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Groundwater Contamination in Parts of Nalgonda District, Telangana, India as Revealed by Trace Elemental Studies

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ABSTRACT

The present paper deals with major and trace elements geochemistry of the groundwater from Nalgonda district, Telangana. The study area is very important in terms of anthropogenic activity like rapid industrial, urban development, pesticides, *pharmaceutical,* granite polishing and agro based industries. Inductively coupled plasma mass spectrometer (ICPMS) was employed to determine the concentration of trace elements in collected groundwater samples (bore well). These probe elements were further categorized as toxic elements (Pb, As, Cd, and V), alkaline earths (Sr and Ba), alkali metals (Li, Rb), transition metals (Cr, Mo and Ni), metallic elements (Cu, Fe, Zn, Al, Co), and other non-metallic elements (Se and Si). The groundwater quality was examined in perspective of Indian as well as World Health Organization drinking water standards. Based on the analytical results, groundwater in the study area is found to be slightly alkaline in nature and very hard, the average abundance of the major cations and anions is in the order of $Ca^+ > Na^+ > Mg^+ > K^+$ and $Cl^- > HCO_3^- > CO_3^- > SO_4^- > NO_3^- > F^-$ respectively. The dominant hydro chemical facies of groundwater is $Na^+ - HCO_3^- - Cl^-$ and $Na^+ - Cl^- - HCO_3^-$ types.

The results of trace elements shows that concentration of Pb, As, Cd, V in collected samples exceeding the desirable limits, and in the case of alkaline, alkali, transition, non-metallic elements, seventy per cent of the samples crossed the desirable limits, but all metallic elements viz. Cu, Fe, Zn, Al, Co is within the limits as per Indian as well as World Health Organizations drinking water standards. Factor analysis results shows that seven factors emerged as a significant contributor to the groundwater contamination is about 65.32 per cent. The spatial variation maps decipher trace elemental concentrations both geogenic and anthropogenic origin, by three zones i.e. 'low', 'moderate' and 'high' of the study area based on environment using Arc-GIS. High concentrations of trace elements are indicative of phenomenal rise in chemical composition and likely to have its origin from silicate weathering reactions and dissolution/precipitation processes supported by rainfall and anthropogenic activities, indiscriminate use of fertilizers/pesticides, and disposal of waste and sewage, release of reactive pollutants into the atmosphere by industries. Hence, this work is of immense societal benefit in terms of prevailing human health hazards in the study area with a direct relevance to such industrially populated regions elsewhere.

INTRODUCTION

The trace elements are the elements which are present in water in less quantity (less than 1 ppm). Many of the trace elements are also known as heavy metals (Freeze and Cherry 1979). These metals present in trace concentration play a major role in the human and animal's metabolism and healthy growth of plants: the same metals, however, at increased concentration may have toxicological effects on human beings (Chapman, 1992). The most important and natural sources of trace elements is rock water interaction from which the released metal find their way into the water bodies. In recent years, considerable interest has been focused on assessing the human health risk posed by metals, metalloids, and trace elements in the environment. It has long been recognized that large areas of the globe have human populations characterized by trace element deficiency, or excess including chronic poisoning. The concentration of these elements increase due to waste disposal, vehicular exhaust, atmospheric deposition, use of fertilizers and pesticides, and application of sewage sludge in arable land (Cui et al. 2005; Zheng etal. 2007; Khan et al. 2013; Zhao et al. 2014). Contamination by potentially toxic elements in the natural environment is one of the major problems for human health and environment quality because these elements are indestructible and most of them have toxic effect on living organisms when they exceed certain concentration.

The elemental anomaly in the groundwater regime once created through natural processes or by unintended or unethical human intervention, often goes unabated. The toxicity of an element depends on the dose, the chemical form, route of exposure, bio–availability, and distribution in the body, and storage and excretion parameters. The World Health Organization (WHO) and many national government departments have set standards for trace elements in ground-water, drinking water etc. The groundwater quality is determined predominantly by the geochemical processes, chemical and mineral composition of the aquifer rocks, residence time and other factors related to groundwater flow, addition of effluents through human interference and others.

STUDY AREA

The study area is a typical hard rock terrain where huge stress on groundwater resources has been witnessed due to anthropogenic activities (Brindha et al. 2010). This region is mainly dependent upon groundwater for irrigation, domestic, drinking needs and the groundwater quality of this area for the above mentioned purposes have not been identified earlier.

The area (Fig.1) lies between 79°35'30" and 79°40'35"E longitude and 17°05'00" and 17°10'00"N latitude GSI (1995). This district comprises of Dharwars, peninsular gneissic complex, Cuddapah Supergroup, Kurnool Group (Palnad) (Fig.2). The oldest known geological formations are the Dharwars, which were deposited in shallow basins and subsequently intruded by basic rocks. Later these rocks were subjected to intense structural disturbances and have undergone metamorphism coupled with large scale invasion of granite

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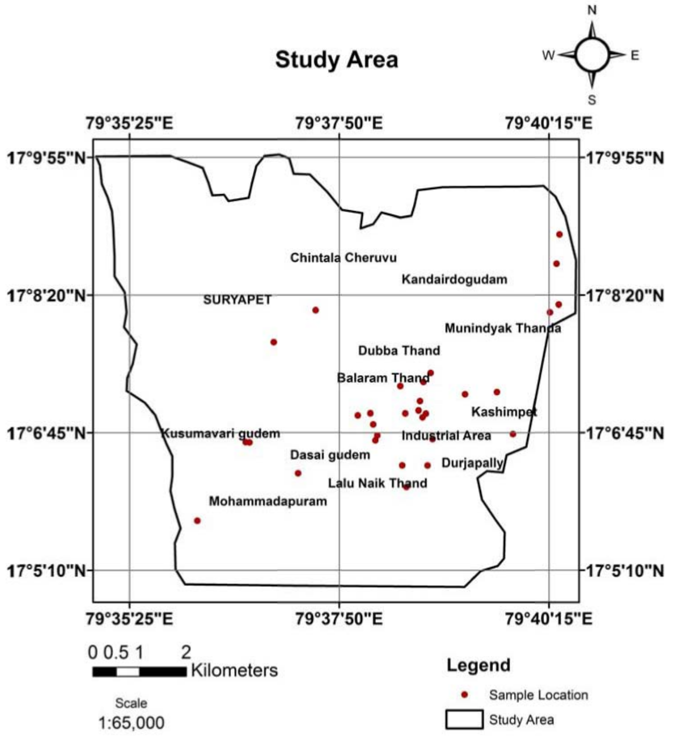

Fig.1. Location map of the study area

magma which by metamorphism assumed gneissic structure at places. The granites and gneisses were subsequently intruded by dolerite dykes, veins of pegmatite and quartz. The drainage pattern in the study area is dentritic to sub-dentritic, groundwater occurs mainly in the weathered and fractured zones under unconfined condition while the deeper fractures are under semi-confined conditions. Thickness of the weathered zone varies from 4 to 20 m, followed by a fractured/ fissured zone.

MATERIALS AND METHODS

Thirty groundwater samples were collected from bore well penetrating the shallow to deep aquifers (~3 to 40m deep) during post-monsoon (December) season in 2014. The samples were collected in one litre polyethylene bottles and acidified in the field by HNO_3. Prior to collecting the samples, the wells were duly pumped so that the stagnant water, if any, is completely removed from storage in the well assembly. Values of pH and electrical conductivity (EC) were measured in the field itself by a portable digital water analysis kit with electrodes. Total dissolved solids (TDS) were calculated by summing up the concentrations of all the major cations and anions.

To assess the groundwater quality as to its type and extent of pollution, groundwater samples were collected with an objective to find out major and concentration of trace elements in the study area. Selection of sample was based on potential areas prone to pollution viz., residential, agriculture, industrial and sewage discharged areas etc. The samples were filtered, acidified by HNO_3 and carried to the laboratory for further analyses of trace elements by inductively coupled plasma mass spectrometer (ICP-MS). The trace elements were analyzed at Geochemical Laboratory, NGRI, Hyderabad, India.

The study aimed at (i) major and trace elements geochemistry from the groundwater (ii) determining the natural background levels of trace elements as a guide for future pollution monitoring with suitable recommendations for mitigation of environment impacts, if any, (iii) examining the groundwater quality in perspective of Indian as well as WHO's drinking water standards, (iv) characterizing the hydro-chemical process that is dominant in the area by factor analysis (FA), and, (v) generating spatial variation maps deciphering different zones of trace element concentration in the groundwater using the geographic information system (GIS) platform.

RESULTS AND DISCUSSION

Major Elements

The quality of groundwater samples that have been analyzed for

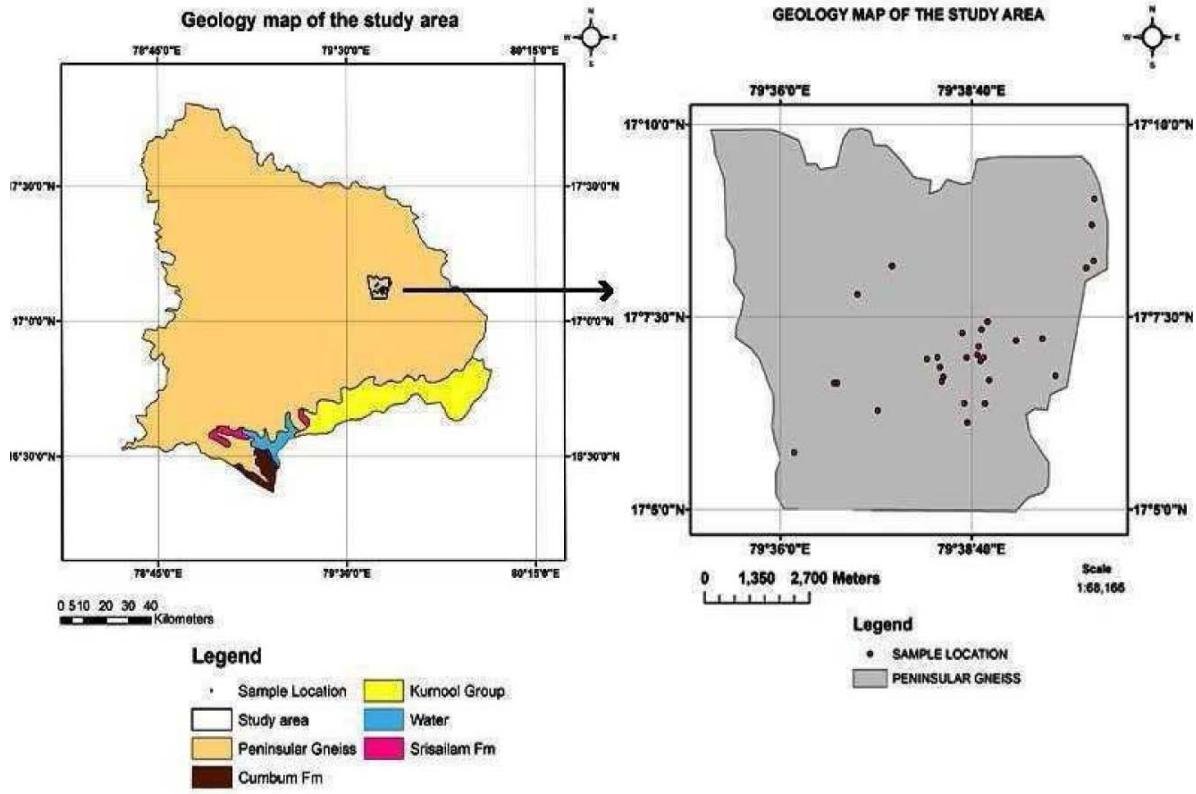

Fig.2. Geology map of the study area

major and trace elements was examined in perspective of BIS (2014) and World Health Organization WHO (2011) drinking water standards as shown in Table 1. In the study area, the wide variation of water quality parameters in space and time was mainly due to anthropogenic sources. The chemical composition of the groundwater in this region is likely to have its origin from silicate weathering reactions and dissolution/precipitation processes supported by rainfall and groundwater flow. The sewage release of reactive pollutants, agricultural development, inadequate management of land, water resources, over exploitation, indiscriminate use of fertilizers/ pesticides are the main causes of anthropogenic pollution.

The pH varies from 7.0 – 8.6, indicating a slightly alkaline condition of groundwater and about 3.3 % of the total samples in the study area exceed the recommended limit of 6.5 to 8.5 mg/l. Electrical conductivity of water is a good indicator of pollution as most of the soluble pollutants exist as ions in water and it varies between 380 – 5910 µs/cm at 25°C reflecting a wide variation in the activities of geochemical processes. About ninety per cent of the total samples in the study area exceed the recommended limit of < 1000 µs/cm. In the study area total dissolved solids (TDS) can be attributed to dissolution/ precipitation processes that occur during groundwater movement along the lineaments, fractures and joints. These control the course of groundwater movement in the hard rock terrains and the local topographic variations in the study region are probably responsible for adding/ removing ions contributing to TDS, although the influence of anthropogenic activities is maximal. It is observed that TDS of groundwater of the study area varies between 190 – 2960 mg/l, about ninety per cent of the total samples in the study area exceed the recommended limit of <500 mg/l, which comes under non-potable category WHO, (2011); BIS, (2014). The total hardness of groundwater of the study area varies between 180 – 2656 mg/l, about ninety six per cent of groundwater samples of the study area exceeds the threshold limit of 300 mg/l as per BIS (2014), and WHO (2011).

The average abundance of the major cations and anions is in the order of $Ca^+ > Na^+ > Mg^+ > K^+$ and $Cl^- > HCO_3^- > CO_3^- > SO_4^- > NO_3^- > F^-$ respectively. The concentration of calcium varies between 43.9 – 774.5 mg/l; sodium varies between 14.5 – 958.0 mg/l; magnesium range between 4.3 – 247.7 mg/l and potassium range between 0.9 – 87.5 mg/l. Eighty per cent of cations of the total groundwater samples, exceed the highest permissible limits prescribed for drinking water BIS, (2014), WHO, (2011) (Table 1). These concentrations in the groundwater are due to the weathering of pyroxenes, plagioclase feldspars, apatite and sphene present in the granites and alaskites. Apart from natural sources, anthropogenic activities have significant influence on the concentration of cations in the groundwater of the study area.

Among the anionic concentrations, the order is $Cl^- > HCO_3^- > CO_3^- > SO_4^- > NO_3^- > F^-$. The concentration of chloride is varying from 11.6 – 1925.5 and sulphate from 16.9 – 726. About eighty five per cent and forty five per cent of samples exceed the highest permissible limits for chloride and sulphate respectively prescribed for drinking water BIS, (2014); WHO, (2011). The concentrations of trace elements are high due to the weathering of phosphate mineral (e.g. apatite) from granites, domestic sewage, industrial effluents (Craig and Anderson, 1979; Karanth, 1987). Similar sources are expected to cause the increase in chloride concentration in the groundwater which leads to salinity, which deterioration of the soil in the study area. The concentrations of bicarbonates are varying from 140 - 600 mg/l, carbonates are varying from 0 – 80 mg/l. It is usually the primary anion in groundwater and is derived from the carbon dioxide released by the organic

Table 1. Drinking water quality standards of trace elements

Elements	Study Area				Percentage exceeding	WHO (2011) µg/l	BIS (2014) µg/l	Adverse effect beyond the desirable limit
	Min	Max	Mean	SD				
pH	7.03	8.6	7.81	0.31	3.3	6.5-8.5	6.5-8.5	Taste, effects mucus membraneand water supply system
EC	380	5910	2631	1377	90	750	1000	Bad taste to potable water
TDS	190	2960	1412	746	90	500	500	Taste, gastro-intestinal irritation
TH	180	2656	777	560	96.6	300	300	Cardiovascular disease
Pb	0.6	40.51	7.951	9.83	33.3	0.01	0.01	Pb toxicity causes nervous system, gastrointestinal, respiratory disorders.
As	0.4	34.1	4.041	6.07	6.6	0.01	0.01	Cardiovascular system, gastrointestinal tract, kidney, skin, blood and liver
Cd	2.23	32.84	9.28	7.23	100	0.003	0.003	Psychological disorders, diarrhea, stomach pains,bone fracture and damage of immune system
V	9.99	36.90	22.13	7.37	100	0.01	0.01	Irritation of lungs, throat, eyes, damage of nervous system
Sr	189.58	4669.25	920.08	1231	100	*0.004	*0.004	Lung cancer and problem in bone growth
Ba	47.89	409.26	143.61	70.65	0	0.7	0.7	Highly toxic, increase in blood pressure
Li	5.44	99.92	19.92	16.86	100	0.0025	0.0025	Cause nausea, diarrhea, dizziness, muscle weakness,
Rb	0.5	16	3.57	3.18	3.3	0.01	0.01	Skin and eye burns, hyper irritation, skin ulcers and extreme nervous system
Cr	2.53	11.35	6.20	2.43	0	0.05	0.05	Skin rashes, upset stomach ulcers, respiratory problems, kidney and liver damage
Al	39.70	772.00	39.70	772.00	23.33	0.2	0.2	Loss of memory, severe trembling and dementia
Mo	12.96	75.55	34.87	14.45	3.3	0.07	0.07	Liver dysfunction, joint pains in the knees, hands, feet articular deformities
Ni	5.13	81.50	39.25	19.05	83.3	0.07	0.02	Lung cancer, respiratory failure, birth effects And heart disorders
Co	8.28	34.07	18.54	6.47	0	0.05	0.05	High concentration causes vomiting and nausea, vision problems, thyroid damage
Cu	3.51	22.95	8.40	3.79	0	2.0	2.0	Liver damage or anemia
Fe	8.83	145.34	25.48	24.49	0	3.0	3.0	Staining of clothing and plumbing material
Zn	13.12	14839.95	771.65	2765	6.6	3.0	5.0	Corrosion of plumbing material, industrial contamination
Se	2.34	146	23.61	30.37	63.33	0.04	0.01	Garlic breath, bronchitis, fever, headache, conjunctivitis, vomiting and abdominal pain
Si	4.42	190	32.03	30.69	50	0.03	0.03	Bronchitis, chronic obstructive pulmonary disease, irritation of skin, eyes and mucus membrane

* US Environmental Protection Agency (EPA); All elements in µg/l; EC: in µS/cm, TDS & TH mg/l

decomposition in the soil (Todd, 1980). The concentrations of nitrate are varying from 1.1 – 341.7 mg/l. About thirty three per cent of the total groundwater samples exceeds permissible limits of 45 mg/l, prescribed for drinking water BIS, (2014); WHO, (2011). The sources of nitrate is industrial wastes containing N-compounds of human, animal wastes and agricultural activities. Urea $CO(NH_2)_2$ and ammonium nitrate NH_4NO_3 are the most commonly used fertilizers contributing nitrates to the groundwater of the study area. The concentrations of fluorides are varying from 0.2 – 2.3 mg/l. About sixty per cent of the total groundwater samples exceeds permissible limits of 1.3 mg/l, prescribed for drinking water BIS, (2014); WHO, (2011) (Table 1).

Trace Elements in Groundwater

Many trace elements are essential nutrients, however, certain trace elements, are known to be persistent environment contamination and toxic to most form of life. Trace elements are generally present in small concentration in natural water system. Their occurrence in groundwater and surface water can be due to natural sources, such as dissolution of naturally occurring minerals containing trace elements in the soil zone or the aquifer material or to human activities, such as mining, fuels, smog smelting of ores and improper disposal of industrial wastes.

Status of trace elements in the groundwater of the study area has been discussed with respect to BIS (2014) and WHO (2011) drinking water standards below (Table 1):

Lead (Pb)

The concentration varies from 0.6 – 40.5 µg/l, highest permissible limit for lead is 0.01 µg/l as per WHO (2011) and BIS (2014). High concentration of lead is observed at the NE of the study area (Fig.3a). Lead concentration in natural waters increases mainly through anthropogenic activities (Goel, 1997). The possible sources of lead in groundwater were diesel fuel consumed extensively in farm lands, discarded batteries, paint and leaded gasoline. Lead was also used in some pesticides as lead arsenate which is also one of the source in the study area. Lead is toxic to the central and peripheral nervous system causing neurological and behavior effects. The consumption of lead in higher quantity may cause hearing loss, blood pressure and hypertension and eventually it may prove to be fatal.

Arsenic (As)

Arsenic concentration ranged from 0.4 – 34.1 µg/l, the highest permissible limit is 0.01µg/l as per WHO (2011) and BIS (2014). High concentration of arsenic is observed at NE of Kandairde Gudem of the study area (Fig.3b). It is a semi-metallic element found in soils, groundwater, surface water, air, and some foods (U.S. Agency for Toxic Substances and Diseases Registry (ATSDR), 2005). Arsenic introduced into groundwater from industrial effluents, atmospheric deposition and also from pesticides, insecticides and herbicides, which are extensively used in the study area. Chronic inorganic arsenic exposure is known to be associated with adverse health effects on several systems of the body, but is most known for causing specific types of skin lesions (sores, hyper pigmentation, and other lesions) and increased risks of cancer of the lung and skin ingesting contaminated foods.

Cadmium (Cd)

Cadmium concentration ranged from 2.23 – 32.8 µg/l, the highest permissible limit is 0.003µg/l as per WHO (2011) and BIS (2014) in the study area. High concentration of cadmium is observed at NE of Durajpalle of the study area (Fig.3c). Cadmium is a cumulative environmental pollutant and its exposure to the body results damage of the kidney, and causes renal dysfunction, arteriosclerosis, cancer etc. (Robards and Worsfold, 1991; Goel, 1997). The concentration of cadmium in water samples of the study area may be attributed to the runoff from the agricultural sector where pesticides as well as cadmium phosphatic fertilizer are being used (Tiwari et al., 2013).

Vanadium (V)

Vanadium concentration varies from 9.9 – 36.9 µg/l, the highest permissible limit is 0.01µg/l as per WHO (2011) and BIS (2014). High concentration of Vanadium is observed south of Mahamunadapuram (Fig.3d). The natural sources of vanadium release to water include wet and dry deposition, soil erosion, and leaching from rocks and soil anthropogenic releases to water and sediments are far smaller than natural sources (Van Zinderen Bakker and Jaworski, 1980. Anthropogenic sources of vanadium include oil and coal combustion, steel alloy tool production and traffic pollution. Anthropogenic releases of vanadium to soil are less widespread than natural releases and occur on a smaller scale. These include the use of certain fertilizers containing materials with a high vanadium content such as rock phosphate (10–1,000 mg/kg vanadium), superphosphate (50–2,000 mg/kg vanadium), and basic slag (1,000–5,000 mg/kg vanadium) (Van Zinderen Bakker and Jaworski 1980) as well as disposal of industrial wastes such as slag heaps and mine tailings. Vanadium is used for treating diabetes, low blood sugar, high cholesterol, heart disease. The acute effects of vanadium are irritation of lungs, throat, eyes and nasal cavities. Cardiac and vascular disease, inflammation of stomach and intestines, damage to the nervous system, bleeding of livers and kidneys, skin rashes, severe trembling and paralyses, Nose bleeds and throat pains, weakening, sickness, headaches, dizziness and behavioural changes.

Strontium (Sr)

The concentration of strontium values range from 189.58 - 4669.25 µg/l, the highest permissible limit is 0.004 µg/l as per WHO (2011) and BIS (2014). High concentration of strontium is observed north of Chintala Cheruvu (Fig.4a). Strontium minerals were widely distributed throughout the earth and are released to the groundwater by the natural re-crystallization of rocks and weathering of rocks and soils (Greve et al., 2007). Higher concentrations indicates that the source could be through agricultural activity causing an input of strontium, to some extent and it depends on the content of fertilizers and carbonate additives and manure like cattle, poultry etc. (Negrel et al., 2004). Strontium concentrations in soil may also be attributed to dumping waste, and industrial wastes. Strontium in soil dissolves in water, so that it would be able to leach deeper into the ground and enter the groundwater. Excessive strontium intakes can alter bone mineralization, such as inhibiting the incorporation of calcium or replacing calcium, and cause bone deformities. Ingestion of large amounts of strontium coupled with a calcium poor diet during infancy and childhood can develop “strontium rickets.” Strontium-90 taken up by bone, attacks bone marrow and soft tissues developing into anemia and leukemia.

Barium (Ba)

Barium concentration ranged from 47.89 – 409.26 µg/l, and highest permissible limit is 0.7µg/l as per WHO (2011) and BIS (2014). High concentration of Barium observed at Chintala Cheruvu, Suryapet and Dubba Thanda of the study area (Fig.4b). Barium enters the environment naturally through the weathering of rocks and minerals. Barium is more mobile and is more likely to be leached from soils in the presence of chloride due to the high solubility of barium chloride as compared to other chemical forms of barium (Lagas et al. 1984; Bates 1988). The accumulation of barium in soils is due to the continued use of fertilizers and soil amendments for increased content of barium in agricultural products. Ingesting high levels of barium compounds that dissolve well in water over the short term has resulted in difficulties in breathing, increased blood pressure, changes in heart

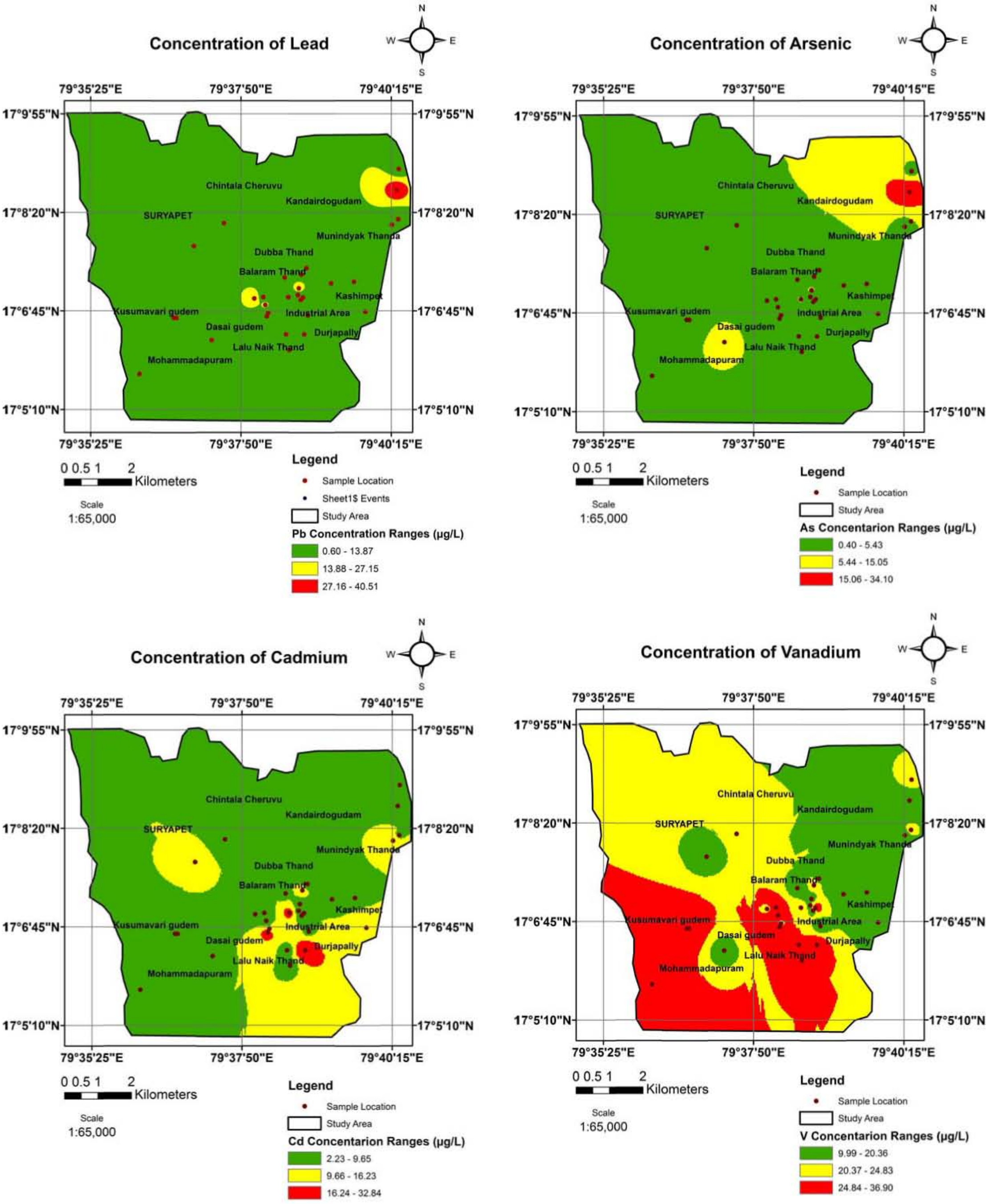

Fig.3. (a-d). Spatial variation maps of Toxic elements (Pb, As, Cd, and V)

rhythm, stomach irritation, brain swelling, muscle weakness, damage to the liver, kidney, heart, and spleen.

Lithium (Li)

The concentration of Lithium values range from 5.44 - 99.92 µg/l, the highest permissible limit of 0.0025 µg/l as per WHO (2011) and BIS (2014). High concentration of lithium observed at industrial area (Fig.5a). Lithium is a highly reactive, light metal, commonly found in drinking water and in many foods, such as grains, vegetables, mustard, kelp, fish, blue corn, pistachios, dairy and meat. Lithium is a geogenic element, being rare in polluted waters, and is contributed to groundwater by time-dependent water-rock interaction and it forms an important tracer element. The enrichment in lithium by water-rock interaction is best expressed by the Li/Cl; (Li/Cl)/Cl, or Li/Na ratios. Lithium may be derived particularly from biotite and other primary minerals. Strong enrichment may be found in some granitic rocks with concentrations in the mg/l range). Lithium can cause nausea, diarrhea, dizziness, muscle weakness, fatigue, and a dazed feeling.

Rubidium (Rb)

Rubidium concentration ranged from 0.5 – 16 µg/l, the highest permissible limit is 0.01 µg/l as per WHO (2011) and BIS (2014). High concentration of rubidium is observed in industrial area (Fig.5b). Rubidium readily reacts with skin moisture to form rubidium hydroxide, which causes chemical burns of eyes and skin, signs and symptoms of over exposure, loss of weight, hyper irritation, skin ulcers and extreme nervousness.

Chromium (Cr)

The concentration of chromium values ranged from 2.53 – 11.35 µg/l, the highest permissible limit is 0.05 µg/l as per WHO (2011) and BIS (2014). High concentration of Chromium is observed north and

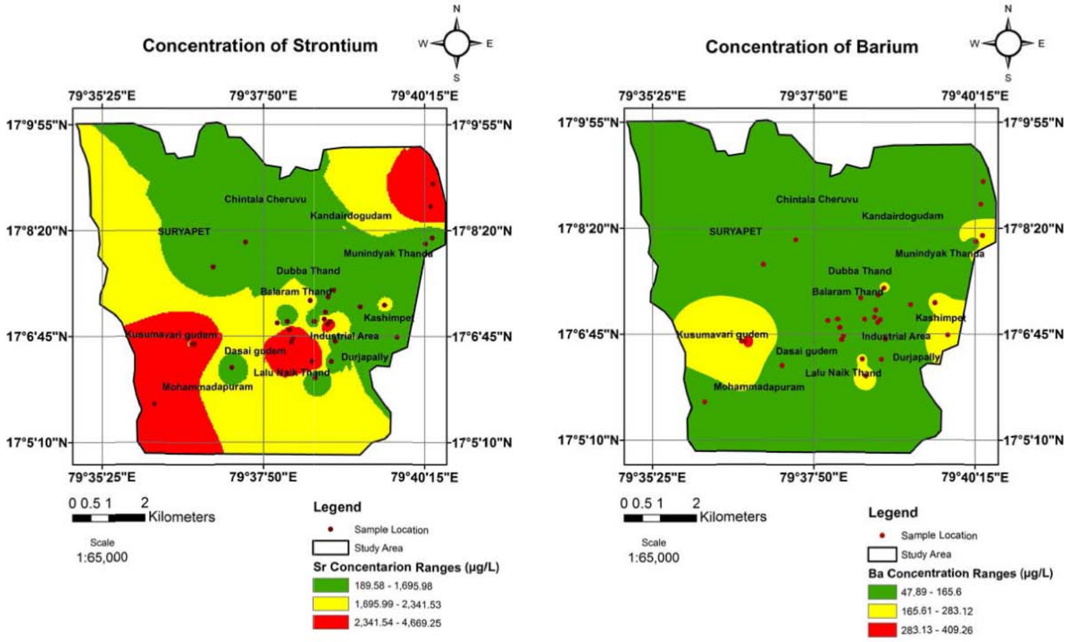

Fig.4. (a- b). Spatial variation maps of Alkaline earths (Sr and Ba)

southern part of the study area (Fig.6a). High concentration of Cr in groundwater may cause ulceration of nasal septum and dermatitis (Singh and Bhayana, 1986). The major source of hexavalent chromium in drinking water is oxidation of naturally occurring chromium present in igneous rocks. There are areas where chromium compounds have been released to the environment via leakage, poor storage, or improper industrial disposal practices.

Nickel (Ni)

Nickel concentration ranged from 5.13 – 81.50 µg/l, the highest permissible limit is 0.02µg/l as per WHO (2011) and BIS (2014). High concentration of nickel is observed at Dasai Gudem, near industrial area (Fig.6b). Nickel is present in a number of enzymes in plants and micro organism (Tiwari et al., 2013). In the human body, nickel influences iron adsorption, metabolism and may be an essential component of the haemopoiitic process. Acute exposure of nickel by the human body is associated with a variety of chemical symptoms and signs such as nausea, vomiting, headache, giddiness etc. (Barzilay, 1999). The primary source of nickel in drinking water is leaching from metals in contact with drinking water such as pipes and fittings.

Molybdenum (Mo)

Molybdenum concentration varies from 12.96 – 75.55 µg/l, the highest permissible limit of 0.07µg/l as per WHO (2011) and BIS (2014). High concentration of molybdenum is observed at the NE part of the study area and some parts of Dasai Gudem, industrial area (Fig.6c). Molybdenum is considered to be an essential trace element in both animals and humans. Safe and adequate intake levels have been suggested for various segments of the population, namely 0.015–0.04 mg/day for infants, 0.025–0.15 mg/day for children aged 1–10 and 0.075–0.25 mg/day for all individuals above the age of 10 (National

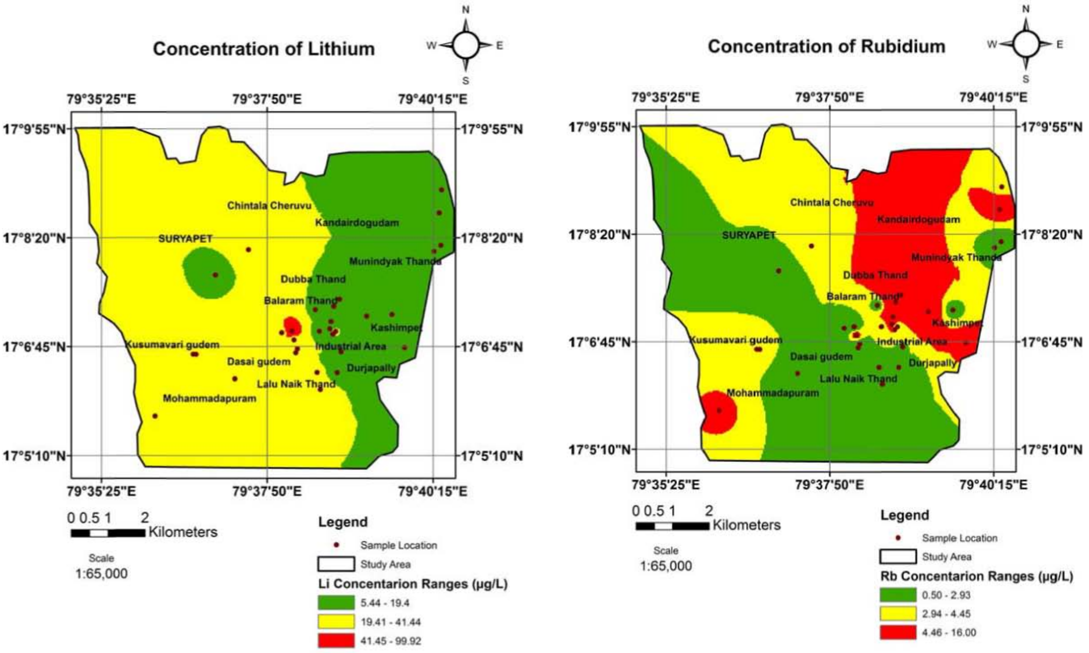

Fig. 5. (a-b). Spatial variation maps of Alkali metals (Li, Rb)

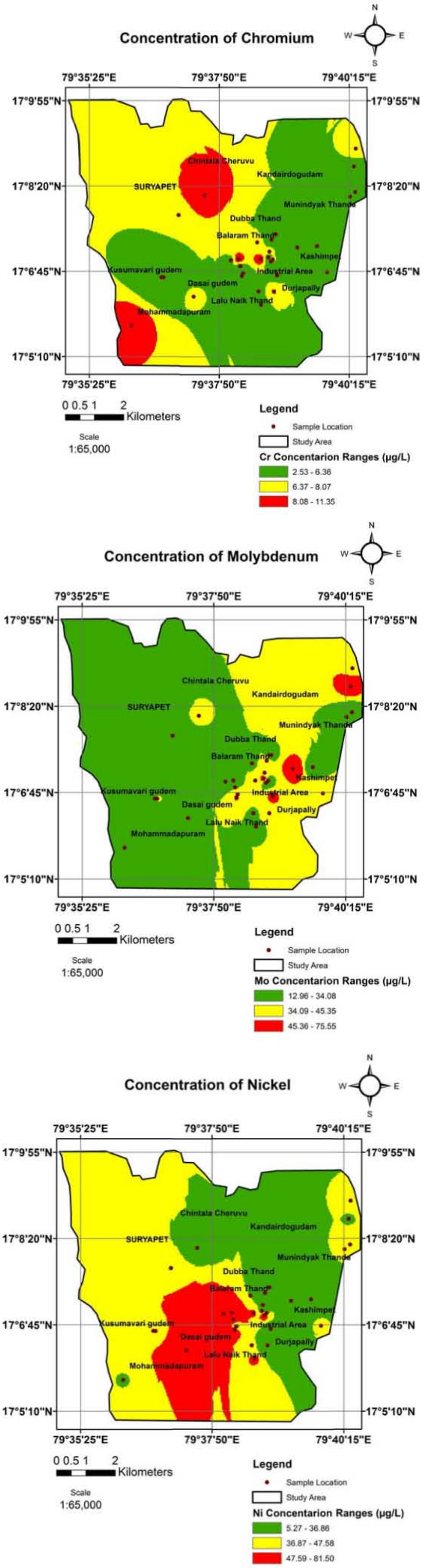

Fig. 6. (a-c). Spatial variation maps of Transition metals (Cr, Mo and Ni)

Academy of Sciences, 1989). An infant with inborn deficiency of the molybdoenzymes sulfite oxidase and xanthine dehydrogenase exhibited abnormal distribution of urinary metabolites, neurological disorders, dislocated ocular lenses and failure to thrive (Johnson et al., 1980). A Crohn disease patient receiving total parenteral nutrition developed tachycardia, tachypnoea, severe headaches, night blindness, nausea, vomiting, central scotomas, generalized oedema, lethargy, disorientation and coma; these symptoms were attributed to dietary Molybdenum deficiency resulting in impaired function of the two molybdoenzymes (Abumrad et al., 1981).

Copper (Cu)

The concentration of Copper values range from 3.51 – 22.95, µg/l, the highest permissible limit is 2.0 µg/l as per WHO (2011) and BIS (2014). High concentration of copper is observed north of the study area (Fig.7a). Copper is an essential element in human metabolism and essential element, concentrated in several enzymes, its presence in trace concentrations is essential for the formation of hemoglobin (Tiwari et al., 2013). An over dose of copper may lead to neurological complication, hypertension, liver and kidney dysfunctions (Krishna and Govil, 2004; Khan et al., 2010). Ingestion of copper causes infant death, short lived vomiting diarrhea etc (Barzilay, 1999).

Iron (Fe)

Iron concentration ranged from 8.83 – 145.34 µg/l (Fig.7b), the highest permissible limit is 2.0 µg/l as per WHO (2011) and BIS (2014). High concentration of iron is observed near industrial area (Fig.7b). It is possible that some Fe concentration could be attributed to the corrosion of pump parts as shown by Langaneger (1987). The higher concentrations of iron may cause toxic effect to human health. Iron is an essential element in human body (Moore, 1973) and is found in groundwater all over the world; higher concentrations of iron causes bad taste, discolouration, staining, turbidity, esthetic and operational problem in water supply systems (Dart, 1974; Vigneshwaran and Vishwanathan, 1995).

Zinc (Zn)

Zinc concentration ranged from 13.12 - 14839.95 µg/l, the highest permissible limit is 3.0 µg/l as per WHO (2011) and BIS (2014). High concentration of zinc is observed all over the study area (Fig.7c). Zinc is also an essential trace element found in virtually all kind of food and potable water in the form of either salt or organic complexes. The groundwater samples were clearly Zn-deficient. Zinc deficiency may leads to dwarfism, dermatitis and loss of taste.

Aluminum (Al)

Aluminum concentration ranged from 39.70 – 772.00 µg/l, the highest permissible limit is 0.2 µg/l as per WHO (2011) and BIS (2014). High concentration of aluminum is observed in some parts of south and northeast of the Chintala Cheruvu of the study area. (Fig.7d). The source of Aluminum in the groundwater samples may be through weathering of bedrock and soil or it may be related sources like industries, which introduced Aluminum into groundwater. Health-wise, there had been a considerable debate on the possible link between Al in drinking water with Alzheimer's disease in humans (Craun, 1990; Epstein, 1990; Flaten, 1990).

Cobalt (Co)

Cobalt concentration ranged from 8.28 – 34.07 µg/l, the highest permissible limit is 0.05 µg/l as per WHO (2011) and BIS (2014). High concentration of cobalt is observed in industrial area and in Balram Thanda of the study area (Fig.7e). Cobalt may enter the environment from both natural sources and human activities. Cobalt occurs naturally in soil, rock, air, water, plants, and animals. It may

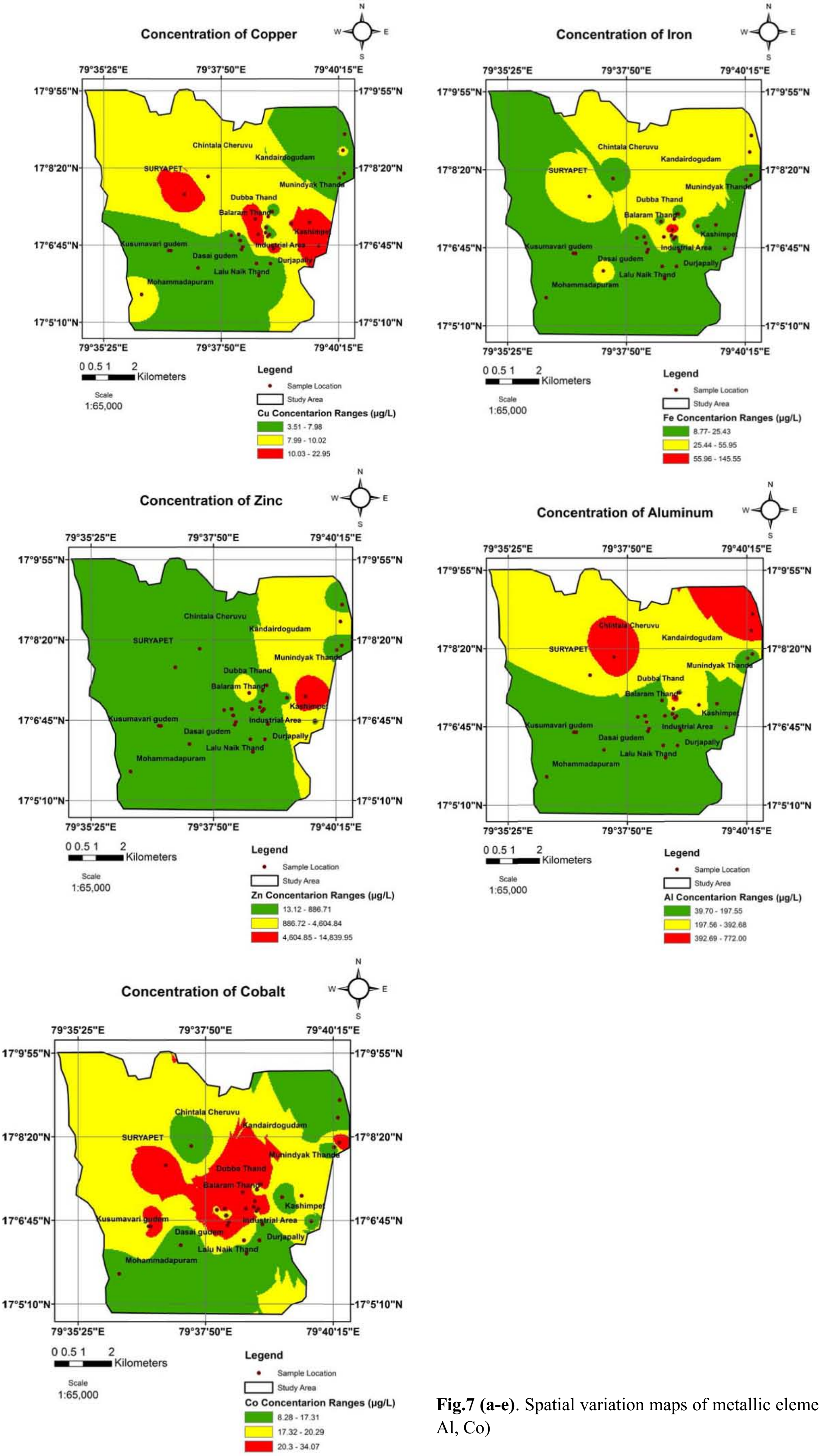

Fig.7 (a-e). Spatial variation maps of metallic elements (Cu, Fe, Zn, Al, Co)

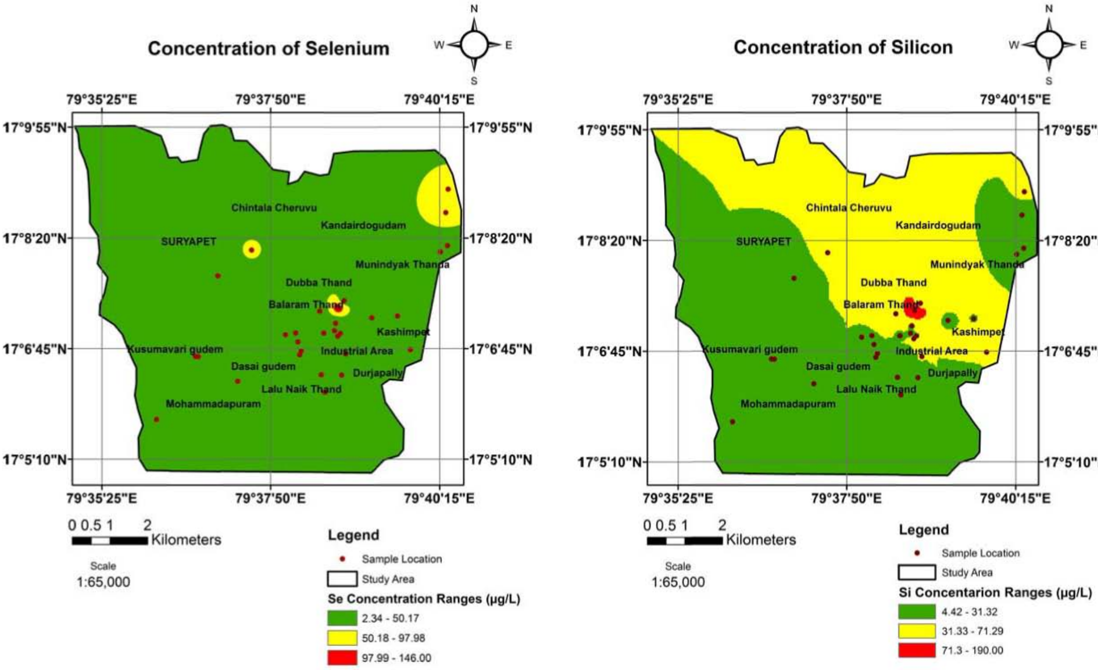

Fig.8. (a-b). Spatial variation maps of Non-metallic elements (Se and Si).

enter air and water, and settle on land from windblown dust, and may additionally get into surface water from runoff and leaching when rainwater washes through soil and rock containing cobalt. Phosphate rocks, other industrial pollution may contain high concentrations of cobalt. Cobalt is an essential metal and a component of vitamin B_{12}, it has been found in most tissues, such as muscle, lung, lymph nodes, heart, skin, bone, hair, stomach, brain, pancreatic jui, kidneys, plasma, urinary bladder, and liver (highest levels), of non-occupationally exposed subjects (Forbes et al., 1954). An excessive intake of cobalt may damage the heart muscles, and may cause an over-production of red blood cells or damage to the thyroid gland.

Selenium (Se)

The concentration of selenium values ranged from 2.34 – 146 µg/l, the highest permissible limit is 0.01 µg/l as per WHO (2011) and BIS (2014). High concentration of selenium is observed north of the study area (Fig.8a). The maximum contaminant level for selenium is 0.01 µg/l micro grams per liter U.S. Environmental Protection Agency, (1976). Small amount of selenium was beneficial, but excess amount was toxic. The potential health effects were on hair, finger nail loss and numbness in fingers or toes.

Silica (Si)

The concentration of silica values ranged from 4.42 – 190.00 µg/l, the highest permissible limit is 0.03 µg/l as per WHO (2011) and BIS (2014). High concentration of silica isobserved at NE of Balaram Thanda of the study area (Fig.8b). The most common of the quartz silica is the alpha-quartz, which is a major component of igneous rocks - granite and pegmatites. Due to the abundance of silica in the tropical regions, it has become a major chemical constituent of natural water bodies. According to Hem (1985), the primary source of dissolved silica in natural waters is the chemical breakdown of silicate minerals in rock and sediments by chemical weathering process (Jansen et al. 2010). Previous studies have shown that exposure to airborne crystalline silica normally results in silicosis (Cherry et al. 1997, 1998). Silicosis is a serious lung disease caused by the accumulation of silica dust in the lungs. The scarring of the lungs causes stiffening and this eventually obstruct breathing and cause shortness of breath. This can lead to permanent heart and lung disease. Silicosis development is directly associated with workplace exposure to silica dust.

FACTOR ANALYSIS

Factor analysis (FA) is a popular multivariate technique, which is

Table 2 Correlation matrix of Trace elements as determined from factor analysis

Variables	Ba	CO	Cd	Cr	Cu	MO	Ni	Sr	V	Zn	Fe	Li	Si	Al	Pb	Se	As
Ba	**1**																
CO	0.159	**1**															
Cd	-0.028	0.164	**1**														
Cr	-0.428	-0.076	0.144	**1**													
Cu	0.014	0.213	0.261	0.247	**1**												
MO	-0.118	-0.125	0.175	-0.039	0.083	**1**											
Ni	0.037	0.004	-0.272	-0.180	-0.191	0.052	**1**										
Sr	0.176	0.116	-0.170	-0.256	-0.214	0.142	0.034	**1**									
V	-0.020	0.061	0.135	0.278	-0.405	-0.318	-0.086	0.158	**1**								
Zn	0.063	0.063	-0.057	-0.072	0.235	-0.210	-0.306	0.027	-0.248	**1**							
Fe	-0.290	-0.083	-0.086	0.172	0.044	0.005	-0.001	-0.158	-0.190	-0.016	**1**						
Li	-0.054	0.030	-0.330	0.365	-0.189	-0.170	0.227	-0.089	0.425	-0.114	-0.151	**1**					
Si	-0.064	-0.102	0.085	-0.182	0.049	0.096	-0.140	-0.173	0.013	-0.020	-0.011	-0.079	**1**				
Al	-0.270	-0.395	-0.179	0.186	-0.059	0.249	-0.184	-0.008	-0.125	-0.059	0.303	-0.161	0.343	**1**			
Pb	-0.185	0.021	-0.086	0.094	-0.075	-0.010	-0.057	-0.176	-0.115	-0.046	0.928	-0.128	-0.031	0.144	**1**		
Se	-0.132	-0.289	0.006	-0.058	0.122	0.259	-0.211	-0.005	-0.156	0.059	0.144	-0.241	0.779	0.722	0.001	**1**	
As	-0.064	-0.274	-0.055	0.015	0.085	0.326	0.030	0.294	-0.330	0.101	0.262	-0.217	-0.075	0.335	0.097	0.448	**1**

Table 3. Factor loadings of trace elements as derived from factor analysis

	F1	F2	F3	F4	F5	F6	F7
Ba	-0.266	**0.317**	-0.228	0.049	0.148	0.010	0.100
CO	**-0.313**	-0.006	-0.169	-0.237	0.162	-0.006	0.058
Cd	-0.001	0.114	0.141	**-0.763**	0.154	-0.525	-0.056
Cr	0.052	**-0.589**	0.520	-0.345	-0.503	0.082	0.034
Cu	0.172	0.080	-0.137	**-0.576**	-0.174	0.212	-0.038
MO	0.342	0.191	-0.053	0.000	-0.248	**-0.349**	-0.255
Ni	-0.191	-0.049	-0.163	0.379	-0.094	-0.058	**-0.400**
Sr	-0.094	0.260	-0.132	0.334	-0.152	-0.327	**0.390**
V	-0.459	-0.223	**0.682**	0.166	0.251	-0.283	0.321
Zn	0.068	0.141	-0.216	-0.232	-0.034	0.403	**0.458**
Fe	0.579	**-0.708**	-0.286	0.048	0.202	-0.067	0.060
Li	**-0.374**	-0.269	0.352	0.253	-0.140	0.226	-0.102
Si	0.460	0.342	0.418	-0.009	**0.466**	0.181	-0.168
Al	**0.707**	0.008	0.298	0.214	-0.123	0.013	0.055
Pb	0.416	**-0.715**	-0.316	0.049	0.359	-0.089	0.055
Se	**0.833**	0.379	0.369	0.083	0.100	0.070	0.067
As	**0.519**	0.107	-0.186	0.155	-0.408	-0.223	0.198

Table 4. Summary of the percentage contribution of each factor in the factor analysis for Trace elements

Factors Values	Eigen	Percent Contri-bution	Elements with high loadings
I	2.926	17.21	Ni, Li, Cr, Pb, Fe and Co
II	2.015	11.85	Al, As, Co, Ba, Sr, Cd, Zn, Cu, Mo, Si, Se
III	1.710	10.06	Cr, Li, V, Al, Cd, Se and Si
IV	1.576	9.27	Pb, V, Se, Li, Al, Mo, Ni, Sr and As
V	1.118	6.58	Co, Si, Pb, Fe, V, Ba, Cd and Se,
VI	0.956	5.62	Cr, Cu, Al, Zn, Se, Ba, Li and Si
VII	0.804	4.73	Ba, Se , Pb, As, Li, Cr, Sr, Al and Zn
Total		65.32%	

used in identifying the most important components contributing to the chemical data structure and the interrelationships among various variables (Lall and Sharma 1996). It was used to quantify the contributions of natural chemical weathering and other impacts to the chemical composition of groundwater. It was done as follows: First, the correlation matrix, i.e. the array of correlation coefficients for all pairs of variables, was calculated. Then, the matrix was diagnosed, and its principal components (eigenvectors) were obtained. The so-called factor 1 is related to the larger Eigen value and is able to explain the greatest amount of variance in the data set. The second factor (orthogonal and uncorrelated with the first one) explains most of the remaining variance, and so forth.

The correlation matrix (Table 2) between 17 trace element variables in the groundwater of study area have been discussed in different groups like toxic elements (Pb, As,, Cd, and V), Alkaline earths (Sr and Ba), Alkali metals (Li, Rb), Transition metals (Cr , Co and Ni), Metallic elements (Cu, Fe, Zn, Al, Co), and other Non-metallic elements (Se and Si). In the entire study area seven factors were identified which are controlling the groundwater chemistry.

The contribution of the 1st factor is about 17.21 per cent of the total variance and the eigen value is 2.926. The contribution of the 2nd factor is about 11.85 per cent of the total variance and the eigen value is 2.015. The contribution of the 3rd factor is about 10.06 per cent of the total variance and the Eigen value is 1.710. The contribution of the 4th factor is about 9.27 per cent of the total variance and the eigen value is 1.576. The contribution of the 5th factor is about 6.58 per cent of the total variance and the eigen value is 1.118. The contribution of the 6th factor is about 5.62 per cent of the total variance and the eigen value is 0.956. The contribution of the 7th factor is about 4.73 per cent of the total variance and the eigen value is 0.804 (Table 3). The result of Factor Analysis based on the most significant first seven factors shows that about 65.32 per cent (Table 4) total variance of the ions. Hence, the first seven factors can be used to

Table 5. Major cations and anions data of the study area

Sample Id	Ca	Na	Mg	K	Cl	CO_3	HCO_3	SO_4	NO_3	F
Sample-1	128.6	344.7	54.8	5.1	373.5	0	400	160.8	130.8	1.0
Sample-2	68.5	218.4	92.9	3.9	240.6	60	420	125.2	36.7	1.7
Sample-3	70.0	295.1	121.1	1.6	346.1	80	600	86.4	6.5	2.3
Sample-4	63.1	290.3	38.4	2.5	118.4	60	560	38.1	54.8	1.7
Sample-5	69.2	107.3	17.1	2.4	135.9	0	140	43.8	87.3	0.8
Sample-6	144.7	300.2	76.6	1.2	546.1	0	390	104.9	8.9	1.4
Sample-7	195.3	470.6	123.1	6.6	955.1	0	350	239.8	39.2	0.8
Sample-8	322.1	352.8	188.9	8.3	1231.6	0	340	240.1	54.0	0.7
Sample-9	325.5	764.7	247.7	4.0	1661.6	0	490	524.1	4.6	1.6
Sample-10	92.0	262.5	54.7	1.3	316.2	80	300	113.1	19.8	1.5
Sample-11	162.1	438.1	137.0	3.8	819.8	0	440	234.6	3.6	1.2
Sample-12	132.0	365.0	92.8	1.5	556.3	40	350	191.0	12.5	1.5
Sample-13	180.9	958.0	186.1	7.0	1411.8	40	370	726.4	6.8	1.0
Sample-14	39.8	363.8	60.1	20.6	480.1	40	300	118.4	2.7	1.8
Sample-15	90.5	730.3	89.8	37.8	1110.4	40	180	402.8	4.9	2.0
Sample-16	133.2	368.6	59.3	2.7	525.6	40	400	151.8	1.1	0.8
Sample-17	58.2	549.9	76.4	12.4	739.7	0	220	281.3	4.8	1.6
Sample-18	774.5	506.5	175.5	3.0	1925.5	0	370	343.9	84.6	1.5
Sample-19	96.7	350.8	86.2	0.9	583.8	20	390	102.0	2.3	1.7
Sample-20	358.7	643.3	190.0	87.5	1538.3	60	450	254.4	173.7	1.0
Sample-21	85.1	413.4	41.5	3.5	365.8	80	410	124.0	92.6	2.2
Sample-22	53.6	208.0	47.2	1.4	299.8	60	330	105.5	9.4	1.4
Sample-23	161.1	695.9	114.1	4.1	1197.9	0	490	216.8	3.0	1.3
Sample-24	135.0	257.5	61.3	1.0	203.2	0	590	98.8	109.8	1.4
Sample-25	65.0	14.5	4.3	7.2	11.6	0	160	16.9	3.6	0.2
Sample-26	246.7	598.3	165.4	13.8	897.3	40	590	307.2	341.7	1.4
Sample-27	43.9	59.1	32.3	1.8	16.4	80	240	17.9	21.1	0.8
Sample-28	180.7	155.0	28.3	2.7	215.3	0	410	56.5	22.4	0.5
Sample-29	101.2	45.4	7.8	1.8	24.7	0	280	16.8	44.5	0.5
Sample-30	210.8	534.8	98.2	1.1	852.1	0	520	210.0	113.4	1.1

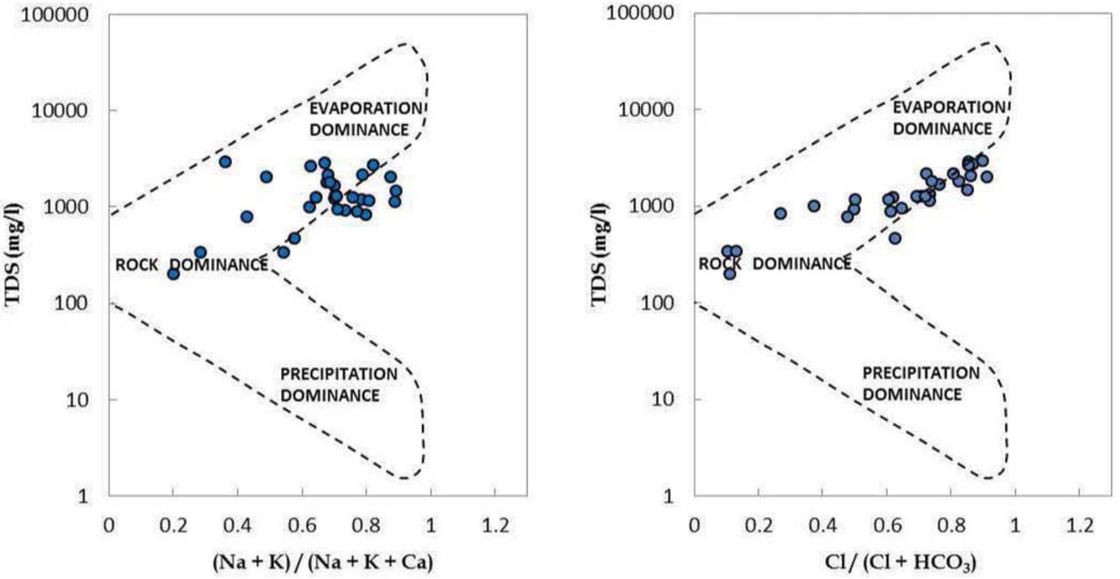

Fig.9. Gibbs diagram of the study area.

explain the main ions that are contributing to groundwater contamination in the study area.

CONCLUSIONS

The present work of immense societal benefit in terms of prevailing human health hazards in the study area and in direct relevance to such industrially populated regions elsewhere. Groundwater in granitic aquifer of the study area shows a large variability in its trace element concentration likely due to the interplay of various processes involving, groundwater mineralization and hydraulic conductivity through fractures/joints. Geochemical relations shows that the rock-weathering is the significant mechanism controlling the groundwater chemistry in the study area. Groundwater quality was initially controlled by rock-water interaction and subsequently modified by anthropogenic activities in the study area (Fig.9).

The groundwater quality as per Indian (BIS) and World Health Organization (WHO) drinking water standards, the analyzed groundwater samples of the study area indicate a slightly alkaline nature groundwater and very hard. EC and TDS values, about ninety per cent of the total samples collected in the study area exceed the recommended limits due to inorganic pollution loads of water, improper drainage system, and ion exchange and solubilisation process within the aquifers. All groundwater samples of the present study area exceeds the threshold limit of total hardness for drinking purpose. The average abundance of the major cations and anions is in the order of $Ca^+ > Na^+ > Mg^+ > K^+$ and $Cl^- > HCO_3^- > SO_4^- > NO_3^- > F^-$ respectively. The dominant Hydrochemical facies of groundwater is Na^+ - HCO_3 - Cl^- and Na^+ - Cl^- - HCO_3 types.

Trace elements study reveals that, about hundred per cent of toxic elements viz. cadmium, vanadium, and thirty five per cent of lead samples exceed the highest permissible limits in the study area. In the case of alkaline elements, hundred per cent strontium samples exceed the highest permissible limits, but all barium samples are within the limits. Regarding alkali elements like lithium, hundred per cent of the samples exceed the highest permissible limits but more than ninety per cent of rubidium samples are within the highest permissible limits. In the case of transition elements, molybdenum and chromium are within the limits but eighty four per cent of nickel samples exceed the highest permissible limits in the study area. In the study area the metallic elements like copper, iron, zinc, and cobalt are within the limits but thirty four per cent aluminum samples exceed the highest permissible limits. Regarding non-metallic elements like selenium and silica, sixty four per cent and fifty per cent of the samples exceed the highest permissible limits in the study area.

In the study area, factor analysis was used to quantify the contributions of natural chemical weathering and other impacts to the chemical composition of groundwater. The results show that seven factors emerged as significant contributors to the groundwater quality, which is about sixty five per cent. The spatial variation maps decipher trace elemental concentration viz. geogenic and anthropogenic origin shows that, anomalous trace elemental concentrations in the study area is indicative of phenomenal rise in chemical composition is likely to have its origin from silicate weathering reactions and dissolution/precipitation processes supported by rainfall and anthropogenic activities, indiscriminate use of fertilizers/pesticides, and disposal of waste and sewage release of reactive of waste and sewage, release of reactive pollutants into the atmosphere by industries. Hence there is a need for regular groundwater quality monitoring to assess pollution from time to time for taking appropriate management measures in time to mitigate the intensity of pollution activity.

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