Assessment of sources for higher Uranium concentration in ground waters of the Central Tamilnadu, India

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Abstract. The uranium concentration in groundwater has attained greater importance considering the health effects in mankind. Groundwater being the major source of uranium; sampling and analysis of groundwater for the major cations and anions along with uranium has been carried out in hard rock aquifers of Madurai district. The sampling has been carried out in varied aquifers like, Charnockites, Hornblende Biotite Gneiss, Granites, Quartzites, Laterites and sandstone. The cation and anions showed the following order of dominance Na+ > Ca2+ > Mg2+ > K+ and that of anions are HCO3− > Cl− > SO42− > NO3− > PO43−. Higher concentration of uranium was found along the granitic aquifers and it varied along the groundwater table condition. Further it was identified that the mineral weathering was the predominant source of U in groundwater. Tritium studies also reveal the fact that the younger waters are more enriched in uranium than the older groundwater with longer residence time.

1.Introduction

The element uranium (U) is distributed throughout the crust of the earth in trace quantities in all the rock types. It is rich in acid igneous rocks like granites, syenites etc. while depleted in basic and ultra-basic rocks. The average concentration of U in Earth crust is 2.7 ppm [1]. In nature, U generally occurs in tetravalent state as insoluble species and hexavalent state as highly soluble species. The U concentration in groundwater depends on lithology, geomorphology and other geological conditions of the region [2 – 4]. Chemically, metallic uranium is highly reactive and can be leached in acidic or alkaline environment. Uranium concentrations in most of the groundwaters are generally low, typically in the range of 0.1 to 1 ppb, but it can
reach several tens to hundreds of ppb when it reacts with U rich minerals in the aquifers. Uranium is easily dissolved and transported in oxidizing groundwater due to the presence of oxygen; hence, it can be transported far away from its original occurrence [5]. Clay minerals and amorphous Fe, Ti and Mn oxides and hydroxides adsorb U from late-stage and post magmatic fluids, or are precipitated during supergene alteration and weathering of the primary minerals [6].

There are seven or more factors, including source rock U content, which can influence the uranium dissolved in water. These are
(1) The uranium content in source rocks, sediments or soils and its leachability.
(2) The proximity of the water to uranium-bearing rocks or minerals.
(3) The degree of hydraulic isolation of the water from dilution by fresher surface or subsurface waters.
(4) Climatic effects and their seasonal variability, particularly the influence of evapotranspiration.
(5) The pH and oxidation state of the water.
(6) Concentrations of carbonate, phosphate, vanadate, fluoride, sulfate, silicate, calcium, potassium and other species which can form uranium complexes or insoluble uranium minerals.
(7) The presence of highly sorptive materials such as organic matter, ferric, manganese, and titanium oxyhydroxides and clays.

These factors have either roughly constant effect. Fairly high uranium concentrations among vegetable foodstuffs were found in cauliflower, carrots, cucumber, white champignon and red peppers. Leaf-rich vegetables, herbs, sauerkraut, dill and parsley. The uranium content of wild mushrooms vary with the site, its geological origin, and with species [7]. Animal products contain lesser concentration of U. Uranium causes both chemical and radiological toxicity which is said to be affecting mainly organs like kidney and lungs [8].

The proposed study area is a complex terrain with varied lithology from hard rock to sedimentary formation along with granitic intrusions. The study aims to understand the sources and distribution of total uranium in groundwater in the aquifers of this region.

2. Study area

Study area is located in Central part of Tamil Nadu comprising of parts of Madurai, Dindigul, Trichy, Pudukottai and Sivaganga districts. Study area occupies a total of 4311 square kilometers and falls between E 09.89-10.35 latitudes and N 78.03-78.81 longitudes as shown in “figure 1”.

![Figure 1. Location of study area showing lithology and sample locations.](image-url)
Vaigai is a major seasonal river. Water level trend in 10 years from 1998 to 2007 showed fluctuation of 0.004 to 1.523 m/year in the study area by comparing the [9] CGWB (2008) reports of various districts, comprising of parts of Madurai, Dindigul, Trichy, Pudukottai and Sivagangadistricts.

3. Methodology
A total of 61 samples were collected spatially from hand pumps and bore wells of study area based on spatial coverage and lithology during the month of February 2014. The pH, temperature, total dissolved solids (TDS) and electrical conductivity (EC) of the water samples were measured in the field using a portable water-analysis kit. Sampling and analysis were carried out using standard procedures. Major ions such as Ca²⁺, Mg²⁺, Na⁺, K⁺, F⁻, Cl⁻, CO₃⁻, HCO₃⁻, NO₃⁻, H₄SiO₄, PO₄³⁻ and SO₄²⁻ were analyzed in lab. Cations such as Ca²⁺, Mg²⁺ as well as anions such as Cl⁻, CO₃⁻, and HCO₃⁻ were analysed by titrimetry method. Na⁺ and K⁺ by flame photometer (ELICO CL 378). SO₄²⁻, PO₄³⁻, NO₃⁻ and H₄SiO₄ were analysed by spectro-photometer (SL 171 minispec). EC, pH and F⁻ were measured using ion electrode meter (Thermo Orion). Precision of analysis was checked by error percentage calculation (1)

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Error \% = \frac{(TA-TC)}{(TA+TC)} \times 100 \quad (1)
\]

(Where TA- total anions and TZc- total cations)
The percentage of error is found to vary between ±1 to ±10 %[10]. Total Uranium concentration in groundwater samples were analysed by Laser fluorimetry.

4. Results and Discussion
The total cations (TZ+) and total anion (TA-) balance [11] shows the charge balance error percentage. The error percentage is observed in the samples between ±10%. Occurrences of errors in chemical analysis of groundwater may also be due to reagents employed, limitations of the methods and instruments used, presence of impurities in distilled water etc. The maximum, minimum and average values for different seasons are given in table.1. The groundwater in the study area is generally odorless and colorless in most of the sampling locations.
Table 1. Minimum, maximum and mean of physico chemical parameters and comparison of chemical composition of water with WHO (2011) in milligram per litre. (Except U in ppb, ORP in mV, EC in μS/cm and pH)

| Parameters | Maximum | Minimum | Average (N=61) | WHO (2011) |
|------------|---------|---------|---------------|-------------|
| Ca         | 104     | 6       | 35.62295      | 100*        |
| Mg         | 57.6    | 8.4     | 26.38689      | 50*         |
| Na         | 158.9   | 2.6     | 44.75262      | NG          |
| K          | 40      | 0.1     | 8.888525      | 20*         |
| Cl         | 116     | 2       | 39.90484      | 250         |
| F          | 2       | 0.1     | 0.595082      | 1.5         |
| HCO₃⁻      | 286.7   | 24.4    | 156.3475      | 125-350*    |
| NO₃⁻       | 420     | 10      | 88.62295      | 50          |
| SO₄²⁻      | 76      | 0.1     | 23.39013      | 500         |
| H₄SiO₄     | 16.09   | 5.591   | 11.38392      | NG          |
| U          | 68.28   | 0.4     | 11.78         | 30          |
| ORP (mV)   | 283     | 270     | 48.54098      | NG          |
| pH         | 8.111   | 6.176   | 7.135541      | 6.5-9.5     |
| EC (μS/cm) | 4000    | 288.8   | 1420.632      | 1400*       |
| TDS (mg/l) | 1890    | 204     | 725.0984      | 1000        |

*NG- not given; * WHO [12]

Quality of drinking water was evaluated according to the WHO standards [8]. pH of majority of groundwater samples collected fall within safe limit, but the TDS of certain samples are higher than the maximum permissible limit. The lithological composition, leaching and dissolution of soil salts and chemical spills from wastewaters play an important role in the TDS values [13]. More likely, many processes influence the relationship between pH and other physico-chemical parameters that even multivariate approach cannot identify them [14]. The large variation in EC is mainly attributed to lithologic composition and anthropogenic activities like disposal of sewage along the riverbeds prevailing in this region. The extremely low values of EC are attributable to short residence time of the groundwater in the rock matrix as suggested by [15] and [16] or due to the effect of dilution [17].

U concentration in groundwater is important in understanding the radiological impact to secure the standard of life. A number of studies have been carried out in different places in order to study uranium concentrations in drinking waters [18-20]. The [8] standard limit for Uranium in groundwater is 30 ppb. In the study area 8 samples are above the permissible limit. Kidneys and bones are the major locates for the accumulation of uranium in the body[21-23] and skeleton is the major site for the long term storage of Uranium [24]. Even lower concentration of Uranium in drinking water also causes the nephrotoxic effects [25].

The orders of dominance of U in different lithologies in various seasons are as follows

Granite > Fissile hornblende biotite gneiss > Charnockite > Hornblende Biotite Gneiss
Uranium and radon in groundwater mainly depend on the fractures and their degree and the angle of inclination to the bedrock [26]. The high concentration of U in Central and north eastern part of the study area (Figure 2) could be due to the leaching of elements present in fractures. Temple (2002) [27] hypothesized that high U concentrations were due to U-rich fractures in the granitic rocks. Only relatively deep wells contained high U concentrations, possibly because U had already been leached from shallow fractures as it behaves as a closed system. The study area also reports presence of pink granitic intrusions [28] and the zone of higher U concentration is found around the granitic terrains that enhance the leaching of U to the groundwater system [29].

High U concentration is generally reported in groundwater of granitic terrains (Figure 3). A large range of U concentrations was observed in groundwaters from the Lac du Bonnet Granite of the Canadian Shield. U concentrations were found to be generally highest at shallow depths (<60 m; depth range of boreholes up to 1000 m) in oxic environment groundwaters which shows evidence of active groundwater circulation.
dominant controls on U concentration were redox potential and the formation of soluble anionic U-
carbonate species. U increases with the accumulation of alteration phases along fractures and around the
primary phases. As weathering progresses, this U is incorporated into the Interstitial spaces of biotite,
feldspar and early alteration phases accumulate within the secondary interstitial aggregates and lose their
discrete character [30]. High-U groundwaters appear not to be a widespread feature of the granites of the
region, perhaps because of the short residence times of the groundwaters and their slightly acidic, low-
alkalinity compositions. The sporadic nature of the U mineralization may also be a factor.

Figure 4. Piper facies for ground water samples highlighting samples with high uranium concentration

The higher value of U concentration which is above 30ppb is observed in few samples and their
hydrogeochemical parameters is plotted in piper diagram (figure 4) to study the migration of U ions in
groundwater samples. The samples are predominantly of HCO$_3$ type as weathering processes affect the
mineral which in turn affects the distribution of elements in groundwater. Firstly Ca would have been
removed from the groundwater, while Na which is absorbed on the surface of the clay minerals in the
aquifer would be released into the groundwater. The Na probably comes from the decomposition of
Plagioclase feldspar. An increase in Na and K is assumed to result from cation exchange of Ca and Mg
ions by mineral-water interaction.
The relationship between U and ionic strength (IS) is plotted in figure 5. It is interesting to note that U concentration increases with increase of IS that may be attributed to the increase in residence time of water [31]. The higher U concentration in the groundwater samples shows that there is a decreasing trend with increase in IS. The study area being a hard rock terrain, residence time of water is generally higher in cracks and fissures if they are not interconnected sufficiently, which ultimately increases U concentration. Increase of ionic strength may also be due to pH induced weathering in the aquifer [32], as U concentrations in groundwater decreased with flow direction due to U-retention by sorption processes.

4.1. Factor Analysis

The purpose of Factor analysis is to simplify the quantitative description of a system by determining the minimum number of new variables necessary to reproduce various attributes of the data. These procedures reduces the original data matrix from one having (n) variables necessary to describe the (N) samples to a matrix with (m) factors (m < n) for each of the (N) samples. It is also aimed at transforming the variables so that the axes become orthogonal, which then allows the definition of new independent variables. The first factor is chosen to explain as much as possible of the total variance of the observations, the second factor to explain as much as possible of the residual variance, and so forth. In other words, the first factor is determined such that the sum of squares of the projections of the points on the factor is highest (factor loadings). Next, to define the second factor, the points are projected on a plane orthogonal to the first factor and so on for the other factors, each explaining less and less of the total variance. On the other hand, the sum of squares of the factor loadings for each variable is the communality and reflects the proportion of the total variability of each variable accounted for by the factoring. It follows three main steps, namely: extraction of initial factors, rotation of factors and calculation of each factor scores.

There were five different factors extracted for the analytical results (table 2) and the fifth factor represents U in ground water showing strong negative correlation with OPR, indicating that oxidation and reduction potential has a significant role in U concentration of ground waters apart from the weathering process.
U must be oxidized before it is transported into groundwater but once in solution, it can travel great distances [33], hence it can be transported far away from its original emplacement [5]. In deeper environments, mobility and attenuation of U are controlled by the composition of fracture coatings and water chemistry. In general, the highest concentration of dissolved U is found in the oxidized zone of the aquifer. As groundwater conditions become reduced, dissolved U concentration decreases due to sorption and precipitation reactions. Deep aquifer systems are recognizable by a constant low U concentration(figure 6)

| Component | 1   | 2   | 3   | 4   | 5   |
|-----------|-----|-----|-----|-----|-----|
| Ca        | .168| .800| -.016| -.162| .042|
| Mg        | .400| .531| .481| .057| -.053|
| Na        | .824| -.173| .149| -.006| .131|
| K         | .786| -.199| -.095| -.186| .008|
| F         | -.251| .223| .034| .775| -.145|
| Cl        | .731| -.345| -.210| -.075| .153|
| HCO₃⁻     | .866| .164| .043| .177| -.081|
| NO₃⁻      | .139| .223| .896| -.054| .040|
| SO        | .465| .192| -.756| .014| .044|
| H₂SiO₄⁻   | -.241| .593| .091| .130| -.079|
| U         | .171| -.087| .076| .243| .784|
| ORP       | .088| -.047| .090| .378| -.749|
| pH        | .209| -.337| -.123| .661| .140|
4.2. Factor Score

Factor scores were estimated to find out the spatial representation of the factor and its temporal variation [35]. They are commonly obtained by two approaches such as weighted least square method and the regression method. The regression method is used in the study to compute the factor scores. The positive zones indicate dominance of that factor (hydrogeochemical regime). The spatial variation was estimated by using factor score values of each sampling points and they were plotted by Map Info Professional 10 (figure7).

The spatial distributions of dominant regions irrespective of all seasons are explained in five factors. Weathering is dominant in the NW part of the study area and the water table movement is from the NW to SE direction [36]. It indicates that weathering processes is dominant subsequently by anthropogenic activities. The higher concentration of U is distributed in the central and NE part of region. Higher concentration is mainly due to flushing of U by infiltrating rainfall recharge which results in increase of uranium in groundwater along with the rise in water level [37]. There are different studies of U in groundwater carried throughout the world in various types of granitic terrains and it is evident from the previous studies [38] that most of the regions with higher concentration of Uranium are found in the Granitic terrains of the world.

Figure 6. Schematic diagram of U concentration distribution along a groundwater flow path (Revised from Ivanovich et al) [34]
Figure 7. Overlay of Spatial distribution of uranium factor on lithology

Figure 8. Scatterplot between total U and Tritium in groundwater samples

| Tritium Conc. | Qualitative “Age” (after Clark and Fritz [39]) |
|---------------|-----------------------------------------------|
| <0.8 TU       | Sub modern—recharged prior to 1952            |
| 0.8 to ~4TU   | Mixture between submodern and recent recharge |
| 5 to 15 TU    | Modern (<5 to 10 yrs)                        |
| 15 to 30 TU   | some “bomb” 3H present                       |
| >30 TU        | Considerable component of recharge from 1960s or 1970s |
| >50 TU        | Dominantly the 1960s recharge                |

In the study area based on Tritium values (figure 8) waters can be classified into 3 types such as sub modern, Mixture between sub modern and recent recharge and modern waters. Only selected samples were analyzed for Tritium. Most of the samples belonged to the mixture between sub modern and recent
recharged type. In general highest uranium concentration is observed in this mixed water type belonging to rock types such as Granite, Fissile Hornblende Biotite Gneiss and Quartzite. The inference is found to match with that of Ionic strength which represents higher uranium values associated with hard rocks that have longer residence time for water and hence older waters with respect to tritium has higher uranium concentrations. It is found that modern waters contain lower uranium due to flushing.

5. Conclusion

The Uranium concentration in the present study had an average value of 11.78 ppb with a maximum of 68.28 ppb and 0.4ppb as the lowest reported value. The concentration in 95% of samples were less than 60 ppb - the AERB, Indian standard; whereas considering the WHO standards,88% of the samples were within the permissible limit of below 30 ppb of Uranium. Highest uranium concentration was noted in the central and NE side of the study area which comprises of hard rock terrain. Lithological dominance of Uranium concentration is in the following order; Granite reporting the highest U followed by Quartzite and Fissile Hornblende BiotiteGneiss. Few ground watersamples from Charnockite also showed high U concentration. From the Piper diagram it is concluded that major water type of the area belonged to Na-HCO₃ type responsible for higher Uranium. Few samples also belonged to Ca-HCO₃ type. Tritium results indicate that majority of water belonged to mixture between modern andsub modern water type and higher Uranium also corresponds to this water type. Thus from all these results it’s clearly noted that sources responsible for higher uranium cannot be a single factor as seen in lithological influence; not only granites are responsible for higher concentrations. Similarly Ca-HCO₃ water types in the region also contain few higher Uranium values. Apart from all these sources responsible; redox potential is a major governing factor that contributes to higher Uranium in ground water.

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