

## TO UNDERSTAND THE CHARACTERISTICS OF STABLE ISOTOPES AND TRACE ELEMENTS IN GROUNDWATER OF THIRUMANIMUTTAR SUB-BASIN, TAMIL NADU, INDIA

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**Abstract.** Thirumanimuttar River is the only ephemeral stream passing through the heart of the Salem city and flows towards southwest and joins river Cauvery in the southern region of Kuduthurai at near Paramathi Vellur forms the spinal cord for urban development. A number of industrial units including dyeing/bleaching and sago industries were located within the core zone. The industrial effluent and sewage water disposal by conversion of natural streams and water bodies as sewer drains. An attempt has been made to study the characteristics of stable isotopes and trace elements in groundwater of Thirumanimuttar sub-basin. Hence, thirty-four groundwater samples were collected for stable isotope [Oxygen (<sup>18</sup>O), Hydrogen (<sup>2</sup>H or Deuterium)] and trace element studies. The study reveals that the groundwater samples undergone some evaporation prior to infiltration. The *d*-excess of the groundwater were varied between -4.89 to 10.08 ‰ indicating that the water undergone strong evaporation during recharge into the local groundwater system. The trace element study indicates that some trace metals such as Al, Ni and Pb exceeds the acceptable limit. The spatial distribution map shows higher concentration of Cr is increased from north to south due to the textile dyeing units were located around in the region.

**Key words:** Thirumanimuttar, Groundwater, Stable Isotope, Trace Element, Industrial Effluent, Recharge

### 1. INTRODUCTION

Isotopic and trace element techniques are valuable in the assessment and management of groundwater resources, especially in the mountainous areas and where there is a scarcity of water. Stable isotopes such as <sup>2</sup>H and <sup>18</sup>O are influenced directly by the atmospheric processes and during groundwater recharge (Clark & Fritz, 1997). Stable isotopes of water and its solutes have been widely used over the past 40 years to address problems related to groundwater recharge (Paternoster et al., 2005; Zhu et al., 2007; Palmer et al., 2007; Bouchaou et al., 2008; Saravana Kumar et al., 2009). It can also provide information about the hydrogeological characteristics of aquifers including origin, time rate of recharge and aquifer interconnections (Song Xianfang et al., 2006;

Axel Horst, 2007). Some of the researchers also used for to identify the sources of groundwater salinity/pollution (Jørgensen et al., 2008; Said et al., 2006; Marimuthu et al., 2005; Mukherjee et al., 2007). Often, interpretation of isotope data is complicated because a number of simultaneous processes may affect the evolution of isotope character of particular rain event and surface/groundwater (Gupta & Deshpande, 2005).

In igneous and metamorphic rocks several trace elements can be accommodated in the crystal structure of different minerals. Fe, Mn, Cu etc., are expected to occur as major trace elements in the rocks and sediments. The distribution and occurrence in the water samples depends upon the degree of weathering and mobility of these elements during weathering (Handa, 1986).

Trace elements geochemistry in the groundwater has also been significant in geochemical studies due to their toxicity (Calderon, 2000) when their concentration exceeds a certain limit (Lu et al., 1998). Beyond permissible limits, Pb, Cu, Ni, Zn and Mn are reported to be more toxic (Rosborg et al., 2003). Higher concentration of Cu in drinking water can cause metabolic disorders and gastrointestinal adverse effects (Sidhu et al., 1995). It can affect the liver and brain in persons having Wilson's disease, which is a genetic disorder that causes excessive Cu accumulation (Roberts & Schilsky, 2003). Mn in drinking water in concentration greater than permissible level can produce adverse neurological effects (Woolf et al., 2002). Pb produces gastrointestinal adverse effects in the human body (Saboor Javaid et al., 2008; Mameli et al., 2001). Pregnant women, infants and children are more susceptible to the toxic effect of Pb (Watt et al., 2000). In higher concentration, Ni is very toxic and carcinogenic (Denkhaus and Salnikow, 2002) and its higher level in drinking water can lead to cirrhosis of liver in children. Zn in higher concentration in drinking water can lead to toxicity (Salzman et al., 2002). Provision of clean drinking water is therefore necessary from the public health perspective. Several authors have discussed in detail on the potential health impact due to water (Olas et al., 2008; Frengstad et al., 2000; Kouping Chen et al., 2007; Manavalan Satyanarayanan et al., 2007). Hence the trace metals such as Cd, Fe, Cr, Mn, Zn, Pb and Cu are used to understand the variations in the study area.

Groundwater is a major source of water for agricultural, industrial, and domestic uses, and often it may be only source of water supply for the people in the study area. A rapid growth activity has brought about a steep increase in water demands which has to be met from available groundwater resource. The problem gains importance in hard rock terrain where the water table has gone below weathered zone and extraction is possible only from deeper fractured zone. Scarcity of monsoon and withdrawal of groundwater in excess to replenishment of aquifer system in many parts results into continuous declining of water table causing deterioration in water quality. The salinization of water resources is one the most widespread processes that deteriorated water-quality and endangers future water utilization (Vasanthavigar et al., 2012). The purpose of this paper is to better understand the characteristics of stable isotope and trace element variations of groundwater with respect space to space.

The water exchanges among reservoirs by changing its isotopic compositions through equilibrium and/or kinetic processes. Hence, the origin and the circulation of water can be traced by

the hydrogen and oxygen isotope abundance. Stable isotopes are ideal traces for estimating the recharge areas and flow path of groundwater. Because it is made up of the water molecules and are sensitive to physical process such as mixing and evaporation (Aji et al., 2008).

## 2. STUDY AREA

Thirumanimuttar Sub-basin lies between North Latitudes 10°58' and 11°48' East Longitudes 77°53' and 78°21' with a total drainage of about 2438 km<sup>2</sup> of which 35% area is in Salem district 65% in Namakkal district. The river Thirumanimuttar originates in the Shervaroy hills and Manjavadi Ghat at the altitudes of 1200 m and 1000 m respectively from the North and North East of Salem town (Fig. 1). Thirumanimuttar River is the only ephemeral stream passing through Salem city and flows towards southwest and joins river Cauvery in the southern region of Kuduthurai at near Paramathi Vellur. River at present is used mainly as a sewer drain by the municipal corporation for their liquid waste during monsoon period carries some rain water and very rarely flood waters. The mean temperature varies from 30.2°C to 33°C. The normal annual rainfall over the study area is about 1590 mm (Vasanthavigar et al., 2011). The area receives major part of rainfall from northeast monsoon. The Thirumanimuttar has 14 small water bodies, of which 10 located in Salem district and 4 are in Namakkal district.

### 2.1. Hydrogeology

The study area is underlain entirely by Archaean crystalline formations with recent alluvial and colluvial deposits of limited areal extents along the courses of major rivers and foothills respectively. Weathered and fractured crystalline rocks and the recent colluvial deposits constitute the important aquifer systems in the basin. The area lying at the foot hill zones which are seen in the northern parts of the basin is underlain by the colluvial material derived from the nearby hill ranges comprising boulders, cobbles, gravels, sands and silts. The porous formations are represented by alluvium and colluvium. The alluvial deposits are confined to the major river courses only. Ground water occurs under phreatic conditions in the weathered mantle and under semi-confined conditions in the fractured zones, it is developed by means of dug wells. The depth of the dug wells tapping weathered residuum ranged from 10 to 38 m bgl. The maximum saturated thickness of these aquifers is < 1m to more than 25 m depending upon the topographic conditions.

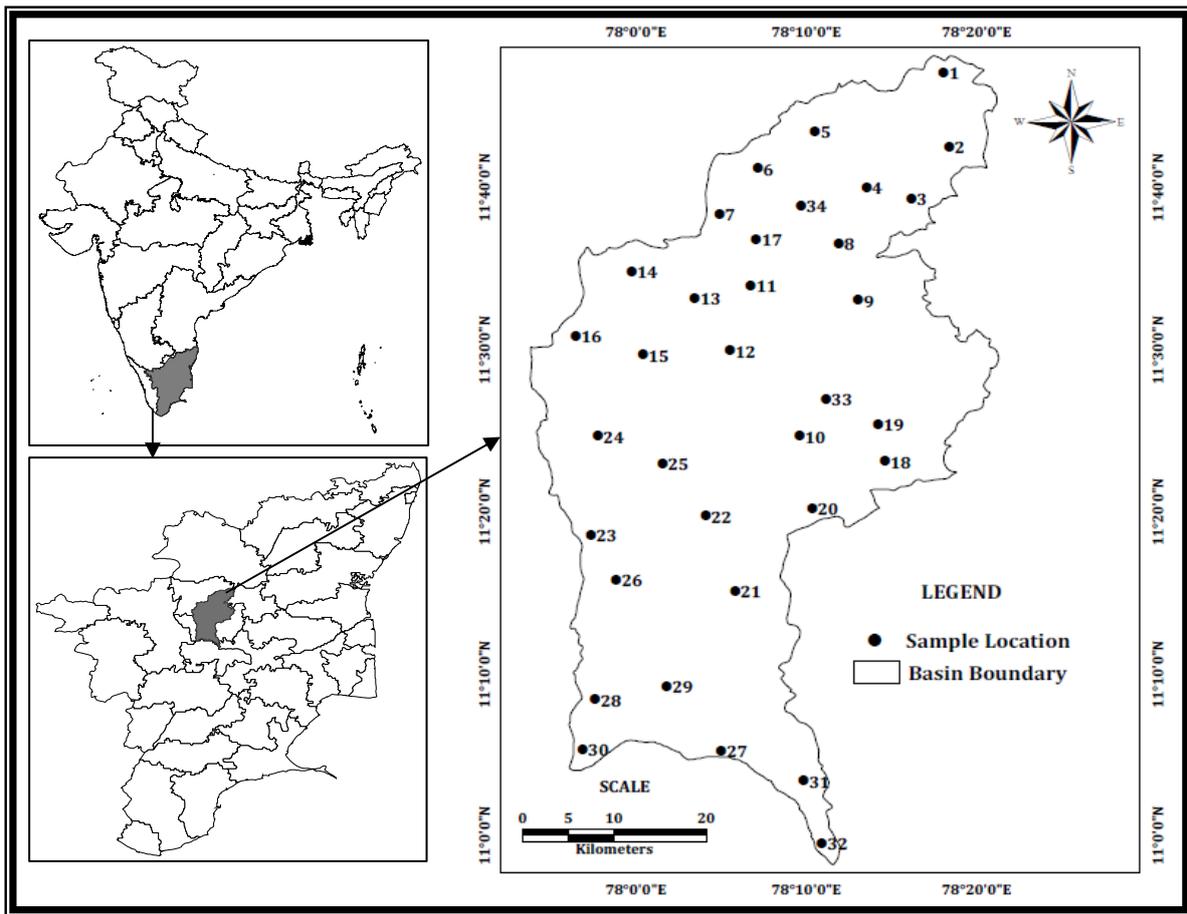


Figure 1. Groundwater sample location map of the study area.

The hard consolidated crystalline rocks of Archaean age represent weathered and fractured formations of granitic gneiss, calc granulite, charnockite, syenite and other associated rocks. Ground water occurs under phreatic conditions in the weathered mantle and under semi-confined conditions in the fractured zones. These rocks are rendered porous and permeable with the development of secondary openings by fracturing and their interconnection. The thickness of weathered zone ranges from <1 m to 30 m.

It is within the depth of 20 m in major part of the area while in the western and extreme north-north-eastern parts of the study area, they are more than 20 m. The depth of the dug wells ranged from 7 to 45m bgl (Srinivasamoorthy et al., 2011; CGWB, 2008). The yield of the open wells ranges from <50 to 200 m<sup>3</sup>/day in weathered crystalline rocks and up to 400 m<sup>3</sup>/day in recent alluvial formations along major drainage courses.

## 2.2. Groundwater Related Issues and Problems

The development of groundwater in the study area in general, is high. Most blocks of the study area have been categorized as over exploited or critical. Incidence of fluoride in ground water in

excess of permissible limits for drinking has been reported from parts of the area, especially from the fracture zone. Pollution of groundwater due to industrial effluents is another major problem in the basin. Industrial effluents of Sago units were located around Sivadapuram and Kondalampatti regions. Sewage water disposal by conversion of natural streams and water bodies as sewer drains.

Excessive use of fertilizers and pesticides in agriculture has also reportedly resulted in localized enrichment of nitrate in the phreatic zone (Vasanthavigar et al., 2011). In over view of the comparatively high level of ground water development in the major part of the study are and the quality problems due to geogenic and anthropogenic factors, it is necessary to exercise caution while planning further development of available ground water resources in the area.

## 2.3 Land use land change

Land use refers to man's activities on land, which are directly related to land. Knowledge of land use and land cover is important for many planning and management activities concerning the surface of the Earth. The land use classification map

for the study area has been sketched from IRS-IC LISS-III dated 2<sup>nd</sup> 1990 and 2007, Geo-coded data on 1:50,000 scale by visual interpretation (Fig. 2).

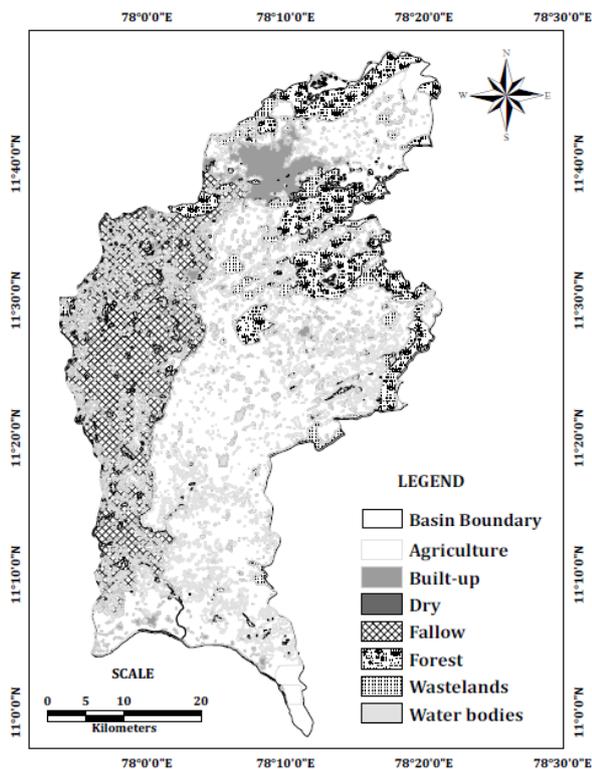


Figure 2. Land use land cover map of the basin

The map shows that about 75% of the area is covered by agricultural activities. The principal food crops are Paddy, Solam, Maize, Kambu, Ragi and sugarcane. Groundnut, cotton and tapioca are the important cash crops cultivated. Nearly 11% (Table 1) of the area is covered under reserved forest is located in the study area. Deciduous tree, Sandal wood, oak and teak wood occupy the Shervaroy hills. Coconut trees are found in plain particularly along the river course. Tamarind, Neem, Palmyra, Nuna, Vengai, Banyan, Vekkali are some important trees found in the study area. About 119 sqkm (4 to 5%) of the area is covered with waste lands which are found in central, eastern and western region; only 2.5% of the region is occupied by surface water bodies.

### 3. MATERIALS AND METHODOLOGY

Thirty-four groundwater samples were collected in tinted glass bottles for Oxygen (<sup>18</sup>O) and Hydrogen (<sup>2</sup>H or Deuterium) isotope analysis (Fig. 1) during July 2009. The bottle was completely filled with water taking care that no air bubble was trapped within the water sample. Then to prevent evaporation, the double plastic caps of the bottles were sealed. During sampling time a proper care was

taken to avoid air bubbles and sealing the mouth of the bottle. Precaution was also taken to avoid sample agitation during transfer to the laboratory.

Table: 1. Results of classified images in 2007

Classes	Area	
	in Sq.km	in Percentage
Agriculture	1835	75.24
Forest	274	11.20
Build up	153	6.25
Wastelands	119	4.85
Water bodies	60	2.46

The stable isotope analytical work was done by using isotopic ratio mass spectrophotometer (Finnigan Deltaplus Xp, Thermo Electron Corporation, Bremen, Germany) in Indian Institute of Technology (IIT), Department of Geology and Geophysics, Karagpur, India. The analyses were standardized against the international references Vienna-Standard Mean Ocean Water (VSMOW). Both  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values are expressed in per mil with reference to the standard mean ocean water (SMOW). Measurement accuracies are  $\pm 0.07\text{‰}$  and  $\pm 0.50\text{‰}$  for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  respectively.

Stable isotope results were expressed with respect to VSMOW in  $\delta$  unit's ‰:

$$\delta^{18}\text{O} = \left\{ \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{standard}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} \right\} \times 10^3 (\text{‰}) \quad (1)$$

$$\delta\text{D} = \left\{ \frac{[(\text{D}/\text{H})_{\text{sample}} - (\text{D}/\text{H})_{\text{standard}}]}{(\text{D}/\text{H})_{\text{standard}}} \right\} \times 10^3 (\text{‰}) \quad (2)$$

Further 34 groundwater samples were collected (i.e. where the trace samples collected area) in 500 ml polyethylene bottles scattered over the entire region of the study area during July 2009. To ensure the removal of organic impurities from the samples and thus prevent interference in the analysis, the samples were digested with concentrated nitric acid. The sample was analyzed by Atomic Absorption Spectrometer (AAS), (ELICO double beam SL 176) in Department of Earth sciences, Annamalai University, Tamil Nadu, India.

### 4. RESULTS AND DISCUSSION

#### 4.1. Stable isotope

##### 4.1.1. Altitude Effects

The isotope-altitude gradient, or altitude effect, has turned out to be the most powerful tool for tracing

groundwater as it distinguishes groundwater recharged at high altitude from those at low altitude. Such kind of information could not otherwise be obtained. For the last several decades, the altitude effect has been established over the world and successfully applied in a number of hydrological studies, even in watersheds with elevation contrasts of less than a couple of hundred meters (Clark & Fritz, 1997).

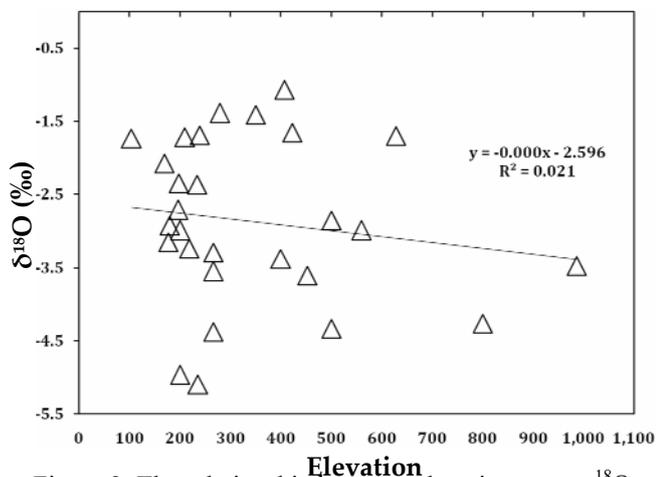


Figure 3. The relationship between elevation versus  $^{18}\text{O}$

The figures show the relation between  $^{18}\text{O}$  against altitude (Fig. 3). It is represent the enrichment of  $^{18}\text{O}$  at lower altitudes and depletion in higher altitudes. This combined reaction indicates the evaporation process having a significant influence on the groundwater, which may be due to presence of flushing processes. Depletion of  $^{18}\text{O}$  is also noted at lower altitude may be due to the partial evaporation of infiltrating rain water.

#### 4.1.2 $\delta^{18}\text{O}$ Vs $\delta\text{D}$

The environmental isotopes of oxygen  $\delta^{18}\text{O}$  and hydrogen  $\delta^2\text{H}$  are excellent tracers for determining the origin of groundwater and widely used in studying the natural water circulation and groundwater movement (Ali M. Subyani, 2004). The figure represents the relation between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in groundwater. The slope of the Local Meteoric Water Line (LMWL) and Global Meteoric Water Line (GMWL) is plotted. An isotope result shows that certain difference existed for groundwater sources and circulation processes in various regions. Moreover, certain degree of relations presents between the hydrogen and oxygen isotope composition in groundwater spatial positions, which to certain degree reflects the interrelationships between rock and groundwater.

The straight lines in the  $\delta\text{D}$ - $^{18}\text{O}$  diagram (Fig. 4) obtained by linear regression for sub-surface water having a slope of  $R^2 = 0.834$ . Majority of the

samples depleted isotopic signature (high negative) and the samples fall within a cluster either close to or to the right of the LMWL, indicating that these samples have undergone some evaporation prior to infiltration (Prasanna et al., 2010).

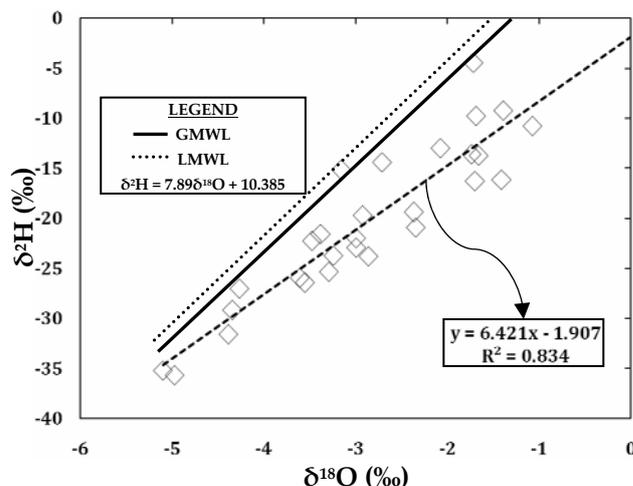


Figure 4. The relationship between  $^2\text{H}$  and  $^{18}\text{O}$  isotope

#### 4.1.3. Deuterium – Excess

The d-excess is defined as a mean relative humidity of the atmosphere above the ocean water i.e. excess deuterium that cannot be accounted by equilibrium fractionation between water and vapour. It is evaluating the meteoric conditions prevailing in the initial moisture source (Merlivat & Jouzel, 1979). Although temperature and wind speed can influence the kinetic fractionation, the relative humidity is the most important factor. Since condensation is most often an equilibrium process ‘d-excess’ is an indicator of kinetic fractionation during evaporation, governed by molecular diffusivity of isotopic molecular species (Dansgaard, 1964; Clark & Fritz, 1997). In addition, it is affected by secondary processes such as the evaporation of raindrops beneath a cloud or evaporation of continental water bodies adding extra moisture to the air mass (Froehlich et al., 2002). The deuterium excess (d-excess) value is defined as:

$$d = \delta\text{D} - 8 \text{ } ^{18}\text{O}\text{‰ VSMOW} \quad (3)$$

A D-excess of 10‰ is the average value for global precipitation and derived waters formed from the vapour that was evaporated in the global average humidity of 85% over oceans (Gonfiantini, 1986). The d-excess of the groundwaters in this region varied between -4.89 to 10.08 ‰ indicating that the water undergone strong evaporation during recharge into the local groundwater system (Fadong Li et al., 2008). In general the range of ‘d-excess’ values between ~ 8 to ~ 10 is, therefore, assumed to be

representative of primary precipitation in the entire study area. Majority of the samples having low 'd-excess' values of  $\leq 6$  suggest that there is significant evaporation of rainwater leaving the residual groundwater. Sample number 28 is showing the D-excess level is equal to the average global precipitation value of 10‰ (Fig. 5).

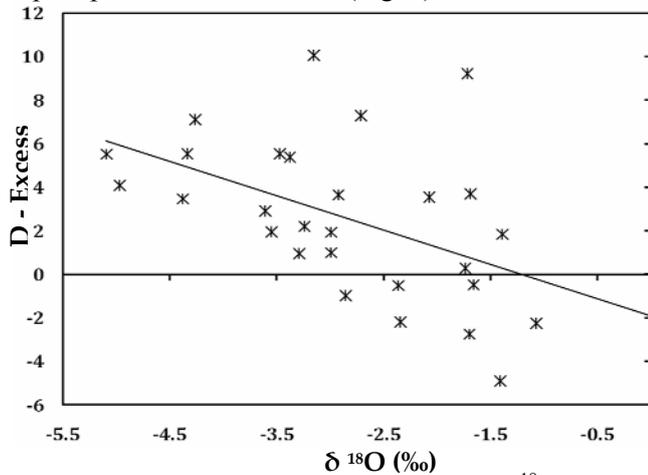


Figure 5. The relation between D-excess and  $\delta^{18}\text{O}$ .

#### 4.1.4. Log PCO<sub>2</sub> Vs. $\delta^{18}\text{O}$ and Log PCO<sub>2</sub> Vs. $\delta\text{D}$

The Log PCO<sub>2</sub> values of the region ranges from -0.561 to -3.16. These values are higher in comparison to the average atmospheric PCO<sub>2</sub> value of -3.5 atm (Raymahashay, 1986; Prasanna et al., 2009; Galip Yuce et al., 2005).

The Log PCO<sub>2</sub> plot (Fig. 6. a and b) suggests that majority of the groundwater samples characterized by higher PCO<sub>2</sub> value and enriched  $\delta^{18}\text{O}$  indicating long residence time. This also suggest that the rainwater charged with atmospheric CO<sub>2</sub> has acquired additional CO<sub>2</sub> from the soils and thereby developing high PCO<sub>2</sub> water on their travel to deep unsaturated zone (Prasanna et al., 2009).

Table 2. Summary of trace elements in groundwater

Parameters	WHO (2008)	BIS (1991)	Sample Range
Fe	1.0 to 3.0	0.3	0.67 to 2.92
Cd	0.003	0.01	0.06 to 0.13
Mn	0.50	0.01	0.21 to 0.84
Cu	2.0	0.05	0.71 to 3.26
Cr	0.05	0.05	0.91 to 4.52
Zn	3.0	5.00	0.37 to 5.33
Pb	0.01	0.05	0.38 to 6.64

## 4.2. Trace elements

The concentration levels of different parameters have been compared with the WHO (2008) standard. Table, 2 shows that some trace metals such as Al, Ni and Pb exceeds the acceptable

limit. As (Fig. 7) can be seen, the ranges of these potential hazardous trace element levels vary much from different sampling stations. Sample no. 21 having higher concentration of Pb, Zn, Cr and Fe.

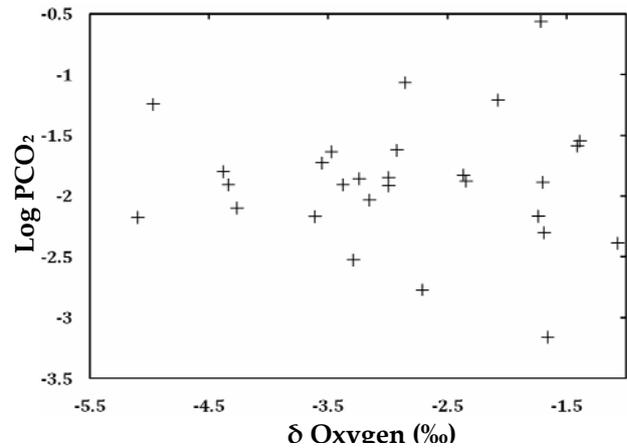


Figure 6 (a). Scatter plot for Log PCO<sub>2</sub> Vs.  $\delta$  Oxygen (‰).

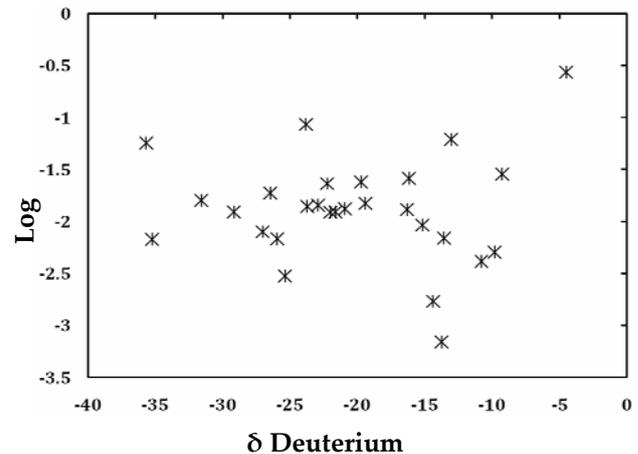


Figure 6 (b). Scatter plot for Log PCO<sub>2</sub> Vs.  $\delta$  Deuterium (‰).

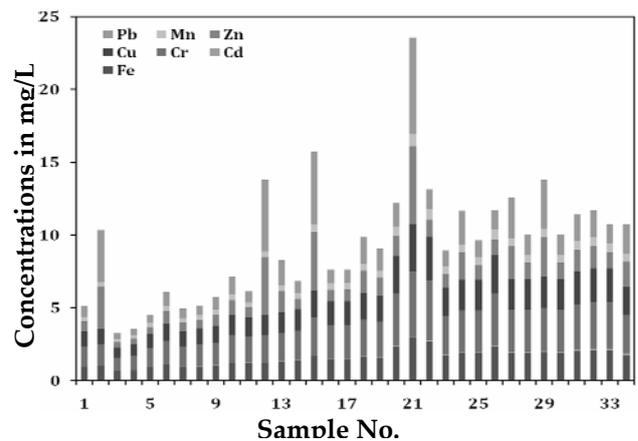


Figure 7. Trace element variations in groundwater.

#### 4.2.1 Cadmium (Cd)

Cadmium is relatively mobile element and occurrence in the environment is from both natural

and anthropogenic sources. It is highly toxic element and producing symptoms such as nausea, vomiting, respiratory difficulties, cramps and loss of consciousness at high doses. Chronic exposure to metal can lead to anemia, anosmia (loss of sense of smell), cardiovascular diseases, renal problems and hypertension (Mielke et al., 1991; Robards & Worsfold, 1991).

The concentration of Cd in the groundwater ranged from -0.06 to 0.05 mg/L with an average of 0.05 mg/L. In the case, majority of the samples (80%) exceeding the guide line value of 0.003 mg/L (WHO, 2008) which is mainly due to the pollutants of dyeing units clustered around the place. The spatial distribution map of Cd shows (Fig. 8) that upstream region having lower concentration when compared with the rest of the study area.

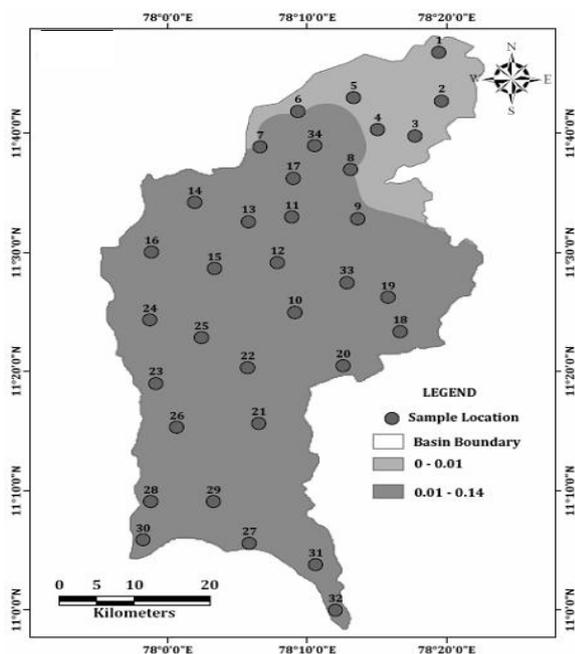


Figure 8. The Spatial distribution map of Cd.

#### 4.2.2. Iron (Fe)

Iron is one of the most abundant metals in the earth's crust. It is found in natural freshwater at levels ranging from 0.5 to 50 mg/L. Iron is an essential element in human nutrition and it estimates of the minimum daily requirement for iron depend on age, sex, physiological status and iron bioavailability and range from about 10 to 50 mg/day. Excessive concentration may promote bacterial activities in pipe and service mains, causing objectionable odors and red-rod disease in water.

A recommended upper limit for iron in public water supplies is 2.0 mg/L (WHO, 2008). The average content of iron in groundwater samples

varied between 1.31 to 2.97 mg/L. The spatial distribution map shows the higher concentration (>2 mg/L) of iron towards the central and southern tip of the study area particularly in locations 19, 11, 18 and 14 (Fig. 9) indicating higher concentrations of iron were confined to 95% of the study area indicating the effect of lithology and anthropogenic activities (Rajmohan & Elango, 2005; Ramesh et al., 1995).

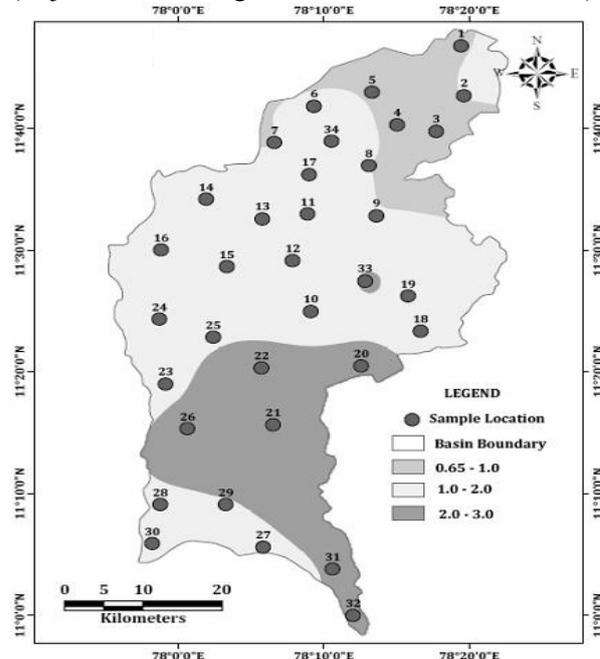


Figure 9. The Spatial distribution map of Fe

#### 4.2.3. Chromium (Cr)

Chromium is widely distributed in the earth's crust. Application of chemical fertilizers like urea, ammonium phosphate, ammonium sulphate and potassium chloride in soils enhances the mobility into water. Chromium is an essential trace element, required for the metabolism of lipids and proteins and to maintain a normal glucose tolerance factor. High doses of Cr cause liver and kidney damage and chromate dust is carcinogenic (SEGH, 2001; Mugica et al., 2002; Srinivasa Gowd & Govil, 2005).

A concentration of Cr, has also prescribed 0.05 mg/L as the guideline value for drinking water. (BIS, 1991; WHO, 2008). In the study area chromium in groundwater varied on an average from 0.91 to 4.52 mg/L. Majority of the samples having higher concentration of Cr, which is derived from ultramafic rocks especially serpentine found in the litho units of the study area along with industrial and agricultural activities (Chi-Man Leung & Jiu Jimmy Jiao, 2006). The spatial distribution map shows higher concentration of Cr is (>4 mg/L) increased from north to south (Fig. 10) mainly induce by the textile dyeing units were located around in the region.

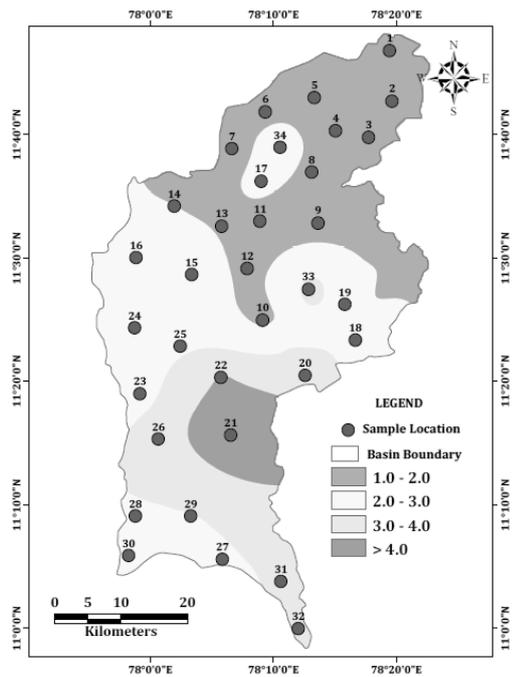


Figure 10. The Spatial distribution map of Cr

#### 4.2.4. Manganese (Mn)

Manganese is one of the most abundant metals in the Earth's crust, which does not occur naturally as a metal but it is found in various salts and minerals frequently in association with iron compounds. It is an essential element for human and other animals. Agricultural practices like fertilizer use, sewage and animal waste disposal and atmospheric deposition from fossil fuel combustion and municipal incinerators constitute significant sources of manganese (Adriano, 1986).

WHO (2008) has prescribed 0.5mg/L as the provisional guideline value for drinking water. In the study area Mn in groundwater varied on an average from 0.21 to 0.84 mg/L. It was observed that a total of 43% groundwater samples exceed the desirable limit. The presence of Mn above the permissible limit of drinking water often imparts an alien taste to water. It is also has adverse effects on domestic uses and water supply structures. The spatial distribution map (Fig. 11) shows the higher concentration of Mn (>0.5 mg/L) is confined along the southern part of the study area which is mainly due to agricultural, sewage and municipal activities eventually distributed all through the study area.

#### 4.2.5. Zinc (Zn)

Zinc is an essential trace element found in virtually all food and potable water in the form of salts or organic complexes. It is essential for the growth of humans, animals and plants. It is potentially dangerous for the biosphere when present in high concentrations. The main sources of

pollution are industries and the use of liquid manure, composted materials and agrochemicals such as fertilizers and pesticides in agriculture (Romic & Romic, 2003). The spatial distribution map of Zn (Fig. 12) shows the groundwater samples 12, 15 and 21 having higher concentrations.

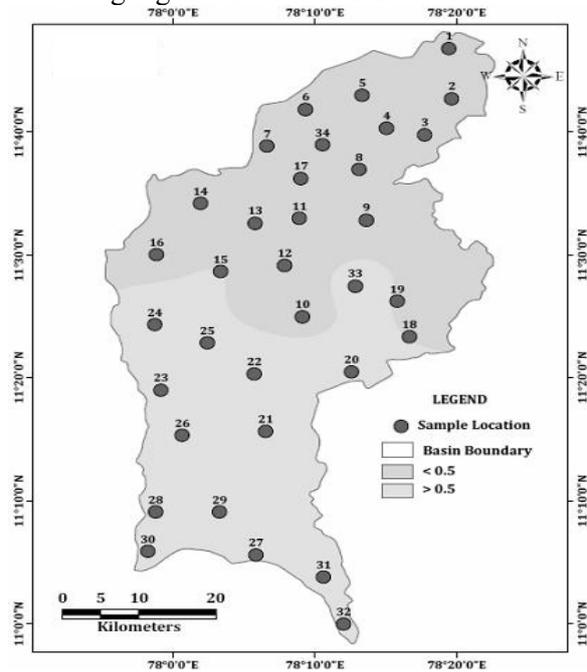


Figure 11. The Spatial distribution map of Mn

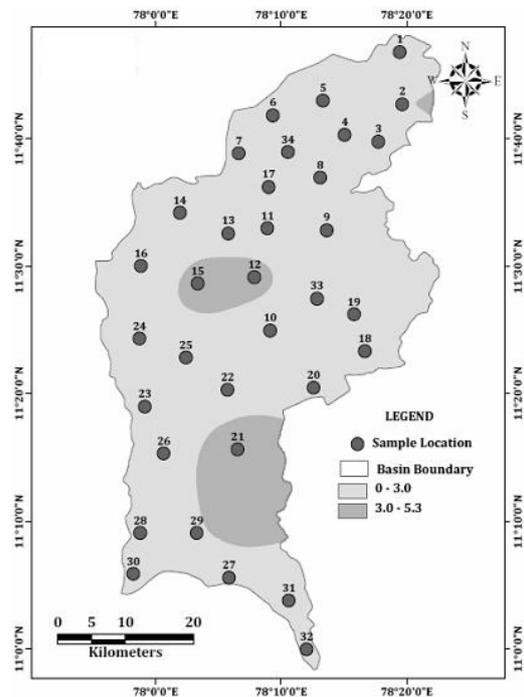


Figure 12. The Spatial distribution map of Zn

#### 4.2.6. Lead (Pb)

The presence of lead in drinking water occurs primarily due to corrosion of lead pipes and solders, especially in areas of soft water. Long term exposure

to lead or its salts can affect adversely to nervous system and kidneys (Mugica et al., 2002). The average concentration of Pb in the study area ranges between 0.38 to 6.64 mg/L for the groundwater. The spatial distribution map (Fig. 13) indicates higher concentrations along the NW and NE parts of the study area for groundwater samples and along the NW and southern parts of the study area dominated by industrial and agricultural activities.

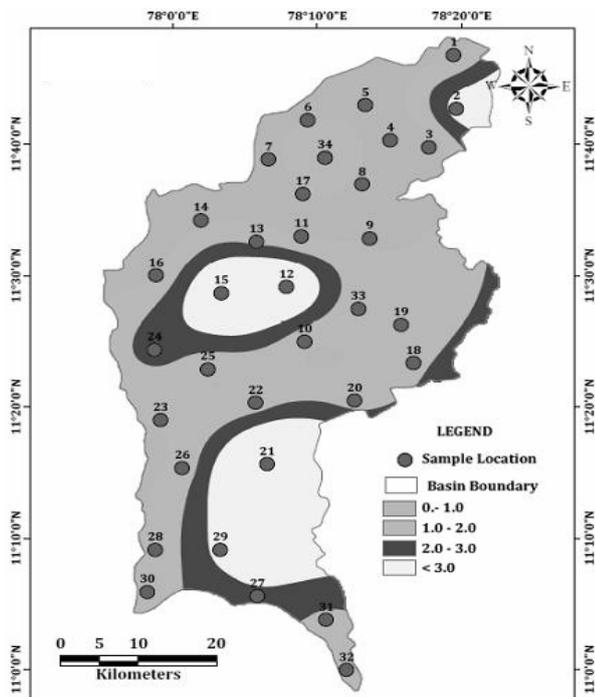


Figure 13. The Spatial distribution map of Pb

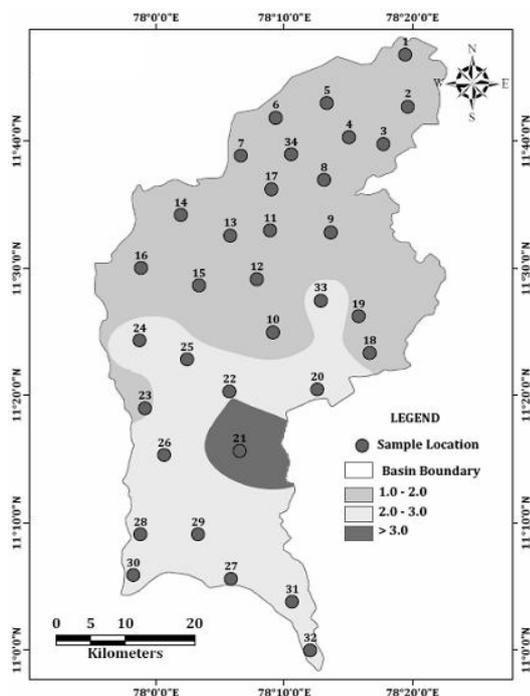


Figure 14. The Spatial distribution map of Cu

#### 4.2.7. Copper (Cu)

Copper accumulation in the water may be due to the plastic industry, blast furnace, steel and application of agrochemicals in the agro-based industry. Overdoses of copper may also lead to neurological complications, hypertension, liver, and kidney dysfunctions (Rao et al., 2001; Krishna et al., 2009).

World Health Organization has recommended 2 mg/L as the provisional guideline value for drinking purpose (WHO, 2008). Copper, average ranges between 0.71 to 3.26 mg/L for groundwater samples. The spatial distribution map (Fig. 14) for groundwater samples indicates higher concentration down south along the downstream direction of the river flow.

### 5. CONCLUSION

The stable isotope study depicting  $^{18}\text{O}$  is enrichment at lower altitudes and depletion in higher altitudes. This combined reaction indicates that evaporation is a significant influence on the groundwater which may be due to presence of flushing processes. The  $\delta\text{D}$  Vs  $^{18}\text{O}$  plot shows majority of the samples depleted isotope and the its falls close to or to the right of the LMWL, which indicates the evaporation prior to infiltration. The  $\text{PCO}_2$  Vs  $^{18}\text{O}$  plot suggest that the rainwater charged with atmospheric  $\text{CO}_2$  has acquired additional  $\text{CO}_2$  from the soils and thereby developing high  $\text{PCO}_2$  water on their travel to deep unsaturated zone. The trace element study reveals higher concentrations of Fe indicating the effect of lithology and anthropogenic activities. The spatial distribution map of Pb shows the higher concentrations were noted along NW and NE parts of the study area due to industrial effluents and agricultural practices. This study has clearly focused on groundwater pollution mainly caused by effluents of the dyeing, sago and sewage water units located mostly within the city and its suburbs which is a major public health hazard. Trace metals are occurring in alarming level in the aquifer and suggested that suitable remedial measures should be taken before they are completely deteriorated.

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