 2nd aquifer (AQ2) of Thar coalfield, DW, and from four samples site of reservoir/Gorano dam are shown in Table 2S The physical parameters of AQ2 have good relationship with all anions and cations (p < 0.05), which showed that they all are contributing for the enhancement values of pH, EC, and TDS of water samples The pH, TDS and EC, and have absolutely high correlation (r > 0.7 and p < 0.05) with \( \text{Cl}^- \), \( \text{F}^- \), \( \text{SO}_4^{2-} \), \( \text{tAs} \), \( \text{NO}_3^- \), \( \text{HCO}_3^- \), \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \), Fe, Cd and Pb for water samples obtained from (AQ2), DW, S1, S2, S3 and S4 at 95% confidence level, which may be due to the high solubilization minerals corresponding to those ions obtained from mining area. The EC and TDS
have positive correlation with K⁺ (p < 0.05), whereas it has weak connection with pH (p > 0.1). Sodium have moderate correlation (r = > 4) with all variable except F⁻ and tAs whereas significant correlation with salinity (p = 0.01). The F⁻ have moderate to significant correlation with Cl⁻, SO₄²⁻, Ca²⁺, tAs, pH, TDS and salinity (p = 0.08 to 0.01). The levels of F⁻ and tAs have + ve association among each other, though, these both elements are enrich in ground water (AQ2) of coal mining area, its drain outlet and storage in a reservoir, signifying the involvement of both elements have general source (Jamshed et al., 2017) [39]. A significant correlation between F⁻ and Ca⁺ also indicates the presence of a mineral like fluorapatite, apatite, and fluor spar indicates geological factors. These results indicates that the high contents of As and fluoride in reservoir can be creates adverse impact on the local population. In some areas of the world, groundwater is polluted with As and F⁻, causes serious health disaster on living beings (Milton et al., 2004). In addition Pakistan (Ayoob et al., 2006; Rafique et al., 2009) and Inner Mongolia also have same problem (Smedley et al., 2002, McCaffrey and Willis, 2001).

The resulted data indicates that the F⁻ have significantly high correlation among pH (r = 0.920, p = 0.012), this might be owing to the same size of ionic radii of F⁻ and “OH, which often replaced with each other, contained by minerals. These results are consisted with future studies (Rafique et al., 2009; Vasquez et al., 2006). It was indicated in literature that the clay minerals in mining area are capable to hold F⁻ ions on their surfaces, however at elevated pH, the OH ions can dislocate the F⁻ ions, which can easily released to groundwater (Rafique et al., 2009; Sreedevi et al., 2006. Thus, the groundwater samples of AQ2 was slightly alkaline which facilitate the dissolution of F⁻ (Saxena and Ahmed, 2003). This information designates that the groundwater samples of 2nd aquifer (AQ2) of Thar coalfield, DW, and from four samples site of reservoir/Gorano dam have elevated concentrations of F⁻ and pH (7.2-7.8). The F⁻ have weak connection with HCO₃⁻ (r = 0.170, p < 0.001).

The high exposure of F⁻ (> 1.5 mg/L) creates adverse impact on the humans especially dental and skeletal fluorosis and in addition high intake of F⁻ for long time might be causes impairment in muscles, kidneys and nerves system (Ayoob and Gupta, 2006). The dilemma of fluorosis involving dental and skeletal system is frequent occur in the areas of crystalline basement rocks, predominantly those have composition granitic in nature in diverse areas of the world (Martinez-Mier et al., 2016). The people around the coal mining area (Tharparkar, Sindh province of Pakistan) are rigorously suffer from bone deformation, skeletal and dental fluorosis in human as well as in cattle (Rafique et al., 2009 Kazi et al., 2018).

3.5. Sediment Analysis

The average concentration of the iron, sodium, potassium, arsenic, cadmium and lead in the sediment samples collected from four sites of reservoir (SD1, SD2, SD3 and SD4) for subsequent two month, are shown in Table 4. The resulted data based on dry weight basis. It was observed that the concentration all elements were inversely proportion to those values obtained from corresponding water samples, might be due to settling of them with distance of reservoir (2.0 km). The concentration of As was found in the
range of 6.7–11, 10.8–13.7, 17.3–20.8 and 22.7–28.6 in SD1, SD2, SD3 and SD4, respectively. It was observed that the contents of As was enhance three fold of those value observed in first site adjacent to drain outlet. The contents of Cd at SD1, SD2, SD3 and SD4 were found in the range of 7.65–9.45, 10.5–12.8, 12.4–14.7 and 16.4–20.4 mg/kg, respectively. The concentration was found in the ranges of (16.5–18.6) (30.5–33.9) (45.3–48.4) (53.6–55.7). The Cd was enhanced from SD1 To SD4 $\geq$ 2.0, whereas the Pb concentration increase upto 3 time. The sediment serves as a reservoir or sink of the metal pollutants in water reservoir However the concentration of all elements in sediment was much higher than in water, which is consistent with previous studies (An and Kampbell, 2003; Anazawa et al., 2004).
Table 4
Concentration of toxic elements in bottom sediment of reservoir.

| Variables/parameters | F1   | F2   | F3   | F4   |
|----------------------|------|------|------|------|
| pH                   | 0.610| 0.758| 0.218| -0.031|
| EC                   | 0.872| -0.477| 0.002| 0.111|
| TDS                  | 0.368| 0.915| 0.155| 0.038|
| Sal                  | 0.658| 0.283| -0.697| 0.000|
| F^-                  | 0.433| 0.891| -0.087| 0.099|
| Cl^-                 | 0.300| 0.950| -0.087| 0.001|
| NO3^-                | 0.988| -0.100| -0.085| -0.070|
| SO4^-2               | 0.450| 0.891| 0.017| -0.046|
| HCO3^-               | 0.880| -0.274| 0.067| 0.383|
| Na^+                 | 0.692| 0.150| 0.703| -0.058|
| K^+                  | 0.985| -0.122| -0.097| -0.075|
| Ca^2+                | 0.896| -0.422| -0.113| -0.074|
| Mg^2+                | 0.842| -0.517| -0.078| -0.065|
| Fe^3+                | 0.978| -0.159| -0.008| -0.136|
| Cd^2+                | 0.961| -0.268| 0.058| 0.006|
| Pb^2+                | 0.853| -0.504| 0.131| -0.022|
| tAs                  | 0.411| 0.907| -0.088| -0.006|
| Eigenvalue            | 9.67 | 5.95 | 1.14 | 0.216 |
| Variability %)        | 56.9 | 35.0 | 6.67 | 1.27  |
| Cumulative %          | 56.9 | 91.9 | 98.6 | 99.8  |
| Elements              | SD1  | SD2  | SD3  | SD4  |
| As                   | 8.5 ± 1.7 | 12.4 ± 1.01 | 18.8 ± 1.4 | 25.4 ± 1.8 |
| Cd                   | 8.5 ± 0.6 | 11.8 ± 0.9 | 13.5 ± 0.8 | 18.6 ± 1.2 |
| Pb                   | 17.6 ± 0.8 | 32.4 ± 1.2 | 46.5 ± 1.06 | 54.4 ± 0.8 |
4. Conclusion

It was observed that the discharge of groundwater of aquifer 2 of coal mining area due to construction of power plant, in a newly prepared reservoir/gorano dam. The variation in physico-chemical characteristics, anion, cation and toxic elements was determined. The resulted data indicated that the all parameters in water samples are sequentially decrease from AQ2 to S4. The multivariate technique, principle component analysis helped in recognized the causes responsible for the variations water quality from AQ2 to S4 are only geologic in nature. The cluster analysis grouped six sampling sites into two clusters on the basis of similar characteristics of water samples of different origin. It was observed that all selected physico-chemical parameters, cations, anions, and toxic elements were higher than the suggested limits by WHO. The high values of sodium absorption ratio of water samples of reservoir indicates that they are not suitable for agricultural purposes. Further studies should be focused on the bio-accumulation of As and F\(^{-}\) in aquatic biota and hazards associated with their consumption.

Declarations

Conflict of interests

The all authors declared not any conflict of interest

Consent to Participate

Not applicable

Consent to Publish

Not applicable

Ethical Approval

Not applicable

Credit authorship contribution statement

Tasneem Gul Kazi and Shahabuddin Memon: Made a project of this whole research work, composed the work, Asif Ali Unar: had done sampling and analyzed all physicochemical parameters

Availability of data and materials

The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.

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