ROLE OF CRITICAL CONTAMINANTS IN GROUNDWATER OF KALAHANDI DISTRICT OF ODISHA AND THEIR HEALTH RISK ASSESSMENT

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Abstract
Trace metals (Al, B, As, Be, Cd, Ba, Co, Cu, Fe, Cr, Sb, Ni, Li, Sn, Mn, Zn, V and Se) plays a vital role in various enzymatic activities within living organisms. Concentrations of trace elements can be determined in water samples using inductive coupled plasma mass spectrometry (ICP-MS). Although it is one of the most complex and expensive methods of inorganic elements analysis, its high reproducible value, accuracy and recovery make it more dependable. This paper provides a method for elemental analysis in water samples, which can be used for regular monitoring of heavy metal contamination of water and may reduce the risk of severe health hazards.
Keywords: Heavy metals, health risk, ground water, pollutants, chemical contamination

Introduction

Groundwater is one of the most valuable freshwater sources of drinking water worldwide and safe drinking water is essential to human development based on population growth, social development, and urban, industrial and agricultural water demand, groundwater is usually reserved for drinking, irrigation and industrial activities[1]. Human activities such as mining, industrialization and urbanization have produced a large amount of heavy metals. Pollutants pass through eluviation, leaching and osmosis into groundwater, thereby affecting its quality. Heavy metals refer to elements with atomic masses between 63.546 and 200.590 g/mol and densities greater than 4.0 g/cm3. They are generally stable pollutants that are different from their compounds[2]. After being discharged from the Earth's crust, they stay in the environment for a long time due to nondegradability and have toxicological effects on animals, plants and humans. Cadmium (Cd), chromium (Cr), arsenic (As) and plumbum (Pb) are toxic heavy metals and these toxic heavy metals tend to accumulate in different tissues of the human body and may be very toxic even at low concentrations. Among them, Cd, Cr and As are called carcinogenic heavy metals, which are widely distributed in the Earth's crust. Ferrum (Fe), cuprum (Cu), manganese (Mn) and zinc (Zn) are essential for human metabolism and are essential elements for various biomolecules, but if their concentration exceeds a certain limit, human health may be harmed[3]. Heavy metals can enter the human body through direct ingestion, skin contact, and inhalation through the mouth and nose. Inhalation is the research category of atmospheric exposure, which

is not included in this paper[4]. The intake of shallow groundwater in this article refers only to the ingestion of drinking water and skin contact. Health risk assessment is an excellent method for assessing the harmful effects of environmental pollutants on the human body. Therefore, it is particularly important to carry out a comprehensive health risk assessment of heavy metals in groundwater. Trace elements are found naturally at several levels in the hydrosphere, and many are required for the physiological and metabolic processes of organisms[5]. These metals are also referred to as microminerals and are part of enzymes, hormones, and cells in the body. Insufficient intake of trace minerals can cause symptoms of nutritional deficiency. Water is our most precious resource, a 'blue gold' to which more than 2 billion people do not have direct access[6]. It not only is essential to survival but also plays a sanitary, social and cultural role at the heart of human societies. Currently, 2.2 billion people have limited access to safe drinking water, and by 2025, half of the world's population will be living in water-stressed areas. Worldwide, 71% of the population access clean drinking water while 844 million people across the world still lack clean drinking water. This issue is more severe in rural areas where only one out of three people use safe drinkable water Due to industrialization, the number of factories and population has increased rapidly. Over the last few decades, contamination of freshwaters with a wide range of pollutants has become a matter of concern[7]. It is unfortunate that we, human works without realizing the consequences of pollution and do a lot of activities that terribly ruin nature, resulting in the denial of a healthy environment to our successors. In India, most rural and suburban regions rely on groundwater to meet water demand for drinking and domestic purposes. Among all contaminants, inorganic trace elements are of much concern as they are xenobiotic compounds and can accumulate in water resources for a long period. Polluted groundwater contaminated with industrial wastewater, agricultural, and domestic wastes, etc. contains trace metals that can reach the water table and pollute it [8]. However, depletion in water quality is related to public health concerns, so it is essential to estimate the exposure risk to understand groundwater sources' toxicity levels imposing health hazards. In 1993, EPA (Environmental Protection Agency, U.S.A) issued interim guidance, allowing dissolved metal concentrations to be used to set and measure compliance with water quality standards excluding any metals adsorbed onto large particles, the use of dissolved metals takes one of the bioavailability limits into account[9]. The inductively coupled plasma (ICP) is the most widely used ionization source for inorganic mass spectrometry. When argon gas (99.999% purity) passes through a quartz torch placed in an induction coil (also called the load coil) to which a radio frequency (RF) power between 750 and 1700 W is applied, an alternating current oscillates within the field. The frequency of oscillation is governed by the type of RF generator used, but most commercial instruments use a frequency of either 27.1 MHz or 40.6 MHz. These oscillations set up electrical and magnetic fields at the top of the torch[10]. If a spark is then applied to the argon gas via a Tesla coil, electrons are stripped from some of the argon atoms. These electrons then become trapped in the magnetic field and are accelerated in closed circular paths. This process is known as inductive coupling and hence the plasma so formed is referred to as an inductively coupled plasma (ICP). Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most promising techniques for multi-elemental determination

of trace metals[11]. ICP-MS is ideal for trace metals analysis, because it allows fast multi-elemental and isotopic analysis with high sensitivity, as well as a broad dynamic range.

Kalahandi area is known for its Bauxite mines, alumina industry, and steel industries. Shallow groundwater in the mining area is an important water source for rural life and agricultural irrigation. Different mining activities like mining products washing, chemical used and other mining production activities commonly occur[12]. These clustered mining activities produce multiple pollutants, which has resulted in the pollution complexity of groundwater in the Kalahandi mining area. At present, although previous studies on some trace elements have been carried out in the mining area of different regions of Odisha, the types of trace elements tested have been relatively limited and the sampling area involved has not been carefully determined[13]. In addition, the health risk assessment of trace elements in groundwater in mining areas has focused mainly on deep groundwater. Despite some efforts were done by researchers to study the groundwater quality of Odisha, limited investigations are attributed to ground water study of Kalahandi district, Odisha. Various dug wells and tube wells in and around Kalahandi are the source of drinking water for public use[12]. The main objectives of this study are to assess the physico-chemical properties of water samples collected from dug well and tube well of the study area. To determine the trace metals among the collected samples. To evaluate the physico-chemical properties of soil samples collected from the study area and also assess the human health and ecological risks associated with contaminants.

Materials and methods

Study areas and climate

Kalahandi is one of the economically backward district of western Orissa with a geographical area of 7920 Sq. Km and is an integral part of Western Orissa Development Council constituted by Govt. of Orissa very often reels under severe drought condition. About 92.5% percent of the population of the district live in rural areas and agriculture is the main stay of the people. The agriculture is mostly rain fed and due to lack of adequate irrigation facilities and recurring severe drought conditions in the district, the agricultural production is very often curtailed. Kalahandi district lies between North latitudes 19°03' and 20°45' and East slongitudes 82°18' and 83°48', falling in Survey of India top sheet nos. 64 L, 64P, 65 I and 65 M. It is bounded on the north by Balangir and Nuapada districts, on the east by Phulbani district, on the south by Koraput district and on the west by Nawarangpur district of Orissa and Raipur district of Chhattisgarh. The river Tel and its tributaries constitute the main drainage system in the district[1,14]. Some important rivers like Indrāvati, Nagavalli and Vansadhara, owe their origin to the hill ranges in the south-eastern parts of the district. The hilly streams are perennial in nature and many of the tributaries are ephemeral in nature[12].
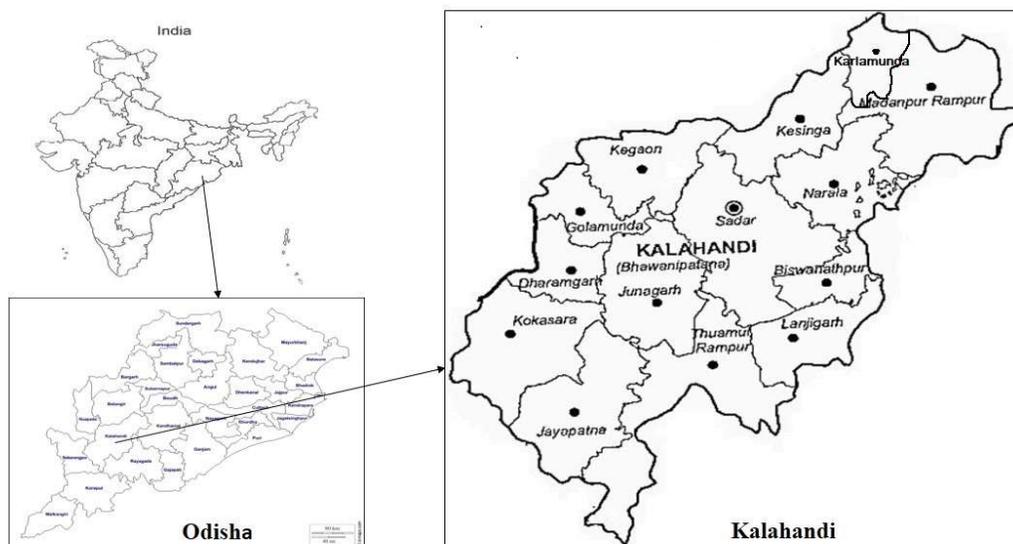
Fig. 1. Representative map showing sampling sites in Kalahandi, Odisha

The climate of the district is sub-tropical with hot and dry summer and pleasant winter. The summer season extends from March to middle of June followed by the rainy season from June to September. The winter season extends from November till the end of February. Humidity is high during middle of June and it's less in post-monsoon period. The average relative humidity in the district varies from 27% to 80% throughout the year. The mean monthly potential evapo-transpiration value ranges from 45mm in December to 470 mm in May. Wind is generally light to moderate. According to 2011 census data, the total population of the district is 15, 76,869 constituting 3.75% of the total population and 5.09% of land area of Orissa. The rural and urban populations are 14 54,882 and 1, 21,987 respectively. The rural population constitutes 92.5 % of the total population[15]. The density of population is 199 against the state figure of 270 persons per sq. km. The south-west monsoon is the principal source of rainfall in the district. Average annual rainfall of the district is 1378.2mm. About 80 to 85% of the total rainfall is received during the period from June-September. Droughts are quite common in the district. Block-wise average annual rainfall varies from 1111.8 mm to 2712.9 mm[12,15].

Sampling

Collection and analysis of soil samples

 Soil samples of the respective study sites will be collected in sterile zipped pouches in triplicates. Samples would be collected in 3 different seasons like summer, rainy and winter to check the seasonal variations among the collected samples. Temperature, pH and electrical conductivity (EC) will be measured adhering to standard methods (APHA 2012)[16]. Alkalinity will be studied by titrimetric method. Total phosphate will be determined by persulphate method. Total solid suspended will be studied by photometric method. Biochemical oxygen demand will be studied by

Winkler method and Chemical oxygen demand will be studied by colorimetric method. Physicochemical characterization of the samples was performed with parameters typically used to ascertain general soil fertility characteristics: pH (H_2O), electrical conductivity (EC), total nitrogen (N), and the extractable fraction of phosphorous (P) and potassium (K).

Collection and analysis of water samples

The drinking water samples would be collected from randomized tube wells and dug wells of Kalahandi district, Odisha in triplicates in high density polyethylene bottles using standard sampling protocol. Samples would be collected in 3 different seasons like summer, rainy and winter to check the seasonal variations among the collected samples[17]. All samples will be kept in refrigerated condition at 4^0C till the completion of experiment. pH analysis would be done by handheld pH meter on the sampling site. Other parameters like Electrical conductivity analysis, Total Conductivity, Total Hardness, Dissolved Oxygen, Total dissolved solids, Dissolved silica, major ions ($Ca+2$, $Mg+2$, $Na+$, $K+$, $Cl-$, $HCO3 -$, $SO4\ 2-$) will be carried out in the laboratory adopting standard procedures[18]. Total organic carbon and Total Nitrogen will be analyzed by TOC/TN analyzer. Trace metals in the water samples will be analyzed by ICP-MS method. Standard methods of APHA (2012) would be followed for the assessment of water quality[19].

ICP-MS Sample preparation and analysis

Ground water samples (14 mL) collected from different locations (n=18) were digested by HNO_3 (1mL, 70%, #225711 Sigma Aldrich, ≥99.999% trace metal basis) in HVT50 vials using microwave digestion system (Anton Paar Multiwave PRO). A temperature ramp from xx -170°C in 15 minutes followed by a hold of 10 minutes was used for digestion. After digestion, processed water samples were filtered using wwPTFE filter (0.22µm) and immediately taken for elemental analysis using iCAP^{TM} TQ ICP-MS (Thermo Scientific)[20].
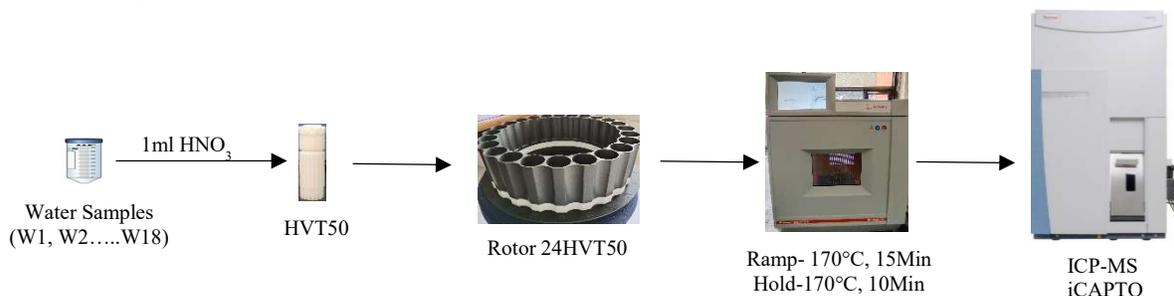

Fig 2: Experimental pathway for water samples digestion and analysis.

ICP-MS data acquisition

Details on instrumental operating conditions are given in table 1.

Table 1: ICP-MS operating conditions and measurement parameters.

Nebulizer	MicroMist DC
Peristaltic pump speed	40 rpm

Dry Pump Speed	77 rpm
Torch	Quartz
Plasma exhaust	0.53 mbar
Cool flow	14 l/min.
Helium flow	4.925 ml/min.
Sample cone	Nickel, 1 mm orifice diameter
Skimmer cone	Nickel, 0.5mm orifice diameter
Dwell time	0.1 sec.

Quantification using inductively coupled plasma-mass-spectrometry (ICP-MS)

Selected trace elements (As, Pb) were analyzed in groundwater samples using inductively coupled plasma mass spectrometry (ICP-MS; Thermofischer, Model iCAP TQ-00240). Thermo Scientific Qtegra Intelligent Scientific Data Solution (ISDS) software was used for operating the instrument. Helium gas flow rate was set at 4.9 mL min^{-1}, while nebulizer argon flow rate was 1.05 min^{-1}. The ICP-MS was calibrated using a multielement standard mix (#92091, Sigma Aldrich) according to the manufacture's instruction prepared in 1% HNO_3[16]. A calibration curve (10 ppt- 10 ppb) was drawn for absolute quantification of ^{75}As and ^{208}Pb (R^2= 0.99). The calibration line was forced through zero, the blank 1% HNO_3. Water samples were taken up by ICP-MS self-aspiration using sample capillary (0.55 mm) to a V grooved Micromist DC nebulizer and spray chamber. Samples were passed through a quartz torch with injector diameter of 2 mm. Samples were ionized by plasma and passed through sample cones followed by skimmer cone[21–23]. In order to avoid any polyatomic ion interference experiment was conducted in KED (Kinetic energy dissociation) mode. 1% HNO_3 was pumped through the nebulizer between all samples. A wash out time of 30 sec. was used to remove elements carryover from one run to another. Ions of interest were passed through Q1 (quadrupole) and received by the detector. Concentration average of three runs for each element were noted by QTEGRA software for respective samples. Concentration average were exported and analyzed further[24].

ICPMS operating conditions and measurement parameters

A MicroMist DC nebulizer was used in the system. During the run, nebulizer flow was 1.04 l/min with a pressure of 3.17 bar. The peristaltic pump was revolving clockwise (40 rpm). The quartz torch produces plasma and the exhaust was maintained at 0.49 mbar. Interface temperature was

maintained at 29.98°C with a cool flow of 14 l/min[25]. Both sample and skimmer cones used in the system were nickel with orifices of 1 mm and 0.5 mm respectively. Between sample runs, HNO_3 (1%) was pumped through the nebulizer with a washout time of 30 sec to remove any carryover[23,24]. The complete experiment was carried out with a dwell time of 0.1s. The average of three runs for each element concentration was calculated and exported for further statistical analysis.

FTIR sample preparation and analysis

Sample preparation is an important part of analytical study even if an analytical technique does not require it, such as FTIR. Many scientific works, which are connected with an investigation on FTIR, are describing the process of sample preparation in the same way. All of the viewed articles accented that, in the process of sample preparation for FTIR, it is very important to be a dried and finely ground sample because wetness and particle size strongly influence the resolution of the spectrum[26]. The next step is mixing the sample with KBr powder. Working with an IR spectrum of minerals requires understanding several factors which influence the position of characteristic absorption bands. The powdered fine samples (soil) are densely treated with potassium bromide (KBr) pellets (small sphere) and analyzed by FTIR Benchtop system, The Agilent Cary 670 spectrometer. For Fourier transform infrared (FTIR) analysis, spectral scanning obtained at 4000–500 cm−1 wave number to evaluate mass soils[27]. The FTIR peaks were analyzed by Essential FTIR v3.50.185 from Operant LLC, Searchlt-KnowltAll®information system, ID expert from BioRad laboratories, Inc. and IRPal 2.0 tabledriven infrared application programming.

Effect of trace metals on human health

Inorganic trace metals are xenobiotic compounds and they sustain in the water for a long period of time. Trace metals in groundwater can be exposed to human beings through two key pathways, direct ingestion and dermal absorption. Some trace metal(loid)s such as arsenic (As), lead (Pb), nickel (Ni), chromium (Cr), copper (Cu), zinc (Zn), cadmium (Cd), and cobalt (Co) are potentially toxicif found above their threshold value in drinking water[17,18]. Continuous exposure to Pb, As, and Cd above the threshold limit can cause various health hazards; Lead (Pb) can cause neurological diseases as it can trigger the central nervous system mostly in children, resulting in fatigue, anaemia, and a decrease in intelligence quotient (IQ) level. Arsenic (As) can cause visceral, kidney, liver and bladder cancer. Cadmium (Cd) can cause bone loss and renal disorder[1,3]. According to WHO, when high concentrations of Mn and Fe are observed, the iron bacteria may cause deposits in the drinking water source and, therefore, may compromise the acceptability of the drinking water. Manganese (Mn) is an essential element in small quantities mainly for bone development and the metabolism of amino acids, lipids, and carbohydrates. In excess amounts, however, Mn has been shown neurotoxin behavior in infants [28,29]. Additionally, areas with a high concentration of Mn in drinking water report higher infant mortality. In the brain, high doses of Mn can cause Parkinson syndrome. A high concentration of Mn in drinking water also causes an unpleasant taste [30]. The moderate

presence of Mn in drinking water has no direct health effects, but the precipitate Mn in water can lead to aesthetic and infrastructure problems.

Table 2. Categorization of the source of chemical constituents (WHO, 2021)

Source of chemical constituents	Examples of sources
Naturally occurring	Rocks, soils and the effects of the geological setting and climate; eutrophic water bodies (also influenced by sewage inputs and agricultural runoff)
Industrial sources and human dwellings	Mining (extractive industries) and manufacturing and processing industries, sewage (including a number of contaminants of emerging concern), solid wastes, urban runoff, fuel leakages
Agricultural activities	Manures, fertilizers, intensive animal practices and pesticides
Water treatment or materials in contact with drinking-water	Coagulants, DBPs, piping materials

Guideline values for naturally occurring chemicals that are of health significance in drinking water (WHO, 2021)

The European Union and World Health Organization (WHO) have set guidelines for drinking water quality. The objective of the drinking water guidelines is to protect the health of consumers. Developing countries need to comply with the EU and WHO guidelines for regulation and set standards for safe drinking water.

Table 3. Guideline value of WHO.

Chemical Inorganic	mg/l
Arsenic	0.01
Barium	1.3
Boron	2.4
Chromium	0.05
Fluoride	1.5

Selenium	0.04
Uranium	0.03

There are two main problems that exist in the current water quality standards: (1) a gap between developed countries and China in water quality standard system; (2) without considering the differences between the regions.

Results:

Physiochemical parameters of Soil

Considering the soils' physicochemical properties that may hinder their fertility (Table 4 & 5), it is possible to have an idea about their range of variation. Soil temperature varies from 20 °C to 24°C. Due to agronomical effect physiochemical parameters varies from site to site (S1=Sripali, S2=Tujung, S3=Turchi, S4=Ghantabahali,S5=Jaring,S6=Baldiamal,S7=Badbasul,S8=Kashibahal,S9=Brahmanchhendia, S10=Haldi,S11=Chichia,S12=Gandamer,S13=Rishida,S14=Putigaon,S15=Jogipala,S16=Dhanra mal,S17=Mundapala,S18=Salebhata). Due to production of bauxite mining areas activities soils are contaminated in the study areas. So variations arises in the chemical characterization data. Phosphorus, Potasium, Organic carbon,Sulphur, Boron, Zinc, Copper, Magnesium, and Ferrous concentration also depends on the ground water due to rocky surface in the study areas. All the above mobile ion and its retention in the soil correlated with the amount and rate of water percolating into the soil zone which depends on the soil permeability. Everyday falling down of leaves may increase the soil organic carbon and thus the total organic matter. In the study area soil organic matter content varies from very less to more than sufficient and its directly influenced by soil texture and moisture content.

Table 4. Physical parameters of all study sites soil samples.

Site Name	T(°C)	pH	E.C	ALKALINITY
S1	20.3±2.9	5.6±0.8	160.7±2.3	5.8±0.4
S2	21.7±2.5	6.5±0.5	209.0±5.7	7.5±0.3
S3	21.7±3.3	7.0±0.3	152.0±3.7	7.3±0.6
S4	22.3±4.o	2.2±4.7	250.5±3.0	7.7±0.4
S5	23.0±2.4	7.5±0.3	263.0±4.3	7.5±0.2
S6	23.7±3.4	7.1±0.1	237.3±1.2	7.6±0.4
S7	23.7±2.9	7.3±0.2	174±3.1	7.7±0.2
S8	23.3±3.1	6.6±0.1	189.3±0.5	7.1±0.3
S9	24.3±3.3	7.0±0.1	61.8±3.2	6.9±0.2
S10	23.0±2.4	7.3±0.4	517.0±0.8	7.3±0.5
S11	21.7±2.6	7.3±0.2	193.8±0.3	7.5±0.4
S12	21.7±6.2	7.8±0.2	686.2±3.2	7.8±0.3
S13	22.±2.1	7.6±0.4	251.7±2.2	7.5±0.4

S14	22.7±2.9	7.9±0.3	211.6±0.4	7.8±0.5
S15	22.7±2.1	8.1±0.3	1392.3±1.7	7.9±0.3
S16	21.0±2.2	8.0±0.1	288.0±0.3	7.9±0.1
S17	20.7±2.9	7.4±0.5	1.1±0.1	7.2±0.4
S18	22.7±2.9	7.3±0.6	437.4±0.4	7.1±0.5

Table 5. Chemical characterisations of all study sites soil samples.

Site Name	P	K	OC	S	B	Zn	Cu	Mg	Fe
S1	1.5±0.4	603.0±2.2	1.9±0.1	1.0±0.1	0.2±0.1	1.9±0.1	1.9±0.1	99.0±0.4	21.6±1.1
S2	1.5±0.4	346.0±4.1	2.0±0.1	1.0±0.1	0.4±0.1	0.9±0.1	1.4±0.1	21.7±0.4	13.5±0.4
S3	1.4±0.3	112.7±2.1	1.8v0.2	1.1±0.1	0.2±0.1	0.8±0.1	1.1±0.1	9.2±0.1	6.4±0.6
S4	1.6±0.4	610.3±6.5	1.3±0.1	1.1±0.1	1.2±0.1	2.6±0.3	3.6±0.1	9.1±0.2	4.1±0.1
S5	1.5±0.2	603.7±2.9	1.2±0.1	1.1±0.1	0.3±0.1	4.8±0.2	2.5±0.2	12.7±0.3	0.8±0.2
S6	1.8±0.3	220.7±0.9	1.2±0.1	1.1±0.1	0.4±0.1	1.0±0.1	4.1±0.2	31.8±0.2	1.8±0.2
S7	1.5±0.2	343.0±2.2	1.4±0.5	1.1±0.1	0.5±0.1	0.7±0.1	3.7±0.2	11.8±0.3	2.8±0.1
S8	1.9±0.2	440.0±0.4	1.6±0.1	1.1±0.1	0.4±0.1	0.2±0.1	2.6±0.1	19.9±0.2	1.0±0.1
S9	1.5±0.3	603.3±4.7	1.0±0.2	1.0±0.1	0.3±0.1	0.4±0.1	1.2±0.1	18.6±0.2	3.2±0.1
S10	1.9±0.3	188.7±47.9	2.2±0.1	1.1±0.1	0.5±0.2	1.9v0.2	3.7±0.3	4.6±0.2	1.0±0.1
S11	1.6±0.3	603.3±4.7	1.2±0.1	1.0±0.1	0.2±0.1	2.8±0.2	3.3±0.2	42.8±0.2	23.9±0.2
S12	2.2±0.3	599.7±1.2	2.0±0.2	1.0±0.1	0.3±0.1	0.5±0.1	2.0±0.1	2.2v0.2	0.4±0.2
S13	2.0±0.3	60.3±0.5	1.2±0.1	1.1±0.1	0.4±0.1	1.5±0.2	0.8±0.1	4.1±0.2	0.8±0.2
S14	2.5±0.5	42.7±2.1	1.9±0.1	1.1v0.1	0.3±0.1	0.3±0.1	1.0±0.1	1.5±0.2	0.9±0.1
S15	1.8±0.2	599.3±0.9	1.6±0.1	1.0±0.1	0.2±0.1	1.9±0.2	1.1±0.1	5,2±0.2	0.2±0.1
S16	1.6±0.2	604.0±5.0	1.5±0.1	1.1±0.1	0.2±0.1	2.0±0.1	1.3±0.1	12.2±0.3	0.2±0.1
S17	1.7±0.2	480.7±0.9	1.2±0.1	1.1±0.1	0.3±0.1	1.0±0.1	1.6±0.1	2.5±0.1	0.2±0.1
S18	1.5±0.2	603.3±4.7	1.4±0.2	1.0±0.1	0.4±0.1	1.5±0.2	1.3±0.1	7.6±0.2	2.9±0.1

Physiochemical characterization of water

The theme of the present research is to examine underlying relationship between groundwater potential
and quality parameters. This research also focusses critically on the variation of groundwater quality parameters. These datas indicate a fair amount of availability of groundwater resource and a reasonable reliability on groundwater sources (Table 6 & 7). The concentration of chemical characterisation data shows the effect of Fl, Pb, Cl, As and Mg in the study sites. The higher concentration in this region owes to over application of fertilizer, which paves its way with water towards ground water reservoir. Chloride is also found to be widely distributed in the present study area. The river Tel and its tributaries constitute the main drainage system of the district. Some important rivers like Indravati, Nagavalli and Vansadhara owe their origin to the hill ranges in the southeastern parts of the district. The hilly streams are perennial in nature and many of the

tributaries are ephemeral in nature. The drainage pattern of the district is of dendritic, radial and centripetal types. The drainage is effluent in nature. So water contamination occur in some study sites.

Table 6. Physical parameters of all study sites contaminated water samples.

Site Name	T	PH	E.C	TDS	T
S1	31.7±0.5	7.3±0.2	269.3±0.8	333.3±2.3	0.9±0.2
S2	31.3±0.5	7.4±0.1	852.6±5.5	351.3±24.9	0.7±0.2
S3	30.7±0.5	7.2±0.1	630.1±0.5	354.0±207.9	2.1±0.1
S4	30.0±2.2	7.8±0.2	497.0±3.3	695.0±54.4	0.9±0.1
S5	31.0±1.6	7.9±0.2	1350.0±3.1	207.7±10.1	1.2±0.1
S6	30.3±0.9	7.5±0.4	630.9±2.2	398.3±38.4	1.5±0.1
S7	31.7±0.5	7.3±0.2	691.5±3.9	725±224.1	2.0±0.1
S8	31.7±0.6	7.4±0.2	203.8±4.0	519.3±310.7	1.2±0.1
S9	31.7±1.2	7.2±0.2	257.8±3.9	219.0±90.9	1.0±0.1
S10	31.3±0.6	7.5±0.3	1009.3±2.3	577.0±21.9	1.5±0.5
S11	30.7±0.5	7.1±0.2	489.7±2.7	376.3±64.6	2.1±0.1
S12	29.7±2.1	7.1±0.7	973.3±4.5	333.7±4.0	0.6±0.1
S13	30.0±0.8	7.6±0.3	1052.6±1.5	594.7±28.8	1.2±0.1
S14	30.3±1.2	7.3±0.2	605.7±1.9	476.7±52.7	0.6±0.1
S15	30.3±0.6	7.5±0.1	940.7±2.1	756.0±28.6	1.8±0.1
S16	30.3±0.6	7.2±0.1	799.1±1.7	491.3±166.5	2.3±0.1
S17	30.3±0.9	7.1±0.2	805.7±1.1	873.7±40.6	0.3±0.1
S18	31.0±0.8	7.3±0.1	876.2±0.7	535.3±3.8	0.7±0.1

Table 7. Chemical charaterisations of all study sites water samples.

Site Name	Ca+	Mg+	Fe	Cl-	Fl	Na	TN	OC	K
S1	73.0±0.8	15.7±0.5	3.1±0.1	33.3±0.5	0.4±0.1	19.1±0.2	0.32±0.2	0.52±0.3	26.1±0.2
S2	59.7±1.7	7.0±0.8	1.3±0.1	79.3±1.2	1,3±0.1	21.0±0.1	0.42±0.1	0.57±0.4	23.3±0.4
S3	38.7±1.7	20.3±1.2	1.8±0.1	29.0±1.4	0.6±0.1	32±0.2	0.53±0.3	0.67±0.5	25.1±0.1
S4	94.7±1.2	14.0±0.8	1.0±0.1	190.0±2.4	0.6±0.1	49.5±0.3	0.36±0.2	0.57.±0.7	17.3±0.6
S5	64.7±1.7	23.3±5.2	1.6±0.1	45.7±1.7	0.8±0.1	49.2±1.1	0.29±1.2	0.54±.0.2	24.4±0.2
S6	46.3±1.2	39.0±0.8	0.3±0.1	55.0±2.2	1.4±0.1	16.7±0.7	0.47±0.5	0.48±0.1	21.1±0.1
S7	162.0±1.6	11.0±0.8	1.1±0.1	56.7±1.2	1.4±0.1	23.1±0.1	0.29±1.1	0.47±.0.5	18.9±0.4
S8	95.7±2.5	10.3±0.6	1.2±0.1	74.3±2.5	0.7±0.1	38.9±0.5	0.39±0.3	0.52±0.1	24.1±0.2
S9	33.3±1.5	20.0±1.0	0.5±0.1	72.7±0.6	0.8±0.2	45.1±0.2	0.32±0.2	0.20±0.1	21.1±0.1
S10	46.3±0.6	8.7±0.6	0.4±0.6	81.0±4.6	1.1±0.2	41.2±0.2	0.52±0.4	0.25±0.5	19.7±0.3
S11	70.0±2.2	44.0±0.8	0.8±0.1	47.0±2.8	0.8±0.1	17.3±0.1	0.61±0.2	0.41±0.1	19.2±0.2
S12	64.0±0.8	7.7±0.5	1.1±0.2	67.3±1.7	1.2±0.1	22.1±0.4	0.35±0.1	0.46±0.2	26.2±0.4

S13	144.3±1.2	24.3±1.2	0.4±0.1	44.0±1.4	1.3±0.1	18.2±0.6	0.27±0.2	0.62±0.1	22.5±0.6
S14	154.3±2.1	11.7±1.2	0.7±0.4	34.0±0.8	1.7±0.1	31.1±0.1	0.33±0.1	0.36±0.3	18.4±0.5
S15	121.7±1.5	11.0±1.0	1.4±0.4	60.0±2.0	1.0±0.1	21.3±0.3	0.48±0.4	0.38±0.1	21.1±0.5
S16	67.0±1.0	87.7±1.5	1.1±0.2	110.0±1.0	0.7±0.1	23.2±1.1	0.42±.03	0.53±0.2	22.3±0.4
S17	51.3±1.2	25.7±1.2	1.1±0.1	54.0±0.8	1.5±0.1	19.7±0.2	0.40±0.1	0.23±0.1	23.6±0.7
S18	95.3±1.2	63.7±2.1	1.2±0.2	121±0.5	1.0±0.1	20.0±0.7	0.39±0.2	0.77±0.4	17.2±0.2

ICP-MS analysis

Table 8. ICPMS detected compounds available in water samples.

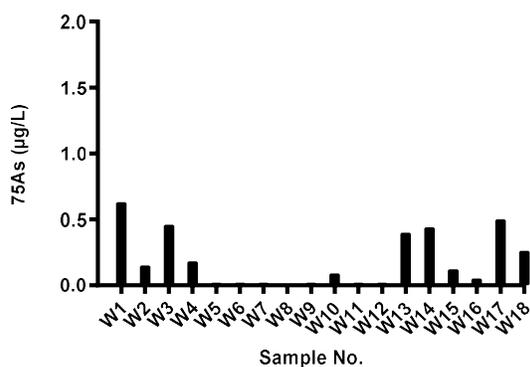| Sample name	^{75}As (PPB)	^{208}Pb (PPB)
W1	0.63	0.00
W2	0.15	0.21
W3	0.46	0.43
W4	0.18	1.01
W5	0.00	0.20
W6	0.00	0.00
W7	0.00	1.00
W8	0.02	0.35
W9	0.00	0.00
W10	0.09	1.60
W11	0.00	1.05
W12	0.00	0.00
W13	0.40	0.00
W14	0.44	3.33
W15	0.12	0.00
W16	0.05	0.00
W17	0.50	0.19
W18	0.26	0.28
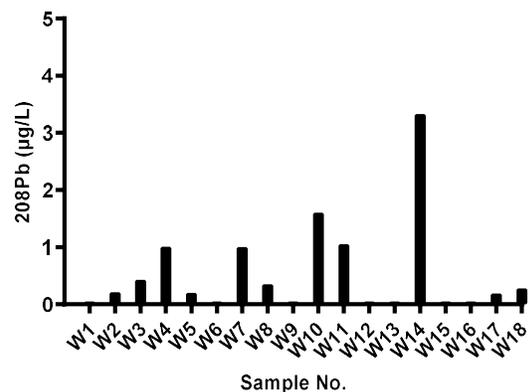
Fig. 3 compound detected in all sites water samples by ICPMS spectroscopy. Data presented Zero were below limit of detection (LOD).

Contamination control

The quality of data generated by a mass spectrometer is more affected by contamination. To decrease the risk of contamination, strict control of impurities in all reagents and water. The addition of chemicals and transfer between containers should be restricted to a minimum. For better results, all tubes must be pre-cleaned with 1% HNO3. Pre-cleaning of the ICPMS system must be done with 1% HNO3 to avoid any memory of the previous experiment. In addition to the above-mentioned factors, impurities in argon (Ar) may contribute to the detection.

Spectral Interferences

While analyzing samples by ICPMS, spectral interferences can originate from isobaric ions, molecular ions, or doubly charged ions[25]. To avoid that, the experiment has to conduct with KED (Kinetic energy discrimination) mode with a non-reactive gas, which avoids cell-formed interferences in collision/ reaction cells of ICPMS. This also reduces polyatomic ion interferences derived from plasma. Polyatomic ions are larger than analyte ions of the same mass, so they collide with the cell gas more often as they pass through the cell, emerging with lower residual energy[23]. These low-energy ions can be excluded from the ion beam by a bias voltage at the cell exists.

FTIR analysis

Fourier Transform Infrared spectrophotometers (FTIR) are mainly used to measure light absorption of so-called mid-infrared light, light in the wavenumber range of 4,000 to 400 cm^{-1} (wavelengths 2.5 to 25 µm), in order to identify and quantify various materials. Strong intensity found between 500 to 1000 frequency level which have C-I, C-Br, C-Cl, and C-F functional groups.
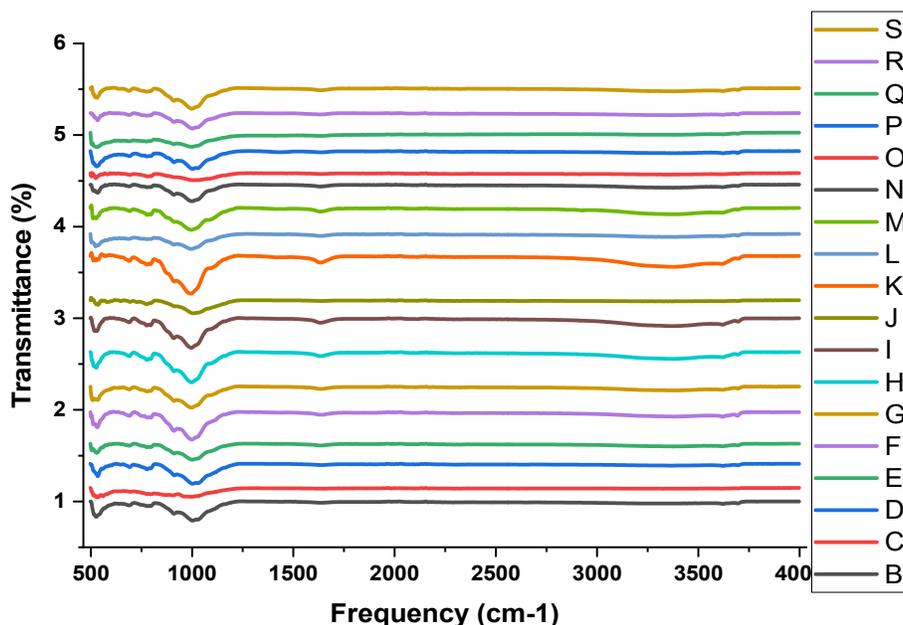
Fig 4. FTIR peaks of all study sites soil samples.(B=S1, C=S2, D=S3, E=S4, F=S5, G=S6, H=S7, I=S8, J=S9, K=S10, L=S11, M=S12, N=S13, O=S14, P=S15, Q=S16, R=S17, S=S18)

Exposure and Health Impact

Heavy metal elements in groundwater are ingested mainly through drinking water consumption (including direct and indirect ingestion pathways) and dermal contact (e.g., washing), the two major exposure routes for entry into the human body[28,30]. Lead pollution exists only in some areas to a certain extent. The analysis comes mainly from the leachate produced during the decomposition of ore and minerals. The second factor is mostly determined by natural activities. The Cu and Zn concentrations in groundwater were largely affected by longterm water-rock interactions and the redox environment of the groundwater system. Cu and Zn are similar elements, and there are no obvious man-made sources of Cu and Zn in the study area. The points with high As and Mn levels in the tested groundwater were distributed mainly in the farmland area near the industrial park areas. As is an important component of agricultural pesticides and herbicides[29]. Combined with related studies in the study area, it has been shown that As pollution is relatively serious and comes mainly from chemical fertilizers and pesticides.

Effect of trace metals on human health

Inorganic trace metals are xenobiotic compounds and they sustain in the water for a long period of time. Trace metals in groundwater can be exposed to human beings through two key pathways, direct ingestion and dermal absorption. Some trace metal(loid)s such as arsenic (As), lead (Pb), nickel (Ni), chromium (Cr), copper (Cu), zinc (Zn), cadmium (Cd), and cobalt (Co)

are potentially toxic if found above their threshold value in drinking water[15,16,18]. Continuous exposure to Pb, As, and Cd above the threshold limit can cause various health hazards; Lead (Pb) can cause neurological diseases as it can trigger the central nervous system mostly in children, resulting in fatigue, anaemia, and a decrease in intelligence quotient (IQ) level. Arsenic (As) can cause visceral, kidney, liver and bladder cancer. Cadmium (Cd) can cause bone loss and renal disorder. According to WHO, when high concentrations of Mn and Fe are observed, the iron bacteria may cause deposits in the drinking water source and, therefore, may compromise the acceptability of the drinking water[28]. Manganese (Mn) is an essential element in small quantities mainly for bone development and the metabolism of amino acids, lipids, and carbohydrates. In excess amounts, however, Mn has been shown neurotoxin behavior in infants. Additionally, areas with a high concentration of Mn in drinking water report higher infant mortality. In the brain, high doses of Mn can cause Parkinson syndrome. A high concentration of Mn in drinking water also causes an unpleasant taste[30]. The moderate presence of Mn in drinking water has no direct health effects, but the precipitate Mn in water can lead to aesthetic and infrastructure problems. The European Union and World Health Organization (WHO) have set guidelines for drinking water quality. The objective of the drinking water guidelines is to protect the health of consumers. Developing countries need to comply with the EU and WHO guidelines for regulation and set standards for safe drinking water. There are two main problems that exist in the current water quality standards: (1) a gap between developed countries and China in water quality standard system; (2) without considering the differences between the regions.

Discussion

 In agricultural production, the use of chemical fertilizers or the pollution by feces increases the concentration of calcium and chlorine ions in groundwater, which may be part of the reason for nitrate exceeding the standard[31]. By studying the correlation between the main chemical components of groundwater and nitrate content, this study reveals that high concentrations of nitrate in this area may be caused by the interaction of groundwater and soil rocks and the application of fertilizers in agriculture. Most groundwater has good water quality and can be used as drinking water[11,32]. Pb, TH, F^-, SO_4^{2-}, and TDS are the most significant parameters affecting groundwater quality. Contaminated groundwater in the study area can pose human health risks to residents through multiple exposure pathways, including drinking water intake and dermal contact. The total non-carcinogenic health risks for males, females, and children are very crucial in the study areas. Additionally, compared with the results of groundwater quality assessment, we found that although most of the water quality of the study area is in good condition, both adults and children face great health risks, especially carcinogenic. Therefore, the overall groundwater assessment should be accompanied by a health risk assessment to better evaluate the suitability of groundwater for drinking.

Conclusion

ICP-MS is an excellent analytical technique for surveying a large number of elements in water. The Information presented above is also extremely useful to the scientific community and public officials involved in health risk assessment and management of environmental contaminants as well as a guide for the analysis of water of different regions that will help in creating a site-specific range[20,33]. FTIR spectroscopy is a useful and nondestructive techniques that does not require difficult sample preparation. New perspectives in the characterization of minerals provides opportunities to combine various FTIR techniques with microscopic system[34]. Currently, the FTIR technique is not a complete alternative to other mineral identification procedures, but it is a useful auxiliary tool. Present wavenumbers and description of most widely used data and processing techniques that will help interpret the IR spectra of geochemical samples as well as contaminated water samples.

Acknowledgements

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