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Research Article

# Evaluation of Physicochemical Characteristics and Change in Concentration of Toxic Elements in Groundwater Collected from Different Sites of 2nd Aquifer of Coal Mining Area and Water Reservoir by Applying Multivariate Techniques

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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/ Goran dam. The ground water samples of 2nd aquifer (AQ2) of Thar coalfield were collected from the depth of 100-120 mand further sampling of water was carried out from drain outlet (DW) from the reservoir. Simultaneously the sediment samples were also collected from the same sites of the reservoir and analyzed for toxic elements. The large datasets of water quality of AQ2, DW and four sampling sites at different spots of reservoir were collected during 2019. The all-water samples were analyzed for physicochemical parameters, 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 described in terms of basic statistical parameters, PCA and CA. The chemical correlations among different parameters were observed by PCA, which was employed to categorize the water samples by CA. The positive correlation of fluoride 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 indicates that the high levels of physicochemical parameters and toxic elements in both ground and reservoir water make it unsuitable for drinking, domestic and agricultural purposes.

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

## 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 plants [Ali et al. 2015; Imran et al. 2014] [1,2]. 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] [3,4]. 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 through mining processes frequently causes considerable changes in its physico-chemical characteristics as well as regularly creates depression of groundwater in the region [Ali et al., 2015] [1].

The feature of groundwater based on different factors, 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] [5,6,7,8]. Ground and surface water, soil and different foods are to be regard as main resources of different forms of Arsenic (As) [Tuzen et al., 2010] [9]. The consumption of contaminated water with Arsenic (As) in the different regions of the world is the main task for the scientists [Smedley et al., 2002; Baig et al., 2009a; Brahman et al., 2013; Farooqi et al., 2007] [5,10,11,12]. The As can be classified as inorganic arsenate ($H_2AsO_4$), arsenate ($H_2AsO_3$) and organic forms (methyl arsenic acid [$CH_3AsO(OH)_2$] and di-methyl arsenic acid [$(CH_3)_2AsO(OH)$]. Different researchers 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] [13, 14,15].

Generally, the organic As compounds are less toxic than inorganic (As compounds). For determining inorganic arsenic in water, very sensitive methods were developed [Marahel et al., 2011] [16]. Cadmium (Cd) is also a dangerous heavy metal to living beings, it can cause injures to the organs of living beings such as kidney, Lungs and Liver [Bernard, 2008; Satarug et al., 2011] [17, 18]. Intake of Cd 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] [19]. The Cd is also discouraging the function of essential elements such as zinc assisted enzymes by exchange it. Due to advance in industrialization the atmosphere is highly contaminated with lead (Pb), which in turn causes contamination of water and air and other things. The lead has no beneficial effects for living beings and creates hazardous impact such as damage of brain, anemia, kidney disorder and hematological disorder [Shah et al., 2010] [20].

To analyze the metals and metalloids in environmental and biological samples numbers of techniques have been comprehensively used including: atomic absorption spectrometry [Detcheva and Grobecker, 2008] [21], inductively coupled plasma optical emission spectrometry [Zhu and Alexandratos, 2007] [22] and others. For coal mining purposes the elimination of water of aquifer system (ground water) might be expensive. The open cut withdrawal system needs the proficient lamination of overload and inter-burden stratum in order to access the coal seams. The dewatering of the surface mine is carried out by use of a pumping-out system 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] [23].

The current study has been in connection with Thar coalfield, where the coal mining and power generation plant is developed by Sindh Engro Coal Mining Company. Initially the ground water of 2nd aquifer of block 2 of Thar coal field, had started releasing into a reservoir, locally called Goran 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 (pH, EC, TDS, salinity, $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $SO_4^{2-}$, $HCO_3^-$ , $Fe^{3+}$, $NO_3^-$, 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/groan dam were analyzed for toxic elements. The accuracy of the methodologies was determined by simultaneously analyzed matrices matched certified sample of water.

The huge data set obtained was calculated effectively 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 a 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, 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. In addition, the sodium absorption ratio of each site was also calculated.

## Material and Methods

### Study area

The huge reservoir of natural coal is present in district Tharparkar, Sindh, Pakistan, detail is reported in our previous work [Ali et al., 2017] [24]. 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 at the depth of 120 m, in Goran reservoir, which is newly developed reservoir in 2017 spread in 1,500 acres. This site completely reserved for dewatering site of Thar coal mining field. The ground water discharge by a pipe which is 27 Km away from coal mine site. The Goran dam/reservoir is geographically located at the southern part of Pakistan. The water sampling was carried out from ground water of 2nd aquafer from 120 m, drain outlet and four sites of reservoir as mention in (Figure 1).

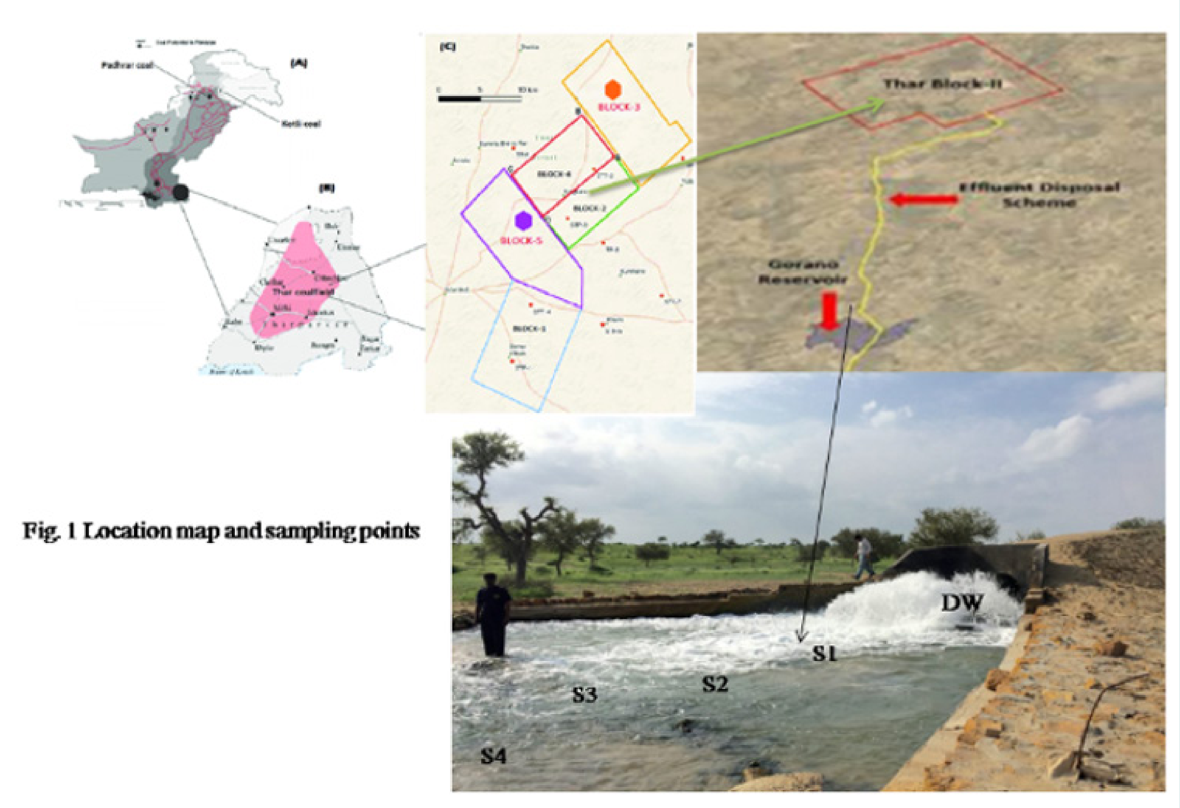

**Figure 1:** Location map and sampling points

## 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) of analytical grade. The standard solution of As, Cd, Pb and other cations were prepared from certified standard solution (1000 ppm) obtained from Fluka Kamika (Buchs, Switzerland) and made up to volume with. 0.1M $HNO_3$. Before analysis all the glassware was kept in 5M $HNO_3$ for 24 hours and then rinsed with deionized water.

## 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 Thermos Scientific™ iCAP™ 7000 Series ICP-OES, anatomic absorption spectrometer Model 700, Perkin Elmer (Norwalk, CT, USA), equipped with hollow cathode lamps and air–acetylene burner has been used. For the physico-chemical parameters such as, electrical conductivity (EC), and total dissolved solids (TDS) by a conductometer (Ino Lab conduc. 720, Germany) was used.

## Sampling and pretreatment

Samples of water were collected in summer of 2019 for two months, 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 groundwater of second aquifer as (AQ2). Then further sampling was carried out from the drain outlet of groundwater of second aquifer of block-2 in a Goran 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(1.5Lcapacity), equipped with a simple pull-ring that allowed for sampling of water at surface and depths of 20 30cm,-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 made 10 composite samples of water samples obtained for AQ2 and DW. Whereas water samples of four sampling sites was made five composite samples of each (surface and lower levels of same site). Then filtered through 0.45 micro-spore size membrane for the removal of suspended particular materials 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 of reservoir (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 the laboratory. In laboratory sediment samples were dried in fuming cupboard under air stream for 24 h. Then crushed and passing through a sieve (200µm). For the preparation of sediment sample, triplicate of each sample (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 one h, for oxidation of the organic matrices. Then cooled the contents of crucible and added 10mL of 0.2M solution of nitric acid ($HNO_3$). Finally, filtered the solution in sample bottles of 100 mL in capacity using Whatman filter paper and subjected to instrument.

## Analytical procedures

The analysis of water samples of different origin (AQ2, DW, S1, S2, S3 and S4) for different physic- chemical parameters was 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 sample was taken in 100 ml of beaker and with the help of pH-meter and conductometer, different physic-chemical parameters such as pH, TDS, EC and salinity were measured (Table 1S). The TDS was not measured in water samples directly due to its high value, and for that purposes each composite sample (n=10) was 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).

**Table 1S:** The water quality parameters associated with their abbreviations, units and analytical method.

| Variables | Abbreviations | Units | Analytical methods |
|---|---|---|---|
| pH | pH | pH Unit | $pH^-$ meter |
| Electric-Conductivity | EC | mS/cm | Conductivity meter |
| Total Dissolved Solids | TDS | mg/L | -------------------- |
| Salinity | Sal | mg/L | -------------------- |
| Fluoride | $F^-$ | mg/L | Ion chromatography |
| Chloride | $CL^-$ | mg/L | -------------------- |
| Nitrate | $NO_3^-$ | mg/L | -------------------- |
| Sulphate | $SO_4^{2-}$ | mg/L | -------------------- |
| Bicarbonate | $HCO_3^-$ | mg/L | Titrimetric |
| Sodium | $Na^+$ | mg/L | FAAS |
| Potassium | $K^+$ | mg/L | FAAS |
| Calcium | $Ca^{2+}$ | mg/L | FAAS |
| Magnesium | $Mg^{2+}$ | mg/L | FAAS |
| Iron | Fe | mg/L | FAAS |
| Total Arsenic | As | µg/L | ICP-OES |
| Cadmium | Cd | µg/L | ICP-OES |
| Lead | Pb | µg/L | ICP-OES |

The other experimental steps were indicated in our previous work (Brahman et al., 2013), to determine the anions a mixed standard of each $F^-$, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$was made at different concentration range (0.5-10 $mgL^{-1}$) from certified stock standard solutions. The major cations, $Ca^{2+}$, $Na^+$, $K^+$ and $Mg^{2+}$ were analyzed in 20-time diluted water samples with ultrapure water using 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 was estimated by the total and comparative levels of cations and stated as sodium absorption ratio (SAR). The method for calculating the SAR is also accounted in previous work (Brahman et al., 2013).

## Statistical evaluation

To analyze the resulted data obtained by the analysis of 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 drawing out the information to facilitate the evaluation of water quality (Liu et al., 2003; Kazi et al. 2009; Brahman et al., 2013) [25,15,11]. 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).

### Application of multivariate technique

Basic statistics was carried out in order to give initial information about the change of water quality of different origin (AQ2, DW, S1, S2, S3 and S4). The multivariate techniques, CA and PCA were applied to evaluate the quality of water samples at different origin (Kazi et al. 2009, Arain et al., 2014 Brahman et al., 2013) [15,26,11]. The CA Involves in calculating either distance or the resemblance among resulted data 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 (replicate average values of observations of all water samples of different origin) using Ward's method with squared Euclidean distances (Arain et al. 2014; Sarbu and Pop 2005) [26,27]. The both multivariate techniques were applied on the resulted data of eighteen thousand, three hundred sixty values (17 factors) determined in ten composite samples in triplicate of each origin such as6 sampling sites in twice (sampling in two month) and analysis in triplicate (17×6×30×2×3=18360).

### Analytical figure of merit

The calibration of standards was 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) of all selected elements were estimated according to $LOD = x\frac{s}{m}$ where "s" is the standard deviation of 10 determinations of the blank and "m" is the slope of the calibration graph attained, the LODs as 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 from the limit of quantification up to 20µg/L using ICP-OES. The LOD were found as 0.02, 0.13 and 0.05µg/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 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 site (AQ2, DW, S1, S2, S3 and S4) were within the ±5%., the ionic balances were 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) Certified values | Measured values | SRM Sediment 1944 (mg/Kg) Certified values | Measured values |
|---|---|---|---|---|
| Na | 20,740±260 | 20,500±284$^{a}$-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±0.81-98.3% | 18.9±2.8 | 18.6±2.9-98.4 |
| Cd | 6.6±0.07 | 6.5±0.06-98.4% | 8.8±1.4 | 8.7±1.3-98.8 |
| Pb | 19.6±1.21 | 19.2±1.25-98.3% | 330±48.0 | 325±49.0-98.5 |

$^{a} means \pm s$

$^{b}$Values in the parenthesis ( ) indicates %Recovery).

## Results and Discussion

The mean values with standard deviation (n=30) of physic-chemical parameters of groundwater (AQ2), drain outlet and four sites of reservoir (Goran 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 $SO_4^{2-}$ 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 was found in the range of 7.75-8.5, 7.6-7.92, 7.5-7.75, 7.2-7.64, 7.0-7.4and 6.7-7.2respectively, which are consisted with WHO regulated levels. However, it is slightly alkaline in nature, which is attributable to the concentration of $HCO_3$ ion, which is relatively high in all sites of reservoir, range das 249 to 397mgL$^{-1}$. However, the pH values of water samples of reservoir were diminished with the distance. The reduction in pH values is taking placed owing to the decline in dissolved minerals (Tripathy 2002).

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**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 Groan 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 mS/cm | 0.25 | 10.8±1.44 | 10.4±1.1 | 9.44±1.12 | 8.24±1.2 | 7.34±0.85 | 6.24 ±0.88 |
| $^{a}$TDS | 1000 | 9350±202 | 9290±147 | 9190±298 | 7280± 435 | 5650±368 | 4930±312 |
| SAL$^{a}$ | - | 9.85±5.80 | 9.71±0.78 | 9.2±1.92 | 7.3±1.55 | 5.7±1.18 | 5.1±1.52 |
| $^{a}$F$^{-}$ | 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 |
| $^{a}$CL$^{-}$ | 250 | 1360±44.4 | 1340±58.7 | 1330±86.8 | 1220±84.2 | 1110±71.1 | 920±47.5 |
| $^{a}$NO$_3^{-}$ | 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 |
| $^{a}$SO$_4^{-2}$ | 500 | 597±71.9 | 565±70.3 | 535±117 | 481.5±106 | 401±88 | 339±74 |
| HCO$_3^{-}$ | - | 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 |
| Pb | 10 | 60.8±7.76 | 59.2±8.55 | 55.8±6.91 | 44.2±6.25 | 36±5.45 | 31.4±4.24 |

Key =$^{a}$ mg/L; $^{b}$ µg/L

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, 5.89-7.45mS/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) , drained 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) [28,29].

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 samples. The EC of groundwater (AQ2) samples was found as24 to 40 time elevated than WHO guidelines for drinking water (Table 2). It was observed that the changes in EC is directly proportional to TDS values. The values of Na$^{+}$ were observed in the range of 1610-1720,1588-1703, 1210-2000, 1117-1847, 1016-1680, and859-1420 mg/L for AQ2, DW, S1, S2, S3 and S4, whereas the levels 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, respectively. The levels of Ca$^{2+}$ were observed in the range of 345-410, 333-391, 339-382, 313-353, 282-318and 241-271mg/L. It was detected that the groundwater samples (AQ2) and DW have elevated concentrations of Na$^{+}$, which indicates that either due to the solubilization of lithogenic Na+ or swap over the soluble Ca$^{2+}$ with Na$^{+}$ via minerals origin in clay of coal mining area (block 2). Guo and Wang, 2007 et al., have also supported the hypo thesis that due to high ratio of Na$^{+}$/Ca$^{2+}$(4.42), 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, and the levels of Fe were found 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, respectively. The levels of Fe were 3 to 5 folds higher in water samples of AQ2, whereas at S4, the concentration of Fe was reduced but still higher than the 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 (1304t1519, 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.

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The obtained results indicate that ground water of AQ2, DW, S1, S2, S3 and S4 is contaminated with high concentration of As, Cd and Pb, which are higher than the suggested WHO limit for drinking water (10 μgL$^{-1}$). The total contents of As in AQ2 was found in the range of 39.2 59.5 μg/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), was found to be decreasing, observed in the range of 35-57, 32-53, 30-48 and 25.5-40.0 μg/L. The total Cd in water samples of 2nd aquifer of Block 2 of coal mining area and drained water was observed in the range of 35-58 μgL$^{-1}$ and 34-51μgL$^{-1}$, respectively, indicates insignificant difference ($p<0.05$). The water samples of reservoir were observed in the range of 33-44, 19-36, 16-25 and 11.5-20.4 μgL$^{-1}$ for S1, S2, S3 and S4, respectively. The resulted data indicate two to four folds higher levels of Cd in all water samples than allowable 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 μgL$^{-1}$, respectively, these all values were three to six folds 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 <S4as shown in (Table 2).

## 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

$$SAR = \left[Na^{+}\right] \Big/ \left\{\left(\left[Ca^{2+}\right] + \left[Mg^{2+}\right]\right)\Big/ 2\right\}^{1/2}$$

Where $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ indicates their respective 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 were 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 samples, 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 into causes infiltration problems in soil. As the study area have shortage of surface water and if the water of reservoir for agricultural purpose, causes adverse impacts on the crops due to excess of Na, can creates transitory saturation of the surface soil. Whereas the high pH and enhanced the potential effects on soil erosion, lack of oxygen and inadequate availability of nutrient. It was reported by Van Vorst, 2003, that water samples from the coal beds have high levels of Na and low in calcium and magnesium, resulting in a high SAR value (Cannon et al., 2007) [30].

## Multivariate statistical analysis

Cluster analysis (CA) was also applied for qualitatively analyze the differences and similarity among the water samples of ground water of aquifer 2, 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 physic-chemical variables (physio-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) [15].

The dendrogram indicates the grouping of all six sampling sites, based on resulted data of all variables, into two statistically important clusters (Figure 2). The results of all physic chemical parameters of water samples of all selected origin after their scaling by z-transformation, to measures the % of similarity and for the construction of a dendrogram have been determine (Chen et al. 2007) [31]. At similarity level of 100%, two clusters were 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, site-2 was involved. The second cluster (B) on the right side is further divided in to two groups. One comprised of AQ2 and DW (where no significant difference was observed in levels of different toxic elements, cations, anions and physic chemical parameters. Whereas the second group is involved the sampling site (S1), that is located at 500-meter distance from the drain outlet, where the levels of all physic- chemical data including toxic elements were considerably decreased from AQ2 and DW, though the dissimilarity was not significant ($p> 0.05$) (Figure 3).

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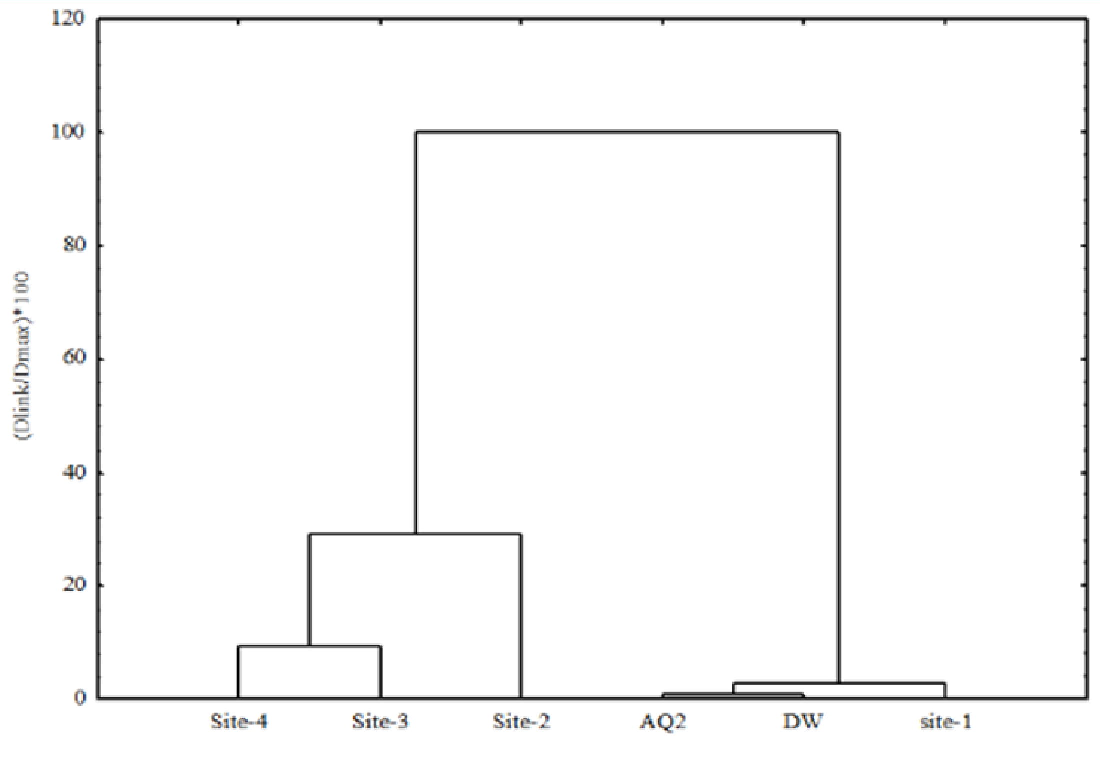

**Figure 2:** Dendrogram showing clustering of different sites based on physic-chemical and toxic elements

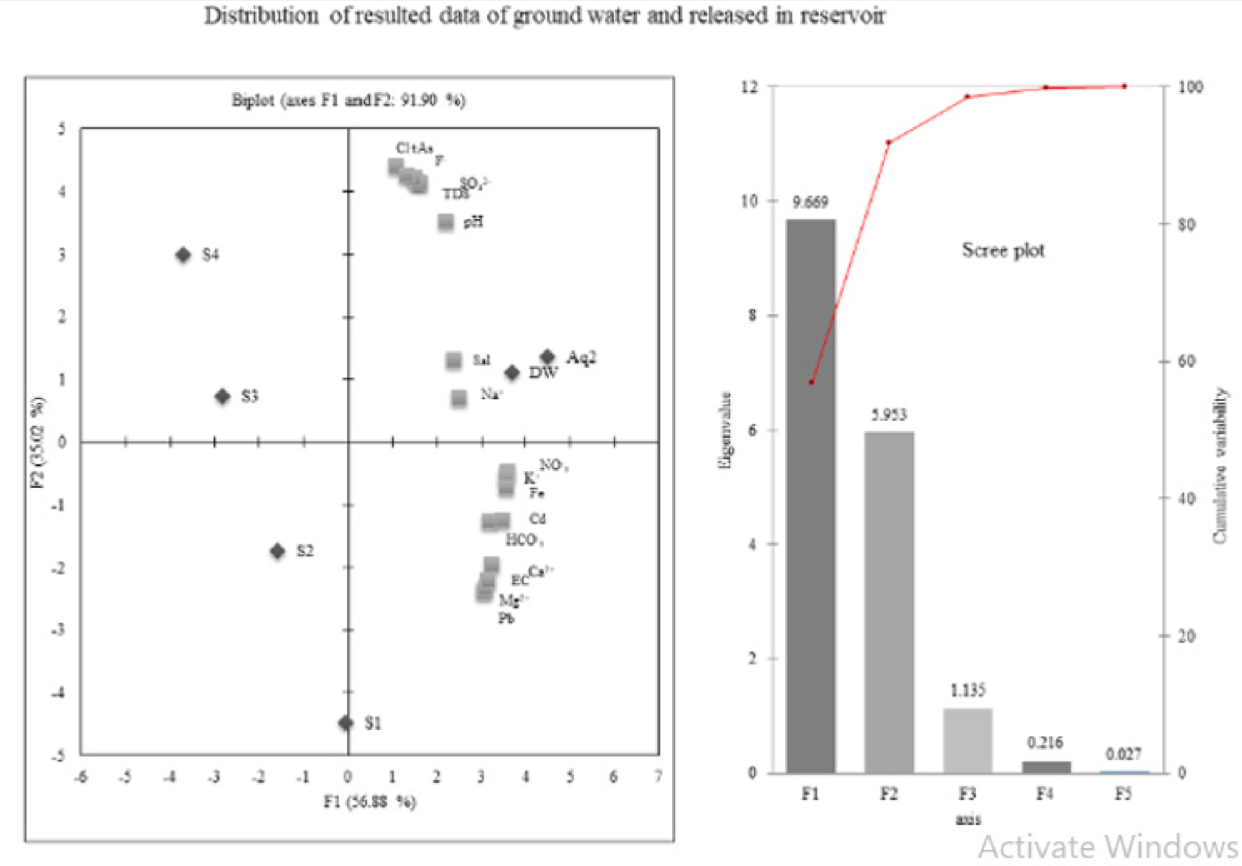

**Figure 3:** Distribution of resulted data of ground water and rereleased in reservoir.

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) [27]. 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 of resulted data set of water samples obtained from different origin is shown in (Table 3). The most important point of view was 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 (Figure 2) indicates high loading data for $Cl^-$, tAs, $F^-$, $SO_4^{2-}$, TDS, PH, $Na^+$ and Salinity especially in AQ2 and DW. The positive loading in 2ndcomponent was observed for, $NO_3$, K, Fe, Cd, $HCO_3$, 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.

**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 | 0.61 | 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 |
| $F^-$ | 0.433 | 0.891 | -0.087 | 0.099 |
| $Cl^-$ | 0.3 | 0.95 | -0.087 | 0.001 |
| $NO_3^-$ | 0.988 | -0.1 | -0.085 | -0.07 |
| $SO_4^{-2}$ | 0.45 | 0.891 | 0.017 | -0.046 |
| $HCO_3^-$ | 0.88 | -0.274 | 0.067 | 0.383 |
| $Na^+$ | 0.692 | 0.15 | 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 | 6.67 | 1.27 |
| Cumulative % | 56.9 | 91.9 | 98.6 | 99.8 |

## 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 of reservoir, have equal distance 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 $HCO^{3-}$ and $Mg^{2+}$. This capacity is might be due to the less accessibility of gypsum and carbonated rocks (Brahman et al. 2013) [11].

The Pearson correlation between physic-chemical parameter, anions, cations and toxic elements in groundwater of 2nd aquifer (AQ2) of Thar coalfield, DW, and from four samples site of reservoir/Goran dam are shown in Table2S 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 $Cl^-$, $F^-$, $SO_4^{2-}$, tAs, $NO^{3-}$, $HCO_3^-$, $Ca^{2+}$, $Mg^{2+,}$ Fe, Cd and Pb for water sam-

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ples obtained from AQ2, DW, S1, S2, S3 and S4 at 95% confidence level, which may be due to the high solubilization of 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 has 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 $Cl^-$, $SO_4^{2-}$ $Ca^{2+}$, tAs, pH, TDS and salinity (p= 0.08 to 0.01). The levels of $F^-$ and tA shave +ve association among each other, though, these both elements are enriched in ground water (AQ2) of coal mining area, its drain outlet and storage in a reservoir, indicated that the involvement of both elements have general source (Jamshed et al., 2017).

A significant correlation between $F^-$ and $Ca^+$ also indicates the presence of minerals like fluorapatite, apatite, and fluorspar 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) [32]. In addition, Pakistan and Inner Mongolia also have same problem (Smedley et al., 2002, McCaffrey and Willis, 2001; Ayoob et al., 2006; Rafique et al., 2009) [5,33,7,8].

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. These results are consisted with reported studies (Rafique et al., 2009; Vasquez et al., 2006) [8,34]. 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 release to groundwater (Rafique et al., 2009; Sreedevi et al., 2006. Thus, the groundwater samples of AQ2 were slightly alkaline which facilitate the dissolution of $F^-$ (Saxena and Ahmed, 2003) [35]. This information designates that the groundwater samples of 2nd aquifer (AQ2) of Thar coalfield, DW, and from four samples site of reservoir/Goran dam have elevated concentrations of $F^-$ and pH (7.2-7.8). The $F^-$ have weak connection with $HCO_3^-$ (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, whereas elevated intake of $F^-$ for long time might be causes impairment in muscles, kidneys and nerves system (Ayoob and Gupta, 2006) [7].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) [36].The people around the coal mining area (Tharparkar, Sindh province of Pakistan)are rigorously suffer from bone deformation, skeletaland dental fluorosis in human as well as in cattle (Rafique et al., 2009; Kazi et al.,2018) [8,37].

### 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 concentrations of toxic 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-folds 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 of Pb was found in the ranges of (16.5-18.6) (30.5-33.9) (45.3-48.4) (53.6-55.7) in SD1, SD2, SD3 and SD4 respectively. The Cd was enhanced from SD-1To SD4 ≥ 2.0, whereas the Pb concentration increase up to 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) [38,39,40,41].

**Table 4:** Concentration of toxic elements in bottom sediment of reservoir.

| 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 |

## 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/Goran dam. The variation in physic-chemical characteristics and toxic elements was determined. The resulted data indicated that all parameters in water samples are sequentially decreasing from AQ2 to S4. The multivariate technique, principal component analysis helped in recognizing the causes responsible for the variations in water quality from AQ2 to S4 are only geologic in nature [42,43,44,45,46]. 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 physic-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.

## References

1. Ali J, Kazi TG, Baig JA, Afridi HI and Arain et al., (2015) Arsenic in coal of the Thar coalfield, Pakistan, and its behavior during combustion. Environ Sci Poll Res 22(11): 8559-66.
2. Imran M, Kumar D, Kumar N, Qayyum A and Saeed A et al., (2014) Environmental concerns of underground coal gasification. Renew Sust Energy Rev 31: 600-610.
3. Singh AK, Mahato M, Neogi B, Tewary B and Sinha A et al., (2012) Environmental geochemistry and quality assessment of mine water of Jharia coalfield, India. Environ Earth Sci65:49-65.
4. Kurwadkar S (2019) Occurrence and distribution of organic and inorganic pollutants in groundwater. Annual Literature Review Water Environ Res 91(10): 1001-1008.
5. Smedley PL, Nicolli HB, Macdonald DMJ, Barros AJ and Tullio J O et al., (2002) Hydrogeo chemistry of arsenic and other inorganic constituents in ground water from La Pampa, Argentina. Appl Geochem 17(3): 259-284.
6. Anwar HM, Akai J, Komaki K, Terao H and Yoshioka T et al., (2003) Geochemical occurrence of arsenic in groundwater of Bangladesh sources and mobilization processes. J Geochem Explore77(2-3): 109-131.
7. Ayoob S, Gupta AK (2006) Fluoride in drinking water a review on the status and stress effects. Crit Rev Env Sci Technol 36(6): 433-487.
8. Rafique T, Naseem S, Usmani TH, Bashir E and Khan F A et al., (2009) Geochemical factors controlling the occurrence of high fluoride groundwater in the Nagar Parkar area, Sindh, Pakistan. J Hazard Mater 171: 424-430.
9. Tuzen M, Saygi KO, Karaman I, Soylak M (2010) Selective speciation and determination of inorganic arsenic in water, food and biological samples. Food Chem Toxicol 48(1):41-46.
10. Baig JA, Kazi TG, Arain MB, Afridi HI and Kandhro GA et al., (2009) Evaluation of arsenic and other physico-chemical parameters of surface and ground water of Jamshoro, Pakistan. J Hazard Mater 166(2-3): 662-669.
11. Brahman KD, Kazi TG, Afridi HI, Naseem S and Arain S et al., (2013) Evaluation of high levels of fluoride, arsenic species and other physicochemical parameters in underground water of two sub-districts Tharparkar, Pakistan: a multivariate study. Water Res 47:1005-1020.
12. Farooqi A, Masuda H, Firdous N (2007) Toxic fluoride and arsenic contaminated groundwater in the Lahore and Kasur districts, Punjab, Pakistan and possible contaminant sources. Environ Pollut 145(3): 839-849.
13. Morales KH, Ryan L, Kuo TL, Wu MM and Chen CJ et al., (2000) Risk of internal cancers from arsenic in drinking water. Environ Health Perspect 108(7): 655-661.
14. Yoshida T, Yamauchi H, Fan Sun G (2004) chronic health effects in people exposed to arsenic via the drinking water: dose–response relationships in review. Toxicol Appl Pharmacol 198(3): 243-252.
15. Kazi TG, Arain MB, Baig JA, Jamali MK and Afridi HI et al., (2009) The correlation of arsenic levels in drinking water with the biological samples of skin disorders. Sci Total Environ 407(3): 1019-1026.
16. Marahel F, Ghaedi M, Montazerozohori M, Nejati Biyareh M and Nasiri Kokhdan S et al., (2011) Solid-phase extraction and determination of trace amount of some metal ions on Duolite XAD 761 modified with a new Schiff base as chelating agent in some food samples. Food and Chemical Toxicology 49 (1): 208-214.
17. Bernard A (2008) Cadmium and its adverse effects on human health. Indian J Med Res128(4): 557-64.
18. Satarug S, Garrett SH, Sens MA, Sens DA (2011) Cadmium, environmental exposure, and health outcomes. CienciaSaude Coletiva; 16(5):2587-2602.
19. Chakraborty S, Dutta AR, Sural S, Gupta D and Sen S et al., (2013) Ailing bones and failing kidneys: a case of chronic cadmium toxicity. Ann Clin Biochem 50: 492-495.
20. Shah F, Kazi TG, Afridi HI, Baig JA and Khan S et al., (2010) Environmental exposure of lead and iron deficit anemia in children age ranged 1-5 years: a cross-sectional study. Sci Total Environ 408(22): 5325-5330.
21. Detcheva A, Grobecker KH (2008) Determination of trace elementsin aquatic plants by means of solid sampling Zeeman atomicabsorption spectrometry (SS-ZAAS). Environ Chem Lett 6: 183-187.
22. Zhu X, Alexandratos SD (2007) Determination of trace levels of mercury in aqueous solutions by inductively coupled plasma atomic emission spectrometry: elimination of the 'memory effect'. Micro-chem J 86(1): 37-41.
23. Liang Z, Ren T, Ningbo W (2017) Groundwater impact of open cut coal mine and an assessment methodology: A case study in NSW. Int J Min Sci Technol 27: 861-866.
24. Ali J, Kazi TG, M Tuzen (2017) Evaluation of mercury and physicochemical parameters in different depths of aquifer water of Thar coalfield, Pakistan. Environ Sci Poll Res 24: 17731-17740.
25. Liu CW, Lin KH, Kuo YM (2003) Application of factor analysis in the assessment of groundwater quality in a black foot disease area in Taiwan. Sci Total Environ 313(1-3): 77-89.
26. Arain MB, Kazi TG, Baig JA, Jamali MK and Afridi HI et al., (2009) Determination of arsenic levels in lake water, sediment and food stuff from selected area of Sindh, Pakistan: estimation of daily dietary intake. Food Chem Toxicol 47(1): 242-248.
27. Sarbu C, Pop HF (2005) Principal component analysis versus fuzzy principal component analysis A case study: the quality of Danube water (1985-1996). Talanta 65(5): 1215-1220.
28. Brahman KD, Kazi TG, Afridi HI, Rafique T and Baig JA et al**.** (2014) Evaluation of fresh and stored rain water quality in fluoride and arsenic endemic area of Thar Desert, Pakistan. Environ Monit Assess 186: 8611-8628.
29. Nag S, Saha S (2014) Integration of GI Sand remote sensing in groundwater investigations: a case study in Gangajalghati Block, Bankura District, and West Bengal, India. Arabian J Sci Engin 1-11.
30. Cannon MR, Nimick DA, Cleasby TE, Kinsey SM and Lambing J H et al., (2007) Measured and estimated sodium-adsorption ratios for Tongue River and its tributaries, Montana and Wyoming, 2004-06. U S Geological Survey Scientific Investigations Report 2007-5072.
31. Chen K, Joao J, Huang J, Huang R (2007) Multivariate statistical évaluation of trace elements in groundwater in a coastal area in Shenzhen, China. Environmental Pollution 147(3): 771-780.
32. Milton AH, Hasan Z, Shahidullah S, Sharmin S and Jakariya M et al., (2004) Association between nutritional status and arsenicosis due to chronic arsenic exposure in Bangladesh. Int J Env Health Res 14(2): 99-108.
33. McCaffrey LP, Willis JP (2001) Distribution of Fluoride-rich Groundwater in the Eastern and Mogwase Regions of the Northern and North-west Province. WRC Report No 526/1/01 Pretoria South Africa 1: 1-985.
34. Vasquez LV, Hernandez JR, Lopez JR, Uribe AS and Mancilla OL et al., (2006) The origin of fluoride in groundwater supply to Hermosillo City, Sonora, Mexico. Environ Geol 51: 17-27.
35. Saxena VK, Ahmed S (2003) Inferring the chemical parameters for the dissolution of fluoride in groundwater. Environmental Geology 43: 731-736.

36. Martinez-Mier EA, Shone DB, Buckley CM, Ando M and Lippert et al., (2016) Relationship between enamel fluorosis severity and fluoride content. J Dent 46: 42-6.
37. Kazi TG, Brahman KD, Afridi HI, Shah F and Arain MB et al., (2018) Effects of high fluoride content in livestock drinking water on milk samples of different cattle in endemic area of Pakistan: Risk assessment for children. Environ Sci Pollut Res 25(13): 12909-12914.
38. An YJ, Kampbell DH (2003) Total, dissolved, and bioavailable metals at Lake Texoma marinas. Environ Pollute 122(2): 253-259.
39. Anazawa K, Kaida Y, Shinomura Y, Tomiyasu T and Sakamoto H et al., (2004) Heavy-metals distribution in river waters and sediments around a ‘‘Firefly village’’, Japan: application of multivariate analysis. Anal Sci 201:79-84.
40. APH Association (2005) American Water Works Association and Water Pollution Control Federation, 1998 Standard methods for the examination of water and wastewater, 20th edn. APHA Washington DC.
41. Guo Q, Wang Y (2007) Geochemical processes controlling the elevated fluoride concentrations in groundwaters of the Taiyuan Basin, Northern China. J Geochem Explor 93(1): 1-12.
42. Kazi TG, Arain MB, Jamali MK, Jalbani N and Afridi HI et al., (2009) Assessment of water quality of polluted lake using multivariate statistical techniques: a case study. Ecotoxicology and Environmental Safety 72(2):301-309.
43. Kazi TG, Wadhwa SK, Afridi HI, Talpur FN and Tuzen M et al., (2015) Comparison of essential and toxic elements in esophagus, lung, mouth and urinary bladder male cancer patients with related to controls. Environ Sci Pollut Res 22(10): 7705–7715.
44. Nergis Y,Khan MJ, Mughal NA, Mughal S (2018)Environmental impacts and mitigation of tlc mine dewatering operation, Sindh, Pakistan. 3, 12-16.
45. (2006) Guidelines for drinking-water quality, 3rd edition: 1st addendum to Volume 1 World Health Organization.
46. Sreedevi PD, Ahmed S, Made B, Ledoux E and Gandolfi JM et al., (2006) Association of hydrological factors in temporal variations of fluoride concentration in a crystalline aquifer in India. Environmental Geology 50:1-11.

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