

Application of sulphur-34 to trace natural and anthropogenic sources of sulphur in groundwater contamination in Hebbal and Challaghatta, Bangalore-a case study

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This paper describes the application of environmental stable isotopes like $\delta^{18}\text{O}$, $\delta^{34}\text{S}$ and certain physico-chemical SO_4^{2-} , F^- in a comprehensive manner to explore the occurrence and quality of groundwater, source of saline water, evaluation of aquifer characteristics and its circulation and to trace the natural and anthropogenic sources of sulphur in the crystalline aquifers of Hebbal and Challaghatta valleys, Bangalore. The average concentration of isotopic $\delta^{34}\text{S}$ in sewage (11.26) and lake (12.10‰VCDT) samples are very close to the isotopic composition of the open (11.86) and bore well (12.84‰VCDT), suggesting a sewage origin of the groundwater sulphate. Fluoride average concentration in groundwater samples during pre-monsoon 2008 and post-monsoon 2009 were 0.99 and 0.11 mg/l respectively. But, the sulphate in the low and high F^- samples cannot be differentiated by their stable isotope values. Sulphur-34 dissolved sulphate varied greatly (4.59 to 16.74‰) in groundwater throughout the basins. There is also apparent relationship between $\delta^{34}\text{S}$ and SO_4^{2-} concentrations to be expected from SO_4^{2-} sources. Finally, the concentration of $\delta^{34}\text{S}$ ‰ in various sources of water samples in entire Arakavathi and Vrishabhavathi basins is interconnected with Terrestrial evaporates, Fertilizers, Magnetic and Hydrothermal SO_4 and Sewage.

Keywords: Fluoride, Groundwater, Oxygen-18, Sewage, Season, Sulphur-34 and Sulphur.

INTRODUCTION

Bangalore harbors no perennial river which resulted in the establishment of many lakes besides serial streams like Arakavathi, Pinakini and Vrishabhavathi which were once the source of surface and groundwater recharge. Currently, following rapid urbanization and industrialization, these lakes have vanished and have been converted into residential and commercial localities. Arakavathi, Pinakini, and Vrishabhavathi streams are today part of open sewage network of the city. An accurate conceptualization is therefore a prerequisite for

realistic understanding of the habitat.

To understand the flow system better and translate this understanding to develop a groundwater model, data on radiogenic isotope with stable isotopes $\delta^{18}\text{O}$, and $\delta^{34}\text{S}$ can be used. Evaluation of available groundwater resources, identification of source and origin of groundwater recharge, recharge chronology and groundwater quality are of great importance for systematic planning, development and management of groundwater to meet the current and future needs. Many a times, hydrological investigations based on conventional methods are too geologically based and non-quantitative, or too engineering based and although quantitative, lack insufficient geological understanding. Isotope techniques are recommended to fill this gap.

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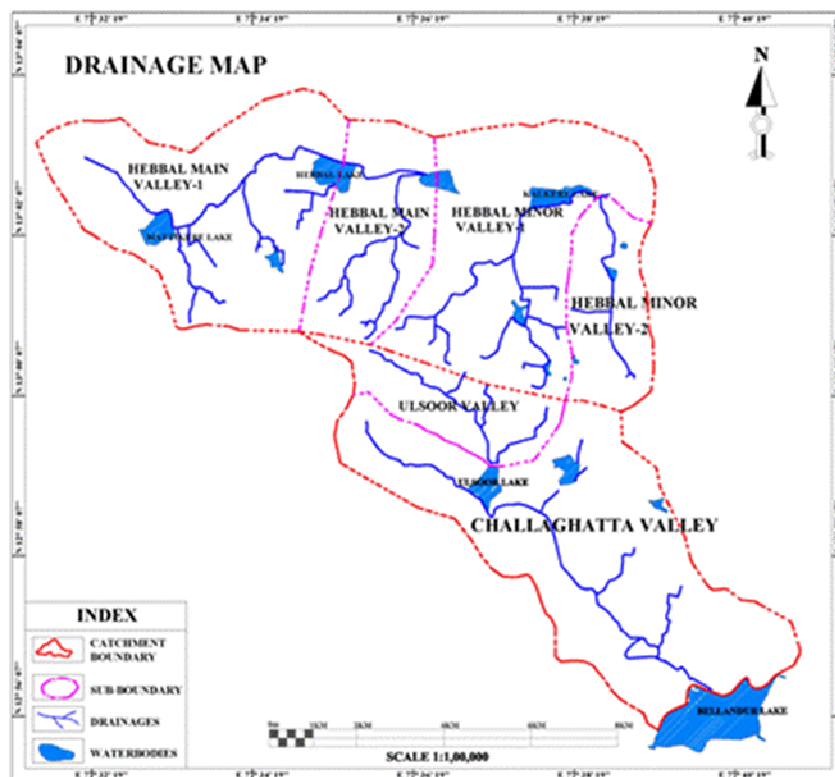


Figure 1. Study area along with sewerage network system.

Study area

The drainage system

The granitic ridge running from NNE to SSE governs the drainage pattern of Bangalore North. Towards east, the drainage is made up of a network of canals generally flowing from west to east with storage tanks along the canals, ultimately feeding the South Pinakini River. In the west also the drainage pattern includes a network of canals generally flowing westwards with storage tanks, ultimately feeding the Arakavathi River. Also the Bangalore south drain towards east, into the Pinakini basin and to the west into the Arakavathi basin. The Vrishabhavathi is a minor river within the city marked with a series of tanks (Figure 1).

Geo-hydrological nature

Geologically the western portion of Bangalore is composed of gneissic granites belonging to Precambrian age. They are exposed as a continuous chain of mounds raising 90-150m above the ground on the western portion constituting the Bannerghatta groups of hills. Inclusions of quartz and pegmatite also occur here and there (Figure 2).

Hydro-geologically western portion shows ground-

water occurrence under water table in the weathered mantle of the granite gneisses and joints, cracks and crevices of basement rocks. Generally, the water table fluctuation in open and bore wells of Challaghatta valley are high around Domlur and Ulsoor Lake respectively, which are the major recharge areas of groundwater. The depth of water table is dependent upon the rate of weathering and topographic factors. Chief source of groundwater is infiltration and recharge by rainwater. Considering the climatic water balance, soil characteristics account for nearly 70% allowing only 20% rainfall being added to groundwater pool. Percolation and recharges in the groundwater account for 10% discharge through wells.

MATERIALS AND METHODS

Estimation of sulphur-34 (^{34}S)

Major forms of sulphur in the groundwater include sulphate and sulphide minerals, dissolved sulphate (SO_4^{2-}), dissolved sulphide (HS^-) and hydrogen sulphide gas (H_2S). Organic sulphur is a component of organic compounds such as humic substances, kerogen and hydrocarbons. Its oxidation and recycling in soil produces the "terrestrial" sulphates found in the semi-arid regions. Atmospheric sulphur sources include natural and

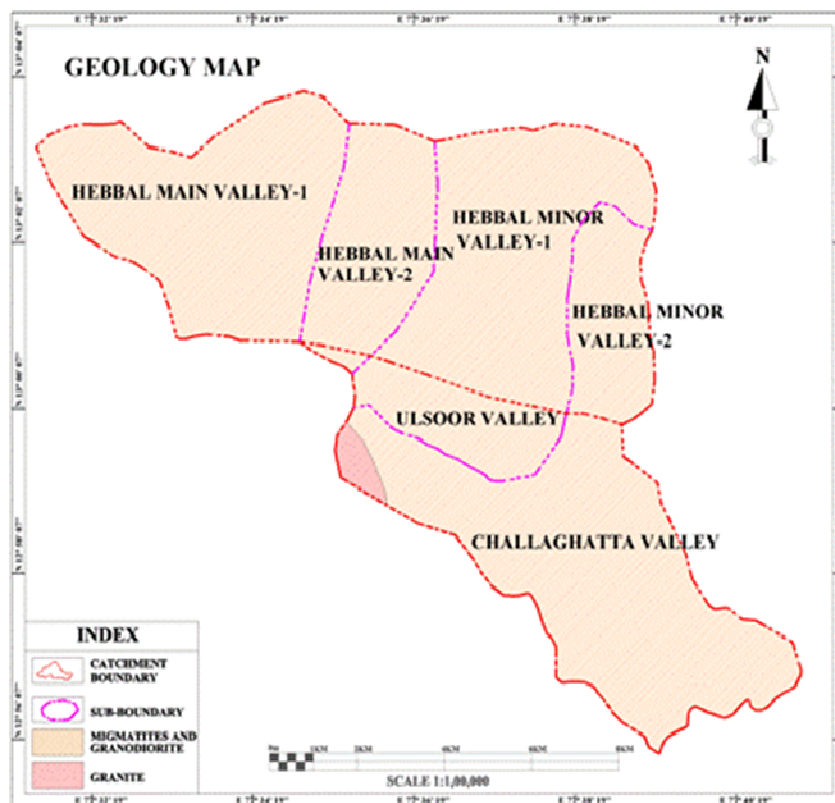


Figure 2. Geological and Geomorphologic background of Bangalore City.

"technogenic" or industrial SO₂, particulate sulphur and aerosols of marine sulphate. Sulphur has four stable isotopes, ³²S, ³³S, ³⁴S and ³⁶S with natural abundance of 95, 0.76, 4.22 and 0.014% respectively. Normally the ratios of two most common isotopes ³⁴S/³²S are measured (Figure 3). The isotopic composition of sulphur are reported as 'δ' values in parts per thousand with respect to standard and defined as;

$$\delta^{34}\text{S} (\text{‰}) = \frac{R_{\text{Stand}} - R_{\text{Sample}}}{R_{\text{Stand}}} \times 1000 \quad \text{..... (1)}$$

Where R = ³⁴S/³²S

Sulphur isotope measurement is performed using a Mass Spectrometer with an analytical error of ±0.3‰ and results are reported in delta notation (δ³⁴S) as part per thousand (‰) deviations relative to Vienna Canon Diablo Troilite (VCDT) standard.

Measurement

Precipitation of sulphate from water is generally carried out using BaCl₂ solution. The graphite reduction method was used to reduce sulphate to sulphide. In this method, an excess of graphite is mixed with BaSO₄ and heated to 1100°C for 10 minutes in a stream of N₂ gas.

In the next stage, pure sulphides are converted to SO₂ by oxidizing agents such as CuO, Cu₂O, V₂O₅ or O₂ at 1000°C temperature (Robinson *et al.*, 1973). Combustion in vacuum with soil oxidant minimizes the contaminant gas (e.g. CO₂) and purification of SO₂ gas is often not necessary. The SO₂ gas is analyzed for sulphur-34 using standard Mass Spectrometer. Sulphur-34 analysis was carried out at the Gas Hydrate Research Group Laboratory of Geological Oceanography, National Institute of Oceanography, Dona Paula, Goa.

Sulphur isotopes in hydrological cycle

Sulphate in groundwater has various sources. It is mainly derived from dissolved evaporates (anhydrite, gypsum), but also from the oxidation of sulphide minerals. Sulphate in precipitation, which occurs in the range of ppm, is derived from marine aerosols and dust from arid areas. Sulphite concentration in surface water can increase considerably due to evaporation. Bacterial reduction (*Desulfohalobium* and *Desulfovibrio*) of sulphate and oxidation of sulphide produce isotope fractionation of stable sulphur isotopes.

$^{32}\text{SO}_4^{2-}(\text{AQ}) + \text{H}_2^{34}\text{S}(\text{G}) \leftrightarrow ^{34}\text{SO}_4^{2-}(\text{AQ}) + \text{H}_2^{32}\text{S}(\text{G}) \quad \text{..... (2)}$
The distribution of sulphur isotopes in a number of natural materials is shown by Krouse

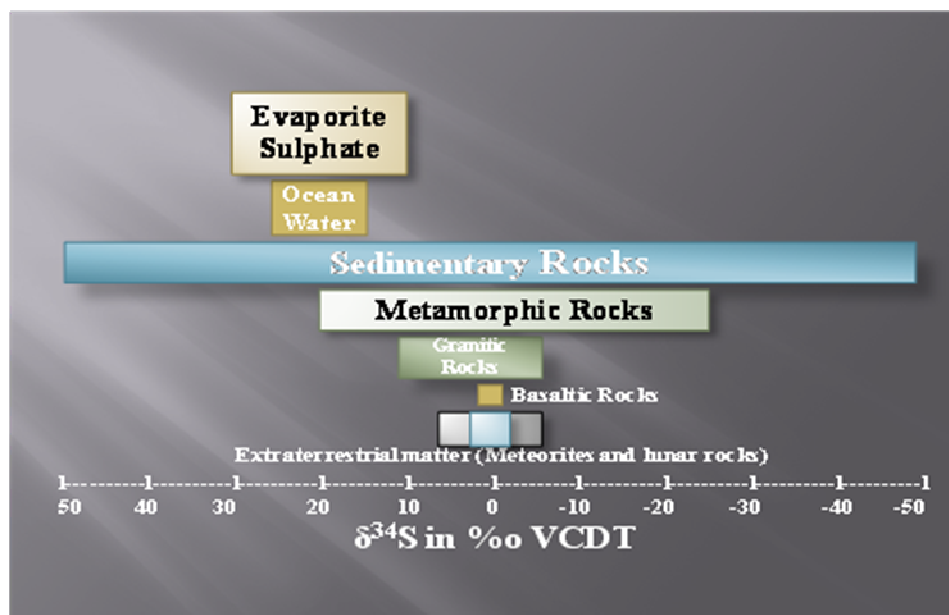


Figure 3. $^{34}\text{S}/^{32}\text{S}$ ratio in some geologically important materials ($\delta^{34}\text{S}\text{‰VCDT}$).

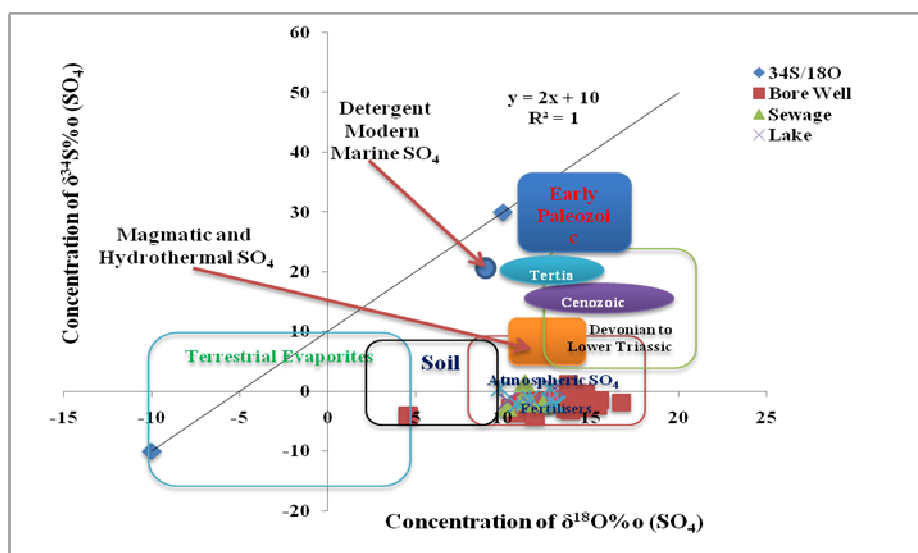


Figure 4. Stable isotopes of sulphate ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) for the Bangalore crystalline aquifer, Ranges of $\delta^{34}\text{S}$ sulphate and $\delta^{18}\text{O}$ sulphate of various origins dissolved in groundwater (Krouse, 2001).

(1980) (Figures 3 and 4).

Modern main sulphate had a constant value of +20 ‰ on the $\delta^{34}\text{S}$ scale. Sulphate and H_2S formed through the oxidation of sulphides or bacterial reduction, respectively, are isotopically significantly lower at about +10 ‰. Sulphate remaining after bacterial decomposition to H_2S has $\delta^{34}\text{S}$ values often above +20 ‰.

The sulphur isotopic composition of sulphate in streams and rivers reflects the isotopic composition of the sulphate sources. Isotopically the sources represent two

groups: relatively heavy (^{34}S enriched) ^{34}S of sulphate derived from evaporate minerals and relatively light (^{32}S depleted) ^{32}S of sulphate derived from reduced sulphur sources such as sulphide minerals or soil organic sulphur. The isotopic composition of a sulphate sources will vary with age of the evaporites in the basin. It could be as light as 10 ‰, from Permo-Triassic evaporites to as heavy as +35 ‰, from late Proterozoic evaporites (Krouse, 1980). The isotopic composition of derived from reduced sulphur will depend on the composition of the

reduced sulphur itself, the size of the reduced sulphur reservoir and the type of process by which the sulphur is oxidized.

Origin

Because of the reactive nature of sulphur, many processes impact its global cycling and isotopic composition. Important processes include: 1) weathering of rocks rich in sulphur; 2) deposition of evaporites; 3) sulphate from sea spray; 4) anthropogenic fluxes from burning of fossil fuels; and 5) cosmogenic ^{35}S entering the atmosphere.

The sulphur cycle consists of the weathering of rocks rich in sulphur that are eventually deposited in the ocean from runoff. The atmosphere obtains sulphate from sea spray, which is eventually rained out over the land. Anthropogenic fluxes and cosmogenic ^{35}S also enter the atmosphere. Sulphur then travels back to the ocean with the runoff that is dissolving more lithospheric sulphur along the way.

Atmospheric sulphur ($-5\text{‰} < \delta^{34}\text{S} < 25\text{‰}$) (Krouse and Mayer, 2000)

More than two-thirds of the atmospheric sulphate in northern industrialized areas is of anthropogenic origin. Anthropogenic input into the atmosphere is in the form of sulphur gases (i.e., SO_2 , H_2S and DMS) from burning of fossil fuels. These sulphur gases usually oxidize to form sulphate once in the atmosphere. The range of $\delta^{34}\text{S}$ values for anthropogenic sulphate in northern hemisphere precipitation usually range from -3 to $+9\text{‰}$ (Krouse and Mayer 2000). In northern industrial areas, fossil fuel burning is greater in the winter months and thus seasonal fluctuations in $\delta^{34}\text{S}$ values can be seen.

Volcanoes also contribute to atmospheric sulphur; the $\delta^{34}\text{S}$ values from this input are around $+5\text{‰}$. The final input to the atmosphere is from marine sulphate. This is incorporated into the atmosphere from sea spray and the $\delta^{34}\text{S}$ values from this input range from $+15$ to $+21\text{‰}$ (Krouse and Mayer, 2000).

Lithospheric sulphur ($-10\text{‰} < \delta^{34}\text{S} < 35\text{‰}$) (Krouse and Mayer, 2000)

Lithospheric sulphur mainly comes from the weathering of metamorphic and sedimentary rocks. Most igneous rocks contain little sulphur and therefore are not a major contributor to dissolved sulphur compounds. Sedimentary rocks that are marine evaporites are the main source of sulphur in groundwater. Two major evaporites are gypsum and anhydrite. The $\delta^{34}\text{S}$ range for these rocks is dependent on which geologic era they are from. These

evaporites, if deposited quickly, reflect the ^{34}S value of the ocean from the time that they were deposited. However, they can contain significantly depleted $\delta^{34}\text{S}$ values compared to the ocean water, due to bacterial fractionation. When these sedimentary rocks are metamorphosed, the S will be retained. As a result, metamorphic rocks have a similar $\delta^{34}\text{S}$ range of -10 to $+25\text{‰}$ (Krouse and Mayer, 2000).

Marine sulphur (modern $\sim 21\text{‰}$)

The ocean is huge sink for sulphur. It is estimated to contain approximately 1.3×10^{15} tons of sulphates (Attendorn and Bowen, 1997). The range of the $\delta^{34}\text{S}$ values for the oceans has changed over the geologic eras.

Groundwater sulphur ($-10\text{‰} < \delta^{34}\text{S} < 35\text{‰}$) (Krouse and Mayer, 2000)

The $\delta^{34}\text{S}$ values of groundwater are highly variable and depend on the nature of the sulphur inputs to the water. Sulphur takes on many forms in groundwater, but is mainly found in the form of sulphates and sulphides. The main source of sulphate is from the dissolution of gypsum and anhydrite. Some dissolved organic sulphur (DOS), elemental sulphur and mineral sulphur might also be present in groundwater.

Cosmogenic origin

Sulphur-35 is formed by cosmic ray spallation of ^{40}Ar in the atmosphere and falls to earth in precipitation. Because of its relatively short half-life (87 days), its presence indicates the water is from recent precipitation.

Sulphur fractionation

Sulphur isotope fractionation occurs by two processes in nature. First, there is equilibrium fractionation during inorganic reactions between sulfur bearing ions, molecules and solids. In this case, ^{34}S is concentrated in the compounds with the highest oxidation state or the greatest bond strength (Bowen, 1988).

Secondly, and more important, is fractionation due to the reduction of sulphate ions. This can occur by inorganic process or by biogenic processes. This fractionation occurs because the ^{32}S form weaker bonds than the ^{34}S and therefore the reduced product tends to be depleted in ^{34}S . The amount of inorganic reduction fractionation is dependent on external factors affecting the system. These factors will vary the rate at which S-O bonds in sulphate are broken (Bowen, 1988). The

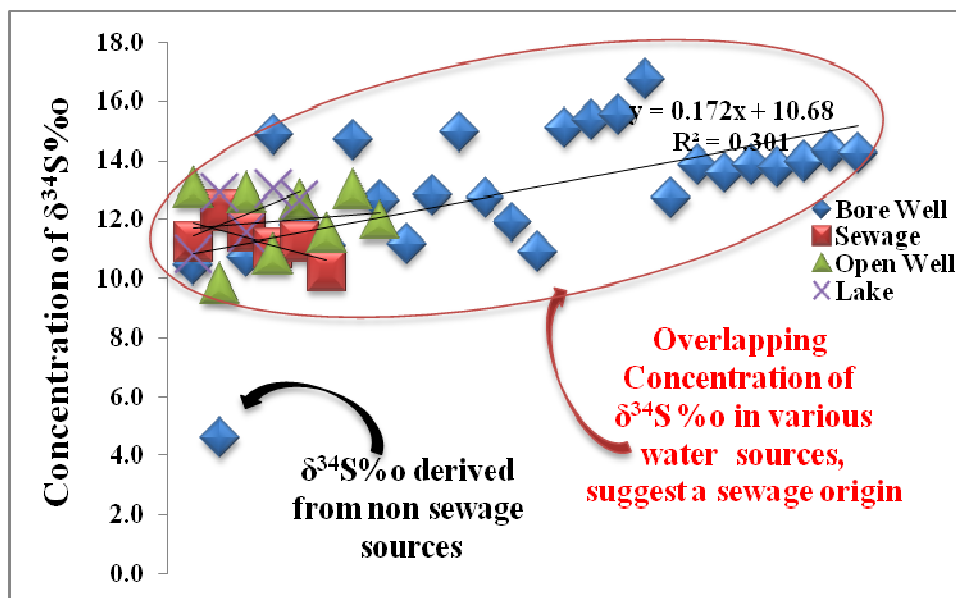


Figure 5. Overlapping concentration of $\delta^{34}\text{S}\text{‰VCDT}$ of various water sources.

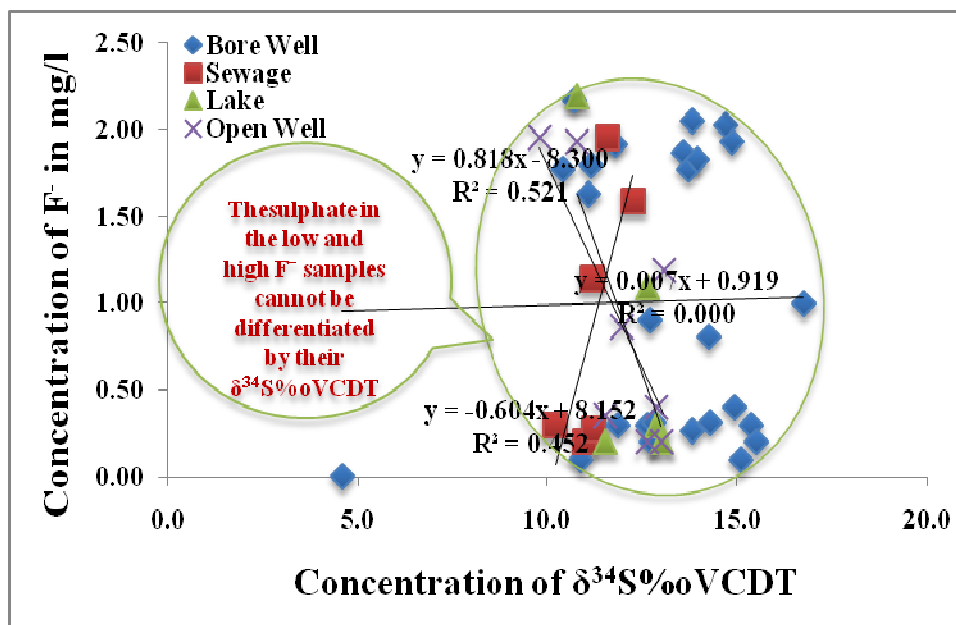


Figure 6. Sulphates in the low and high F^- samples cannot be differentiated by their stable isotope ($\delta^{34}\text{S}\text{‰VCDT}$) values.

reduced sulphur species produced by this process can be depleted in ^{34}S by up to 73‰ from the starting sulphate (Clark and Fritz, 1997). This reduction process is very uncommon in the environment however. The process proceeds very slowly, requiring high temperatures and low pH. Biogenic reduction is the dominant form of sulphur fractionation in nature. Biogenic fractionation is mainly a product of sulphur reducing bacteria such as *Desulfovibrio desulfuricans*.

These bacteria live in the ocean and lake sediment deposits. The bacteria are able to achieve greater rates of sulphate reduction because the process is enzyme catalyzed. Depletions of up to 50‰ in ^{34}S have been reported for reduced products (Krouse and Mayer, 2000). The extent of biogenic fractionation is inversely proportional to rate at which the bacteria reduce the sulphate. This in turn is a function of the surrounding temperature and the concentration of sulphate

(Attendorn and Bowen, 1997).

Hydrological applications

Sulphur isotopes are used in hydrology to trace natural and anthropogenic sources of sulphur, in particular to study the cycling of sulphur in agricultural watersheds, the sources of salinity in coastal aquifers or sedimentary strata, groundwater contamination by landfill leachate plumes, and acid mine drainage.

RESULTS AND DISCUSSION

SULPHUR-34 ($\delta^{34}\text{S}$)

Sulphur-34 is highly fractionated between sulphur compounds due to biological cycling. A summary of the ranges for $\delta^{34}\text{S}$ in natural materials is shown in figures. 3 and 4. Meteorites and magmatic sulphur are close to the standard Vienna Canon Diablo Troilite (VCDT). Values exceeding +20‰ are found in association with evaporites and limestones. Negative $\delta^{34}\text{S}$ values are typical of diagenetic environments where reduced sulphur compounds are formed (Krouse, 1980). The most common reaction product is pyrite, which is present in many shale or other organic rich sedimentary rocks and is formed by bacteria reducing seawater sulphate in marine sediments. The isotopic composition of dissolved sulphate is known to delineate various sources of groundwater sulphate. This approach is particularly successful when sulphate and oxygen-isotope abundance ratios in the sulphate are determined. The isotopic composition of sulphate is controlled by three factors (a) The isotopic composition of the primary- and secondary-sulphate sources (b) Isotope exchange reactions and (c) Kinetic isotope effects during sulphur and oxygen transformations (Krouse, 2001).

In the study area the minimum and maximum concentration of $\delta^{34}\text{S}$ in Sewage, Lake and Open and Bore well varied from 10.2 to 12.3; 10.8 to 13; 8.9 to 13.1 and 4.6 to 16.7 ‰ VCDT respectively. The isotopic compositions of sewage and lake samples are very close to the isotopic composition of the groundwater sulphate (Figures. 4 and 5). At first sight, this would suggest a sewage origin of the sulphate. However, similar isotopic composition would result if the groundwater sulphate originates from atmospheric sources; nonetheless in the present case there is insufficient evidence to prove it. Furthermore, the measured isotope values are similar to those reported for metamorphic rocks (Figure 4).

According to its isotopic composition, dissolved groundwater sulphate may be derived from fertilizer application or from a mixture of atmospheric and soil sources, or from sedimentary rocks (Figure 4). Hence, no clear categorization of groundwater sulphate to a certain

sulphate source is possible. Furthermore, Fluoride is the important anion to determine the water pollution effect even though the origin is purely geological. Fluoride concentration ranged from 0.03 to 2.18 mg/l in various sources of water during all the seasons of the two years. But, the sulphate in the low and high F⁻ samples could not be differentiated by their stable isotopic values (Figure 6). Nevertheless, the sulphate isotope data do not support the assumption of early Paleozoic source for the dissolved groundwater sulphate in Hebbal and Challaghatta valleys (Figure 4).

There is also apparent relationship between $\delta^{34}\text{S}$ ‰ values and SO_4^{2-} susceptible source in the Hebbal and Challaghatta valleys as localized sewerage network. Burtel (1989) measured the $\delta^{34}\text{S}$ ‰ value of gypsum deposits in several mountain blocks in the San Pedro Basin. Permian gypsum from the Epitaph Formation in the Whetstone Mountains had a $\delta^{34}\text{S}$ value of 11.7‰. Pyrite in igneous rocks in the Winchester and Dragoon Mountains had $\delta^{34}\text{S}$ values of 2.0‰ and 4.3‰, respectively. Further, Gu Ailiang, (2008) reported a $\delta^{34}\text{S}$ value (4.9‰) for SO_4^{2-} in Tucson Basin precipitation in 2003. Eastoe *et al.*, (2004) observed a seasonal variation in $\delta^{34}\text{S}$ values in precipitation between 2.1 and 8.5‰.

Because of the overlap in sulphur isotope values between the various water groups, and clear spatial trend, sulphur isotope ratios are regarded as useful tracers of flow paths in the Arakavathi and Vrishabhavathi basins (Fig. 5). But, Sulphur isotope values of precipitation were not measured as part of present study. Similarly, a Sulphur isotope is used to determine the sources of high sulphate water and potential mixing between the different water groups.

The groundwater samples have $\delta^{34}\text{S}$ reflecting sewerage contribution in various location like M.S. Ramaiyanagar, Gokul, Kerena Layout, Campus of Madras Engineering battalion of Indian Army, Domlur 2nd and 11th stage, Krishna Reddy Layout, Bellandur Lake, Devinagar 1st and 2nd cross, Ganganagar, HMT Layout, Anandanagar, Sindy Colony, K.S. Gardens, Ulsoor, Muthyalnagar, RMS 2nd stage, SBM Colony, Mathikere, Divandra palya, GKBK-agriculture College, Kalyannagar, Chalkere 1st cross, Pillanna garden 3rd stage, Batanary Road, Frazer town, Murgesh palya, Indiranagar, Tenment 2nd stage, Kempapur, Marathahalli, Karnataka Course, 100ft. Road, Krishnamurthynagara, Dickinson Road, Shivajinagara, Near Jayamahall road and Jeevanahalli. It suggests that fracture system water primarily has $\delta^{34}\text{S}$ values within the range of sewage contamination.

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