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Simultaneously evaluate the toxic levels of fluoride and arsenic species in underground water of Tharparkar and possible contaminant sources: A multivariate study

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ABSTRACT

The present study investigated total arsenic (tAs), inorganic arsenic (iAs) species and fluoride ion (F^-) contamination in underground water of Mithi and Nangarparkar subdistricts of Tharparkar, Pakistan. Statistical parameters, principal component analysis, cluster analysis, sodium absorption ratio and saturation indices (SI) were used to detect interrelation and sources of concentration of tAs, iAs species (As^{3+} and As^{5+}), F^- and others physicochemical parameters. The concentration of As^{3+} was measured by cloud point extraction using ammonium pyrrolidinedithiocarbamate (APDC) as complexing reagent, while inorganic arsenic (iAs) was determined by solid phase extraction, using titanium dioxide. The positive correlation was observed between F^- contents with As species and other major ions, found in the underground water of the study area. The resulted data indicated that underground water samples of two areas of Tharparkar were severely contaminated with arsenic (0.100–3.83 mg/L) and fluoride ion (13.8–49.3 mg/L), which were exceeded the World Health Organization provisional guideline values, 0.01 mg/L and 1.5 mg/L, respectively. The SI of fluorite and calcite in the underground water samples showed that most of the samples were oversaturated with respect to calcite and fluorite.

1. Introduction

Water is called matrix of life because it is an essential part of all living systems and is the medium from which life evolved and exists (Franks, 2000). Underground water is the major source of drinking water and also used as the alternative source for agricultural and industrial sector in the whole world (Mishra and Bhatt, 2008).

In aquatic systems, elements are present as dissolved ions and complexes, suspended, colloids ions and solid in sediments. Concentrations of these ions strongly depend on biological processes, redox potential, ionic strength, pH, activities of organic and inorganic chelators as well as scavenging processes (Arjonilla et al., 1994).

Arsenic (As) is a toxic element and its aquatic contamination has been receiving worldwide attention by the scientific community (Baig et al., 2009a). The literature studies show that the arsenic in water poses the health hazards to humans, creates non-cancer effects such as hyper-and hypo-pigmentation, keratosis, black foot disease, hypertension, cardiovascular diseases and diabetes, and also typical skin, lung and bladder cancers (Abernathy et al., 2003; WHO, 2011). High contaminated As in water was observed in Bangladesh, India, Argentina, Mexico, Mongolia, Germany, Thailand, China, Chile, USA, Canada, Hungary, Romania Vietnam and Pakistan (Baig et al., 2009b; Berg et al., 2007; Nickson et al., 2005; Dang et al., 2004; Farooqi et al., 2007).

In water, As occurs as inorganic (predominantly As^{3+} and As^{5+}) and organic forms (methyl and dimethyl arsenic compounds). In general, inorganic As compounds are much more hazardous than organic As compounds (Vega et al., 2001). The speciation of As is very important for the assessment of toxicological and environmental impacts of As (Hu et al., 2008; Murata et al., 2005; Zhang et al., 2004).

Fluoride (F^-) in small amounts is an essential component for normal mineralization of bones and formation of dental enamel (Wood, 1974). The main source of F^- for human body is usually drinking water, covering about 75–90% of daily intake (Zohouri and Rugg-Gunn, 2000). Excessive F^- intake level causes fluorosis (Chen et al., 1997), cancer, arthritis and other diseases

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(Li et al., 1995; Waldbott, 1998). Around 200 million people from 25 nations have health risks because of high F^- in underground water (Ayoob and Gupta, 2006). Pakistan, Bangladesh, Argentina, United States of America, Morocco, Japan, South African Countries, New Zealand, Thailand and Middle East countries are facing the problem of fluorosis (Rafique et al., 2009, RGNDWM, 1993).

The chief sources of F^- in natural waters are fluoride-bearing minerals (fluorite, fluorapatite, cryolite and apophyllite) as well as F^- replacing OH^- in the ferromagnesium silicates (amphiboles and micas), and clay minerals (Dey et al., 2011). Its concentration in underground water depends on the pH, the intensity of the weathering process, and the amount of clay in the aquifer material (Adriano, 1986; Saxena and Ahmed, 2001).

The World Health Organization (WHO) provisional guideline values for As and F^- concentration in drinking water are 10 μg/L and 1.5 mg/L, respectively (WHO, 2011).

However, water monitoring management of a long-term period and many sampling sites produces large and complicated data sets consisting of all kinds of water parameters, which are difficult to analyze and interpret and to extract comprehensive information from them, so multivariate techniques were used. The multivariate treatment of environmental data is useful for evidencing temporal and spatial variations caused by natural and anthropogenic factors (Dixon and Chiswell, 1996; Vega et al., 1998). The application of different multivariate statistical techniques, such as cluster analysis (CA) and principal component analysis (PCA) helps in the interpretation of complicated data matrices to better understand the temporal and spatial variances of water quality. In the last decade, comprehensive application of different multivariate statistical techniques has been gradually accepted in water quality assessment (Kazi et al., 2009; Simeonov et al., 2003; Singh et al., 2004; Sojka et al., 2008).

The present study was carried out on water quality parameters of underground water samples of subdistricts Mithi and Nagaparkar during 2011. The level of F^- and As species (As^{3+} and As^{5+}) along with different physicochemical parameters (temperature, pH, EC, TDS, salinity, sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), iron (Fe), nitrite (NO_2^-) and nitrate (NO_3^-) were determined and to identify the formation mechanism of the contaminated underground water. In the present study, a large data set obtained was subjected to different multivariate statistical techniques (PCA and CA) to extract information about the similarities or dissimilarities between sampling sites and identification of water quality variables responsible for underground water contamination. The present study was carried out first time in understudy area to evaluate the mutual relationships of F^- and As species with different physico-chemical parameters of underground water samples. The effects of geochemical factor effect were also evaluated and discuss possible sources of pollutants.

2. Materials and methods

2.1. Description of study area

Nangarparkar and Mithi subdistricts (East to west) of Tharparkar district, are located in south-east edge of the Sindh, Pakistan, were the study area and positioned between 24°21.734′–24°45.626′°N and 69°36.227′–70°45.192′°E (Fig. 1). Tharparkar is spread over about 19,638 km^2 area of which 3862 km^2 and 5340 km^2 area covered with subdistricts, Nangarparkar and Mithi, respectively. The populations of the subdistricts are 201,760 and 331,500 for Nangarparkar and Mithi, respectively. Both subdistricts are rich in minerals resources like china clay, granite, coal, koilin and salt, so underground water is saline in nature (Rafique et al., 2009).

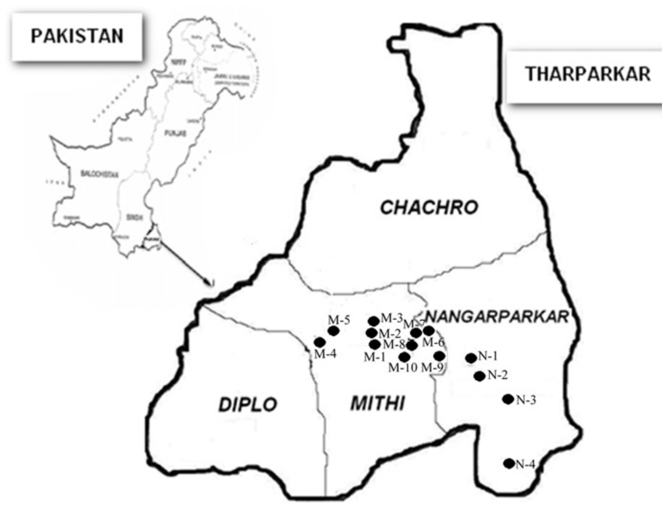

Fig. 1. Sketch map showing sampling sites from subdistrics Mithi and Nangarparkar, Tharparkar, Pakistan.

Stable underground water is lacking in understudy areas, however, a number of brackish to saline open dug wells are present in low lying inter dune playa flats (Mir and Naseem, 2005). Mostly open dug wells underground water having depth 15–160 ft, used for drinking as well as livestock purposes (Rafique et al., 2008). Underground water samples were collected from 14 different villages namely Bhalwa, Danodandhal, Veravah, Nangarparkar, Islamkot, Moryotar, Sakrio, Pabuar, Mithi, Jeeando Daras, Budhe Jo Tar, Mthrao, Lunyo and Haday Jo Tar and sample identification number (ID) for these villages was from N-1 to N-4 and M-1 to M-10, respectively for Nangarparkar and Mithi subdistricts.

The study area has a tropical desert climate. The temperatures during summer remains between 24 °C and 48 °C, while in winter the temperatures range in between 9 °C and 28 °C. Rainfall varies from year to year but average annual rainfall of 200–300 mm.

2.2. Chemicals and glassware

All the glassware was kept overnight in 5 M HNO_3, then rinsed with deionized water before use. All chemicals and reagents were of analytical grade, Merck (Darmstadt, Germany). Ultrapure water obtained from ELGA lab water system (Bucks, UK) was used for solution preparation. The stock standard solution of As^{3+} at a concentration of 1000 mg/L was prepared by dissolving of As_2O_3 Merck (Darmstadt, Germany) in 1 M KOH and adjusting the pH to 7.0 with 10% HCl. While the working standard solutions for tAs were prepared by dilution of certified standard solution (1000 mg/L), obtained from Fluka (Buchs, Switzerland) in 0.2 M HNO_3. Triton X-114 Sigma was used as the non-ionic surfactant. Ammonium pyrrolidine dithiocarbamate (APDC) (Fluka) 0.1% (w/v) was prepared by dissolving suitable amount of APDC in ultrapure water. Titanium (IV) dioxide (TiO_2) (Merck, 99%, 0.5 μm) was utilized as a sorbent. The standard reference material SRM 1643e (water) was purchased from National Institute of Standards and Technology (Gaithersburg, MD, USA).

2.3. Instruments

The pH and electrical conductivity (EC) and total dissolved solids (TDS) in water samples were measured pH meter (781-pH meter, Metrohm) and conductometer (InoLab conduc. 720, Germany), respectively. A global positioning system (iFinder GPS, Lowrance, Mexico) was used for sampling locations. Metrohm ion analysis, 861 (Herisau, Switzerland), employed for anions analysis. WIROWKA Laboratoryjna type WE-1, nr-6933 centrifuge (Mechanika Phecyzyjna, Poland) was used for centrifugation. Mechanical shaker (Gallankamp, England) was used for shaking. Graphite furnace Atomic absorption spectrometer (Perkin Elmer, Model AAnalyst 700 USA), was used for quantitative analysis of total As, inorganic As and As species. The graphite furnace heating program was set for different steps: drying temperature (°C)/ramp/hold (s) (140/15/15), ashing temperature (°C)/ramp/hold (s) (1300/10/20), atomization temperature (°C))/ramp/hold (2300/0/5), cleaning temp. (°C)/ramp/hold (s) (2600/1/3), using a modifier $Mg(NO_3)_2 +$ $Pd(NO_3)_2$ [5 μg Pd + 3 μg $Mg(NO_3)_2$].