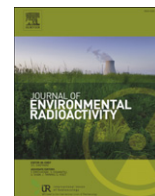Contents lists available at ScienceDirect

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Environmental Tritium (^{3}H) and hydrochemical investigations to evaluate groundwater in Varahi and Markandeya river basins, Karnataka, India

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ABSTRACT

The present study aimed at assessing the activity of natural radionuclides (^{3}H) and hydrochemical parameters (viz., pH, EC, F$^-$, NO$_3^-$, Cl$^-$, Ca^{2+}, Mg^{2+}) in the groundwater used for domestic and irrigation purposes in the Varahi and Markandeya river basins to understand the levels of hydrochemical parameters in terms of the relative age(s) of the groundwater contained within the study area. The recorded environmental ^{3}H content in Varahi and Markandeya river basins varied from 1.95 ± 0.25 T.U. to 11.35 ± 0.44 T.U. and 1.49 ± 0.75 T.U. to 9.17 ± 1.13 T.U. respectively. Majority of the samples in Varahi (93.34%) and Markandeya (93.75%) river basins being pre-modern water with modern recharge, significantly influenced by precipitation and river inflowing/sea water intrusion. The EC-Tritium and Tritium–Fluoride plots confirmed the existence of higher total dissolved solids (SEC > 500 μS/cm) and high fluoride (MAC > 1.5 mg/L) in groundwater of Markandeya river basin, attributed to relatively longer residence time of groundwater interacting with rock formations and vice versa in case of Varahi river basin. The tritium-EC and tritium–chloride plots indicated shallow and deep circulating groundwater types in Markandeya river basin and only shallow circulating groundwater type in Varahi river basin. Increasing Mg relative to Ca with decreasing tritium indicated the influence of incongruent dissolution of a dolomite phase. The samples with high nitrate (MAC > 45 mg/L) are waters that are actually mixtures of fresh water (containing very high nitrate, possibly from agricultural fertilizers) and older 'unpolluted' waters (containing low nitrate levels), strongly influenced by surface source.

1. Introduction

Water quality is an important parameter of environmental studies because it is consumed and also it can transport pollutants in the environment. Groundwater has increasingly taken its place in the provision of safe, potable supply (viz., availability) in the developing world and overexploitation of aquifers, evident in failing boreholes, deteriorating water quality and their regulation has become a world-wide concern. In addition to this, the radioactive contents of water should not be underestimated or disregarded, as they usually are, as an isolated water quality parameter (Sanchez-Cabeza and Pujol, 1996). The extent of water/rock interaction, and hence the groundwater chemistry, depends on the mineralogy of the aquifer rock and the residence time that the groundwater has been in contact with the rock (McNeill et al.,

2003). In this regard, environmental (stable and radioactive) and artificial radioactive isotope hydrologic techniques have proved to be effective tools for solving many critical hydrological problems/processes (Todd, 1959) and in many cases, provide information that could not be obtained by any other conventional means (Clark and Fritz, 1997; Kendall and McDonnell, 1998; Rao, 1984). The use of artificial tracers is generally effective for site specific and local applications (Tirumalesh et al., 2007; Rangarajan and Athavale, 2000; Kulkarni, 1992) due to their cost-effectiveness and investigative empowerment of local investigators (Verhagen, 2003). In contrast, environmental isotope hydrology is increasingly seen as a powerful discipline in assessing groundwater systems especially in developing environments, where historical data is rarely available (Verhagen, 2003). The, environmental isotopes are very useful tracers to study the present and ancient hydrological processes and to understand surface and groundwater interconnections, the source and mechanism of recharge (Sukhija et al., 1996; Shivanna et al., 2004), groundwater circulation and its renewability (Rao and Kulkarni, 1997; Navada et al., 1993), recharge areas and transit times of the aquifer (Sukhija et al., 1998; Agarwal et al.,

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Abbreviations: TU, Tritium unit; MAC, maximum admissible concentration; SEC, specific electrical conductance; TDS, total dissolved solids.
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2006), hydraulic inter-relationships (Navada and Rao, 1991; Jain et al., 1987) and source and mechanism of groundwater contamination (Shivanna et al., 2000, 1993; Tirumalesh et al., 2007a). Environmental isotopes now routinely contribute to more productive water investigations, complementing geochemistry and physical hydrogeology (Al-Katheeri et al., 2009) because radioactive environmental isotopes give information on groundwater dynamics and recharge rates whilst non-radioactive and/or stable environmental isotopes indicate the origins of groundwater and delineate groundwater bodies. The most frequently used environmental isotopes for isotopic hydrological investigations include isotopes of elements of the water molecule [^{1}H (protium), ^{2}H (deuterium), ^{3}H (tritium), ^{16}O and ^{18}O] and that of the element carbon [^{12}C, ^{13}C and ^{14}C].

Tritium [Hydrogen-3 (^{3}H$_2$) or Triton (T$_2$) or ^{3}H], radioactive or unstable isotope of hydrogen having a half-life of 12.32 ± 0.02 yr (~ 4500 ± 8 days), decays to ^{3}He emitting a beta particle having a radiation energy of 0.0057 MeV (Lucas and Unterweger, 2000). It is a gas at standard temperature and pressure and has relatively a high specific activity. Tritium is a naturally occurring radionuclide, produced mainly from interactions between cosmic-ray neutrons and nitrogen in the upper atmosphere (Lal and Peters, 1967), via the reaction: ^{14}N(n, T)^{12}C. The largest anthropogenic source has been atmospheric nuclear testing between 1952 and 1969, which disturbed the natural levels of tritium. It behaves like stable, ordinary hydrogen and is usually found attached to molecules replacing hydrogen, having the chemical properties essentially the same as those of ordinary hydrogen. When Tritium combines with oxygen to form a liquid, the most common forms are tritium gas (HT) and tritium oxide, also called "tritiated water" (viz., T$_2$O/TTO) or partially tritiated water (viz., THO/HTO). In tritiated water, a tritium atom replaces one of the hydrogen atoms so the chemical form is HTO rather than H$_2$O. The tritiated water so formed gets precipitated out of the atmosphere together with ordinary water and migrate with ground and surface waters. The deposition rate of the tritium varies with latitude, but it is also mixed with the bulk of precipitation originating from the ocean (which has a very low tritium content), and thus the average tritium content of precipitation tends to vary inversely with annual precipitation. The combined natural and human-made/anthropogenic emissions of tritium resulted in a current global background level of tritium (Okada and Momoshima, 1993). As part of the water molecule (^{3}HHO/^{1}H^{3}HO), tritium perfectly follows water in atmospheric, oceanic, and hydrological transport and mixing processes (Saito, 2008) and hence can be used as an ideal tracer to date groundwater with a residence time of less than 50 yr. Application of tritium to hydrologic problems was first proposed by Libby (Libby, 1953; Bergmann and Libby, 1957). Tritium analysis has been useful in many areas such as hydrogeology (Lloyd, 1981; Lehmann et al., 1993; Sanchez-Cabeza and Pujol, 1999), nuclear industry monitoring (Mundschenk and Krause, 1991; Castellano and Dick, 1993), dosimetry and health-risk assessment (Okada and Momoshima, 1993; Murphy, 1993), and some special topics such as false labeling of alcoholic beverages (Schönhofer, 1992) and for estimating the groundwater residence time (Fontes, 1983; Yurstsever, 1983) as it is directly incorporated into water molecule.

In the present study, an attempt has been made for first time to estimate tritium (^{3}H) in the groundwater samples from Varahi and Markandeya river basins, using low background liquid scintillation counting system (Wallac Quantulus 1220) to see whether the aquifer in the study area is getting modern recharge or not. The paper also discusses the relationship that can exist between tritium and other hydrochemical parameters like pH, EC, F$^-$, NO$_3^-$, Cl$^-$, Ca^{2+}, Mg^{2+}.

2. Study area

The Location map of the Varahi and Markandeya river basins along with the sampling points are shown in Fig. 1.

2.1. Varahi River basin

River Varahi is a major west flowing river in the west coast in Udupi district, which originates from the high peaks of the Western Ghats near Guddakoppa village in Hosanagar taluk, Shimoga district at an altitude of about 761 m above mean sea level (MSL) and flows for a length of 88 km. A dam (13° 39' 15" N latitude and 74° 57' 0" E longitude) has been constructed across the river Varahi at Hole Shankaranarayana village, which is approximately 6 km from Siddapura village, Kundapura taluk, Udupi district. The stream collects heavy rainfall in the hilly region around Agumbe and Hulikal. Tributaries like Hungedhole, Kabbenahole, Dasnakatte, Chakranadi etc., join Varahi before emptying into the Arabian Sea. Varahi River basin stretches geographically from 13° 26' 34.8" N to 13° 39' 32.4" N latitude and 74° 40' 33.6" to 74° 56' 34.8" E longitude, positioned in the midst of Udupi district in the western part of Karnataka state. The river Varahi has been one of the major sources of water for Mani Dam near Mani village, with diversion weir and Forebay Dam for generation of electricity at the Varahi Hydro-electricity Power Station. The study area is having a catchment area of 293.0 km^2 (29300 ha). The gross command area of 362.41 km^2 covering parts of Kundapura (209.73 km^2) and Udupi (152.68 km^2) taluks of Udupi District, which is the area around the dam, where the benefits of the dam, such as irrigation water reach. The reservoir water has been directed by via Varahi Left Bank Canal (VLBC, 33 km) and Varahi Right Bank Canal (VRBC, 44.70 km). The net irrigable command area is around 157.02 km^2 (15702 ha) covering part of Kundapura (83.24 km^2) and Udupi (73.78 km^2) taluks of Udupi District, area under flow irrigation accounts to 129.79 Km^2 (12979 ha) and 27.23 Km^2 (2723 ha) comes under lift irrigation. The Varahi Irrigation Project is aimed at providing enhanced irrigation facilities and an improved drinking water facility to the villages of two taluks of Udupi district by means of canal system in addition to hydroelectric power generation.

2.2. Markandeya River basin

The River Markandeya is one of the major tributaries of River Ghataprabha, subsequently joins the River Krishna in the Northern Karnataka. River Markandeya originates in Bailur in Western Ghats and flows for a length of 66 km towards east before joining Ghataprabha near Gokak. A dam (16° 2' 0" N latitude and 74° 38' 30" E longitude) has been constructed across the river Markandeya to establish reservoir at Shirur village in Gokak taluk. The study area, Markandeya River basin stretches geographically from 15° 56' to 16° 08' N latitude and 74° 37' to 74° 58' E longitude, positioned in the midst of Belgaum district in the northern part of Karnataka state. The study area is having a catchment area of 432 km^2 (43,200 ha). The gross command area is around 328.31 km^2 covering part of Gokak (237.98 km^2), Saundatti (26.13 km^2), Hukkeri (50.6 km^2) and Belgaum (13.6 km^2) taluks of Belgaum District. The reservoir water is directed via Markandeya Left Bank Canal (MLBC, 15 km) and Markandeya Right Bank Canal (MRBC, 71 km) to irrigate an area of around 8.9 km^2 (890 Ha) and 182.15 km^2 (18,215 ha) respectively. Thus, the net irrigable area is around 191.05 km^2 (19105 ha) covering part of Gokak (95.83 km^2), Saundatti (80.37 km^2), Hukkeri (8.90 km^2) and Belgaum (5.95 km^2) taluks of Belgaum District. Markandeya Irrigation project is aimed at providing enhanced irrigation facilities and an
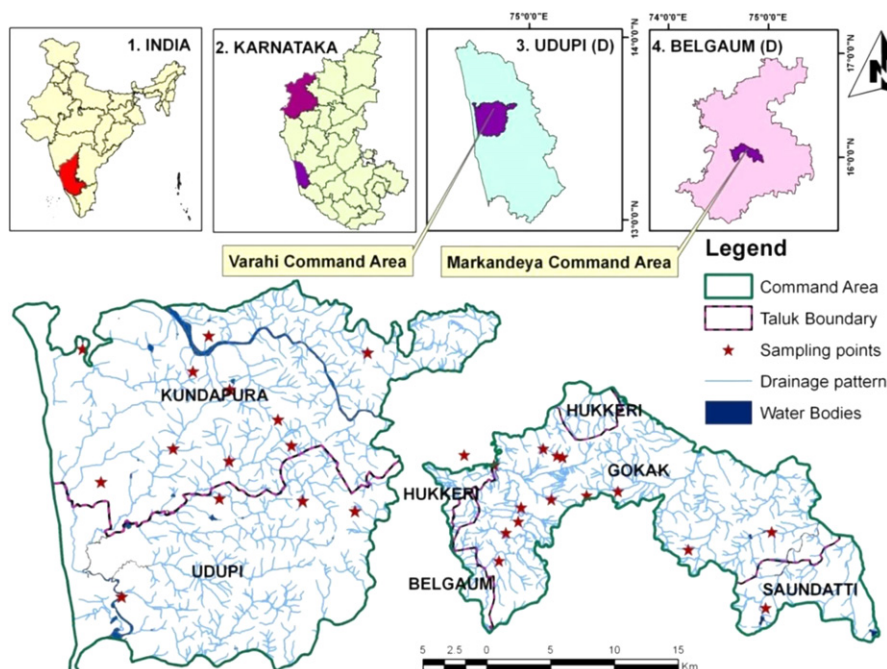
Fig. 1. Location map of Varahi and Markandeya river basins.

improved drinking water system to the villages of four taluks of Belgaum district by means of canal system.

3. Methodology

3.1. Hydrochemical parameter

Groundwater samples were collected in two polyethylene bottles during post-monsoon season (November, 2008), to analyze various anions and cations according to the Standard Methods for the Examination of Water and Wastewater, 21st ed., APHA, AWWA, WEF, (2005) Prior to these analyses, clear pumping for a period of 10 min was carried out in order to avoid the sampling of stagnant annulus water that would be in the region of pump and pump systems. The pH and specific electrical conductivity (SEC or EC; viz., salinity or total dissolved solids) were measured in situ to prevent changes in the chemistry of the water samples before analyses (Appelo and Postma, 1999). The preservation of the samples have been done according to published procedures by acidifying by adding 65% HNO_3 until the pH is ≤2 for major cations and other bottle stored under cool condition at 4 °C for major anions as suggested by Appelo and Postma (1999). In the present study, major anions like nitrate (NO_3^-) and fluoride (F^-) were analyzed by Ion selective electrode (ISE) method (viz., APHA method no. 4500-NO_3 and 4500-F); chloride (Cl^-) was estimated using argentometric titration (i.e., APHA method no.4500-Cl^-) (APHA, 2005), while major cations like calcium (Ca^{2+}) and magnesium (Mg^{2+}) were evaluated by following EDTA titrimetric method (i.e., APHA method no. 3500-Ca and 3500-Mg). High purity reagents were used throughout, using with high purity ion-free, MilliQ water (18.2 MΩ-cm (Mega-ohms-cm)) filtered through 0.22-μm hollow fiber filter (easy pure RF, Barnstead) using Milli-Q® Gradient water purification systems.

3.2. Tritium analysis – experimental setup

Tritium is commonly measured by two methods: β-counting or ^{3}He ingrowth. Natural levels of tritium are only marginally measurable by direct β-counting methods, but fortunately tritium is highly enriched over ordinary H in the H_2 produced by the electrolysis of water. Since, tritium is a very soft beta-emitter (maximum E_β = 18.6 keV), β-detection, either by gas proportional counting (GPC) or liquid scintillation counting (LSC), can then easily measure low-level counting of natural tritium (Taylor, 1981a; Lloyd, 1981; Noakes and Filippis, 1988; Pujol and Sanchez-Cabeza, 1999). For small volumes, gas counting and its better sensitivity have advantage over liquid scintillation counting. In direct liquid scintillation counting, normal, low background liquid scintillation counters with high quality scintillation solutions are used and their detection limit of tritium is about 10 TU. The detection can be reduced to about 3 TU by using 40–75 ml of water instead of 8–10 ml and counting by large volume liquid scintillation counter. In recent years many researchers have been using liquid scintillation counting for environmental studies involving the determination of water radiological quality (Schönhofer, 1989; Salonen, 1993; Blackburn and Al-Masri, 1993, 1994). When analyzing natural waters, the measurement by LSS offers numerous advantages over GPC: (1) the water sample is directly combined with an appropriate aqueous-accepting scintillation cocktail, (2) minimal sample pretreatment is required, and (3) the counting efficiency of LSS is higher than that of GPC (Noakes and Filippis, 1988). When tritium concentration is low, that is, less than 10 TU, electrolytic enrichment is necessary to determine the tritium activity. However, when tritium concentration is higher than 10 TU, electrolytical enrichment might not be necessary. In the present study, tritium measurements in the groundwater samples from Varahi and Markandeya river basins were done at Isotope Application Division (IAD), Bhabha Atomic Research Centre (BARC), Trombay, Mumbai.

3.2.1. Instrumentation

In the present study, radioactive isotope, Environmental Tritium (^{3}H) concentration in the groundwater samples was measured using a low-level background Wallac Quantulus 1220 (PerkinElmer Inc.) (Wallac 1220 QuantulusTM, 2004) beta liquid scintillation counter/spectrometer (Schönhofer, 1992) proceeded by electrolytic enrichment (Nair, 1983) of tritium. The low limit of detection was

calculated according to ISO standard method, and that was 8.4 TU, with 0.750 CPM background and efficiency of 24.72%.

In the present study, the standard, Teflon coated, polyethylene/polythene vials of 20 ml capacity (from Wallac, PerkinElmer Inc.,) were used for the tritium measurements/counting (Nair, 1983). The vials were mechanically tough with high density and a low intrinsic radioactivity in order to maintain the contents at a high degree of stability (Baeza et al., 1997). The liquid scintillator cocktail used was Optiphase Hisafe3 (from Wallac, PerkinElmer Inc.,), which was systematically mixed with the aqueous assay sample (viz., enriched water sample) which will be obtained after distillation, in a polythene vials in the proportion 8:12. This allows the minimum detectable activity to be reduced by using a relatively large volume of water, without producing heterogeneity in the water-scintillator mixture (Baeza et al., 1997) as the environmental samples may induce phase separation (Schönhofer, 1994). The accuracy/precision/reproducibility for tritium was 0.5 TU ($\pm 1\sigma$ criterion/analytical errors), which can vary from $\pm$ 0.3 to $\pm$ 0.6 TU.

3.2.2. Sample collection, pretreatment and enrichment

Tritium analyses are best prepared by electrolytic enrichment in the batch cell followed by liquid scintillation counting (LSC) (Florkowski, 1992; Morgenstern et al., 1992). The low energy of tritium creates difficulty in its detection, since all the natural water samples contain low tritium content and hence water has to be enriched prior to measurement by liquid scintillation counting to improve the sensitivity of measurement and is usually done by concentrating the sample to about 15–30-fold by electrolysis prior using a round bottom double neck flask. The samples for environmental ^3H (tritium) must be collected while the bore is still pumping (Rosen et al., 1999) and the sample was filled completely in polyethylene bottles/vials of 1 L capacity and preserved airtight using inner sealing cap in order to avoid evaporation and head space/air gaps. After collecting water to be assayed, it was pretreated by filtering through 0.45-μm pore diameter membranes and then distilled at atmospheric pressure with no additives. All contact with the atmosphere was avoided by connecting a silicone trap to the condensation flask.

3.2.3. Electrolysis

The equipment used for the electrolytic concentration consists of a power supply unit providing currents of between 0 and 18 A to a series of 20 electrolytic cells placed in a refrigerating container, each cell having a capacity of 250 ml. The concentric cells which are connected in series, have an inner mild steel cathode and stainless steel anodes (Cameron, 1967), electrically insulated by plastic/Teflon on the top and bottom. The electrodes are of stainless steel to avoid corrosion. The anode (A) is external and the cathode (C) is perforated to facilitate the homogeneity of the sample. Each cell presents an outlet tube for gases which is connected to a silicone trap through which the oxygen and hydrogen generated in the electrolytic reaction pass. The cells are placed in a water-antifreeze filled refrigerating container, which is endowed with a stirrer to homogenize the temperature and a thermostat to select the temperature chosen to work at. In general, we work at sub-zero temperatures to counteract the heat generated by the electrolysis, and to have this take place at as close as possible to the freezing point of the solution to be electrolyzed. This allows one to achieve the greatest possible isotopic separation (Sepall and Mason, 1960) and to avoid losses by evaporation, nebulization, or bubbling.

Initially, 250 ml of previously distilled groundwater sample are electrolytically reduced (viz., enrichment/electrolyzed) to about 13 ml in each cell. The quantity is determined by weighing for great precision. The electrolysis was regulated by adding to each sample, 0.5–1.0 g of Na_2O_2, an electrolyte which forms NaOH in water and

yields an alkaline medium favourable to electric conduction and hence to the reaction of water electrolysis. This was followed by passing DC power at a rate of 6.0–8.5 A such that each cell gets 3.0–3.5 V, which was controlled through D.C regulated power supply unit in order to perform the electrolysis at a constant current intensity or quasiconstant current density. A total charge of 705 A-h is passed to bring down the weight of the sample from 250 g to about 13 g in each and every one of the twenty cells. This is to ensure the occurrence of electrolysis in a reproducible manner with good homogeneity due to existence of very similar ionic conditions in all the electrolytic cells. Since the isotopic effect depends on the temperature, to achieve a similar enrichment in all cells requires the reaction to take place in each of them at as homogenous temperature as possible. The cell temperature was measured using a thermocouple, so as to keep the temperature between 2 and 4 °C during electrolysis to control evaporation losses at a minimum rate in order to achieve better separation factor in the round bottom double neck flask. The evolved mixture of hydrogen and oxygen gases is vented out through silicone oil traps. This provides a detection limit of about 0.5 TU, which is generally adequate for most hydrological applications. After electrolysis, the cells are removed from the refrigerator unit, allowed to attain room temperature and condensed water on the outer surfaces of the cells is removed. They are then weighed for their contents and the samples are transferred into 50 ml round bottomed flasks with standard joint (socket), which can be connected to condensers with corresponding cones to facilitate distillation.

3.2.4. Neutralization with $PbCl_2$

After the electrolysis of the sample, the content of each cell was neutralized, since the medium in which the electrolysis took place is strongly alkaline. There exist a variety of methods for this purpose, such as bubbling CO_2 through the cell, or using $Pb(NO_3)_2$ (Benzi et al., 1995) or $PbCl_2$. We used the latter salt, as this is less hygroscopic and dissociates less with heat than $Pb(NO_3)_2$ (Taylor, 1981b). A bout of 3–4 g of finely powdered $PbCl_2$ was added to each flask having 13 ml of sample electrolyzed for neutralization of the alkali present in the sample, till approximately neutral pH is reached. The chemical equation of neutralization using lead chloride is as follows:

$$PbCl_2 \ + \ 2NaOH \rightarrow Pb(OH)_2 + 2NaCl$$

$$Pb(OH)_2 \rightarrow PbO \ + \ H_2O$$
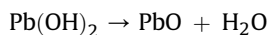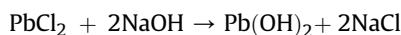
3.2.5. Final distillation

The sample is subsequently subjected to a single distillation using a combination mantle heater in order to eliminate the salts formed in the previous neutralization, since a high degree of salinity may produce heterogeneity in the sample-scintillator mix (García, 1995). The possible interchange of HTO with the atmosphere has to be avoided, using a silicone trap connected to the condensate collection flask. Following the indications of Taylor (1981b), a working temperature of around 150 °C was chosen so that the reduction in the conductivity after a single distillation in these samples can be achieved, which is sufficient to guarantee the homogeneity of the mixture of the distilled sample and the liquid scintillator. Since, the pH and conductivity are considered as very important for a good scintillation measurement; water samples must have pH between 6.0 and 7.0 and conductivity between 2 and 10 μS/cm, after the distillation process. This will not alter the tritium content in the sample, allowing a nearly 100% recovery. Any other value for these parameters requires another distillation process or another preparation process. Even if the pH samples are

Table 1
Tritium based categorization of Groundwater Age (Clark et al., 1997; Zouari et al., 2003).

Groundwater Age (T.U.)	Categorization	Range (No. of samples; %)	
		Varahi river basin	Markandeya river basin
<1	Old (Pre-modern)	−	−
≥1	New (Modern)	−	−
1−8	Mixture of Old + New (Radioactive decay)	1.95−6.66 (14; 93.34)	1.49−8.45 (15; 93.75)
9−18	Recent with activities	11.35 (01; 6.66)	9.17 (01; 6.25)
19−>28	Thermonuclear with activities	−	−

around 7, the conductivity respects the above-specified conditions, there are some interferences in the measurement process that lead to different results for the same water sample prepared by the two methods. Hence, distillation procedure has to be repeated till the conductivity decreases to <10 μS/cm. A low background water sample and a reference sample have been prepared in the same way for each type of water. Another parameter, which influences the result, is the time to hold (viz., holding time) the samples in a dark and cooled place, which varied from 3 to 48 h during the study.

3.2.6. Tritium measurement

The spectrometer required a previous detection efficiency calibration as a function of the quenching, which was performed with ^{3}H standards of known activity subjected to different degrees of quenching with CCl$_4$, which must be renewed periodically (Baeza et al., 1996). Hence, a set of labelled samples (viz., low tritium content waters to be concentrated with the addition of any radioactive tracer) and background samples (viz., low tritium content waters to be concentrated without the addition of any radioactive tracer or tritium-free water) were also electrolyzed together with the groundwater samples whose tritium content has to be determined. Labeled samples will allow us to determine the yield of the electrolysis, while background samples have a twofold purpose: (1) as blanks to be subtracted from the labeled samples so as to correct for the small, but not zero tritium concentration present in the water with which they were prepared; and (2) as background to serve as a check for any possible contamination during the electrolytic concentration process (Florkowski, 1963). With each of these components − labeled samples, background samples, and the problem samples - vials were prepared for the liquid scintillation spectrometric determination of the ^{3}H content. The total counting/measurement time for each sample were about 1000 min (viz., twenty 50-min cycle per sample) between 0 and 18.6 keV energy windows.

To obtain the specific ^{3}H activity, C_s (T.U.) of the water referred to the day of collection of the sample, which was subsequently concentrated electrolytically prior to its assay, the following equations were used to calculate enrichment parameter and measurement yield:

The tritium concentration of the sample on counting date is calculated using the following equation by spikes method:

$$C_s = C_{st}\left(\frac{N_s}{N_{st}}\right)\left(\frac{1}{Z}\right) \quad (1)$$

where

C_s = the tritium concentration in TU of the sample C_{st} = the tritium concentration in TU of the standard.

N_s = the net count rate of the sample.

N_{st} = the net count rate of the standard.

Z = Tritium enrichment factor.

One TU (tritium unit) is 1 atom of tritium in 10^{18} atoms of hydrogen [i.e., 1 TU = 3.231 pCi/L (picocuries/L) or 0.12/0.118 Bq/L (becquerel per litre) of water] or 7.1/7.2 disintegration per minute per litre (dpm/L)/counts per minute per litre (cpm/L). One Becquerel (1 Bq) is one radioactive decay per second. Precautions were taken throughout the study to avoid contamination of samples from atmospheric tritium during storage, pre-distillation and post-distillation of samples.

3.2.7. Contour analysis

The contour analysis involved two-dimensional representation of three-dimensional data in the form of a contour map or iso-concentration map with the help of a surface mapping system, Surfur v. 9.0 (2010) Golden Software, Inc., using kriging gridding method. A contour map is a plot of three values, wherein the first two dimensions are the X, Y coordinates, and the third (Z) is represented by lines of equal value (the contour lines on the map) across the map extents. The shape/relative slope of the surface is shown by the relative spacing of the contour lines and the difference between two contour lines is defined as the contour interval. In the present study, the data collected on the tritium activity (Z), the type of sampling location (well or spring)
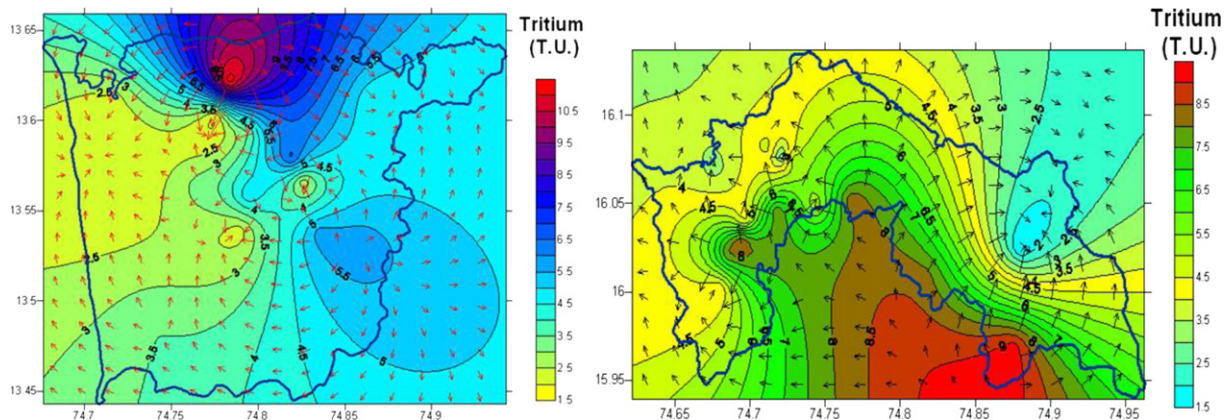

Fig. 2. Spatial distribution of Tritium content in the groundwater of Varahi and Markandeya river basins.
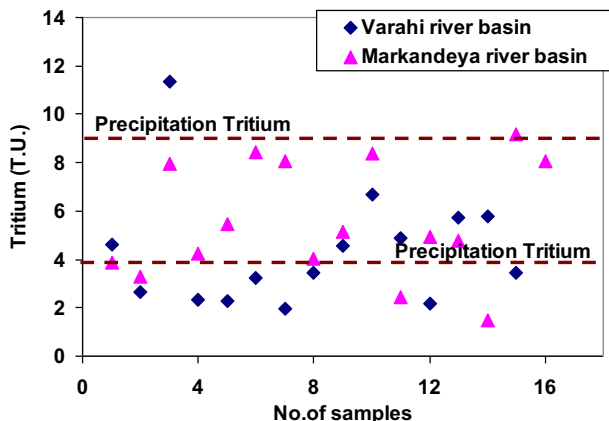
Fig. 3. Comparison between Tritium values in study area with present day precipitation tritium values.

and their geographical location or spatial coordinates (X, Y) from the field work were then transferred into a database that was hosted by a GIS platform for spatial analysis and data visualization to prepare distribution contour map.

4. Results and discussion

4.1. Chemistry of groundwater

In Varahi and Markandeya river basins, the pH values varied from 5.69 to 7.14 and 6.23 to 8.56 respectively, with 46.67% and 12.5% of the samples respectively from Varahi and Markandeya river basins showing pH values either below or above the permissible limit of 6.5–8.5 (BIS 1998). The electrical conductivity values ranged from 30.2 to 400 μS/cm and 345 to 3110 μS/cm in Varahi and Markandeya river basins respectively, with 6.25% of samples from Markandeya river basin crossed the permissible limit of 3000 μS/cm (BIS 1998).

Among cations, the calcium and magnesium concentration varied from 2.8 to 30.0 mg/L and 2.44 to 10.2 mg/L respectively in Varahi river basin and 36–240 mg/L and 14.64–124.4 mg/L respectively in Markandeya river basin. None of the samples from Varahi river basin crossed the BIS permissible limit of 200 mg/L and 100 mg/L respectively for calcium and magnesium While in Markandeya river basin, 12.5% of samples showed both calcium and magnesium concentration crossing the permissible limit.

Among anions, fluoride, nitrate and chlorides values varied from 0.04 to 0.2 mg/L, 0.2–2.0 mg/L and 4–44 mg/L respectively in Varahi river basin, well within their corresponding BIS (1998) and WHO (2004) permissible limit of 1.5 mg/L, 45 mg/L and 1000 mg/L respectively. In Markandeya river basin, fluoride, nitrate and chlorides values varied from 0.2 to 2.0 mg/L, 2.0–50 mg/L and 75–490 mg/L respectively, with 12.5% and 6.25% of the samples respectively showing higher fluoride and nitrate values above their permissible limit.

4.2. Tritium estimation

Tritium concentration alone generally cannot be used to quantitatively date groundwater, but can be used to qualitatively determine whether groundwater is modern (less than about 50 years in age) or pre-modern (older than about 50 years in age) (Clark et al., 1997). Tritium concentrations below 1 TU were considered to indicate that groundwater is at least 50 years old (pre-modern) and tritium values equal to or greater than 1 TU were considered as modern groundwater. Values of tritium of about 3 TU
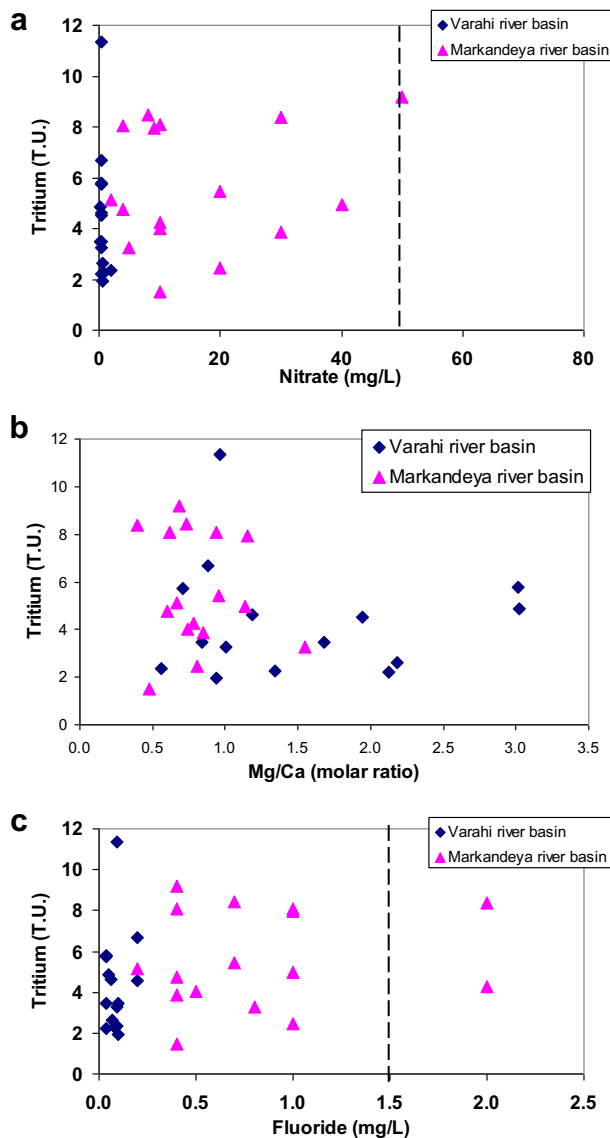

Fig. 4. Plots of Tritium concentrations for the groundwater from Varahi and Markandeya river basins against the following hydrochemical parameters (a) Nitrate concentration (mg/L) with the dotted line indicating the WHO MAC of 50 mg/L; (b) molar Mg/Ca ratio (c) Fluoride concentration (mg/L) with the dotted line representing WHO MAC of 1.5 mg/L

indicate a residence time of the water of about 30–40 years. Again modern age is classified depending on ^3H values wherein the ^3H values ranging from 1 to 8 TU could be attributed as an admixture of recent water with old groundwater and groundwater having been subjected to radioactive decay. Recent water possesses activities between 9 and 18 TU and thermonuclear water with activities between 19 and 28 TU (Table 1). Modern groundwater generally is more susceptible to contamination than old because of the many anthropogenic contaminants introduced during the 20th century (Plummer and Friedman, 1999). Thus, the high tritium content value of the water can be interpreted as being due to mixing phenomena between the 'old' water of the confined aquifer and the 'recent additions' from the hydrological channel network crossing the plain.

The recorded environmental ^3H content in 15 groundwater samples collected in the Varahi river basin varied from 1.95 ± 0.25 T.U. to 11.35 ± 0.44 T.U. with an average of

4.342 ± 0.34 T.U. Similarly, in the Markandeya river basin, the tritium values in the 16 groundwater samples varied from 1.49 ± 0.75 T.U. to 9.17 ± 1.13 T.U. with an average of 5.61 ± 0.84 T.U. The contour analysis was carried out to describe the spatial distribution of tritium concentration in the Varahi and Markandeya river basins (Fig. 2). On comparing these results with standard ^{3}H values given by Clark et al. (1997) and Zouari et al. (2003), it is evident that majority of the samples in Varahi (93.34%) and Markandeya (93.75%) river basins exhibited radioactive decay (1–8 T.U.) having a mixture of pre-modern (viz., old water) water mixed with modern (viz., new water) recharge or recent additions (Table 1). One sample each in Varahi (6.66%) and Markandeya (6.25%) river basins was clearly a modern (9–18 T.U.), recently recharged groundwater. Usually, natural tritium in precipitation varies from ~1 TU in oceanic high-precipitation regions to as high as 10 TU in arid inland areas. All samples from the study area lay

beyond the 1 T.U., indicative of modern water and this inference is in good agreement with the groundwater fluctuations. The Tritium contents of most of the groundwater samples from Varahi and Markandeya river basins are very similar to the present day precipitation tritium for Karnataka varying between 3.8 ± 08 T.U and 8.9 ± 0.2 T.U, indicating modern recharge (Fig. 3), significantly influenced by precipitation and river inflowing/seawater intrusion. In other words, the groundwaters gets recharged with modern rainfalls and have short circulation time in the ground (i.e., that the origin of the waters is meteoric and they have short travel time).

Tonosaki et al. (2000) studied Tritium concentrations of electrolytically enriched natural waters in Takahokonuma Lake which ranged from 0.6 to 1.5 Bq/L, while the tritium concentrations in rivers flowing into the lakes ranged from 0.7 to 2 Bq/L, both being higher than those of the precipitation values in Rokkasho-mura. Borio et al. (2005) investigated the tritium in drinking water in a region of central Italy (Umbria) and observed that the ^{3}H concentrations lower than the minimum detectable concentration activity (8.6 Bq/L) for every sampling site. Wen et al. (2005) recorded the age of groundwater between sub modern (1950s) and recent year recharges in Ejina basin, Northwestern China. Similarly Wen et al. (2008) recorded tritium values in Zhangye basin, Northwestern China varying from 21.55 to 36.62 T.U. for shallow groundwater (depth < 30 m), from 13.57 to 27.36 in groundwater (depth of 30–50 m), 10.11 to 16.76 TU in the samples (depth of 50–100 m) and 3.13 and 5.91 TU in the samples (depth > 100 m). Landstetter and Katzlberger (2009) conducted a study of ^{3}H in Austrian groundwater and drinking water and found that the values of the ^{3}H activity concentration in Austrian groundwater samples are within a range of the low-level detection (LLD) of 1.3 Bq/L and 2.8 Bq/L which corresponds to the natural activity concentration and are far below the 100 Bq/L limit.
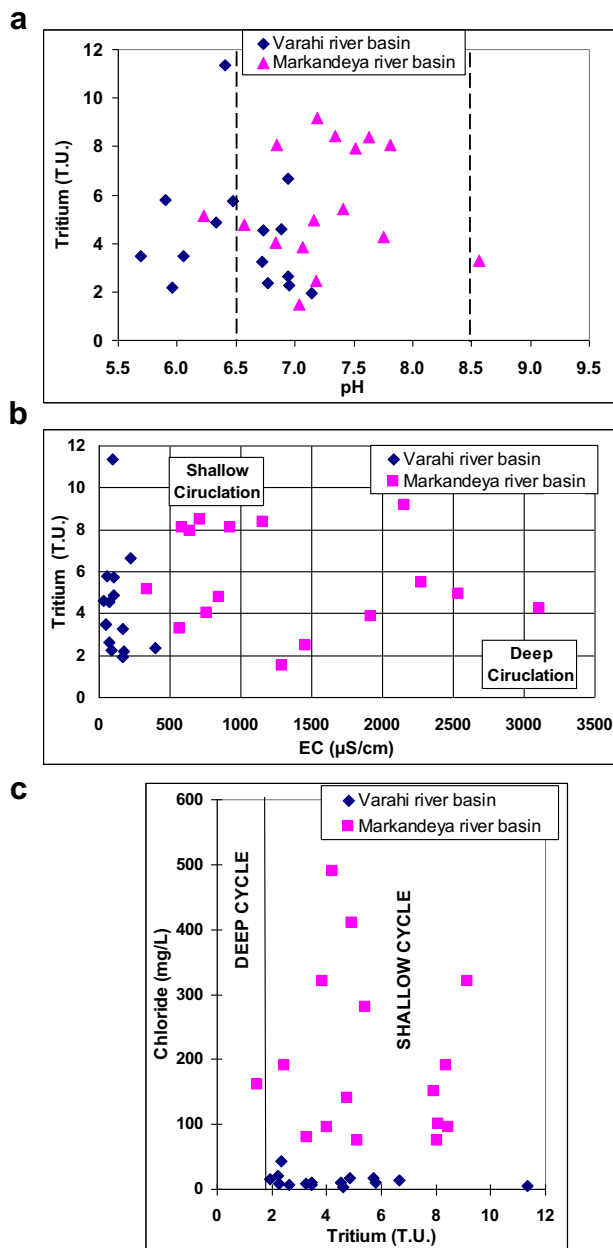
4.3. Plot of nitrate v/s tritium

Isotopes can suggest the source of high nitrate concentrations to an important groundwater supply and can demonstrate the irrigation return flow and pollution hazard in any region. The plot of tritium against nitrate concentrations (Fig. 4a) for the groundwater samples from the study area does not show any clear trend but highlights the fact that the sample with nitrate above the BIS MAC value of 45 mg/L are waters that are actually mixtures of fresh water (containing very high nitrate, possibly from agricultural fertilizers or a leaking cess pit) and older 'unpolluted' waters (containing low nitrate levels), strongly influenced by surface source, anthropogenic contamination with return flow (Verhagen, 2003). The groundwater with the lowest nitrate concentration are also the one with the lowest tritium level indicating that, although the groundwater source lies on agricultural land, it has not (yet) been contaminated by nitrate fertilizers (McNeill et al., 2003).

4.4. Relation between tritium and molar Mg/Ca ratio

The importance of groundwater reaction with dolomite within the study area can be highlighted by the plot of tritium against Mg/Ca molar ratios (Fig. 4b) that show increasing Mg relative to Ca with decreasing tritium (Ó Dochartaigh et al., 1999; McNeill et al., 2003). The relationship between tritium and Mg/Ca means that this chemical ratio could be used as a 'maturity indicator' for groundwater in any aquifer (Elliot et al., 1999). In the present study, some waters have high Mg/Ca ratios suggesting the influence of incongruent dissolution of a dolomite cement phase (Elliot et al., 1999), while some other does not follow this trend, indicating that dolomite is not abundant at those locations.

Fig. 5. Plots of Tritium concentrations for the groundwater from Varahi and Markandeya river basins against the following hydrochemical parameters (a) pH (b) SEC (i.e., Electrical conductivity, μS/cm); (c) Chloride concentration (mg/L).

4.5. Plot of fluoride v/s tritium

The plot of tritium against fluoride concentrations (Fig. 4c) for the groundwater samples from the study area highlights the fact that the majority of the samples had relatively low fluoride (WHO MAC < 1.5 mg/L) might be due to short time for water/rock inter-actions to occur, suggesting lesser contribution from geogenic sources and/or contaminated surface waters except for two samples from Markandeya river basin. The two samples with high fluoride (WHO MAC > 1.5 mg/L) in Markandeya river basin exhibited modern recharge suggesting much contribution from geogenic sources/weathering and/or contaminated surface water. In other words, the relationship between estimated recharge dates and fluoride concentrations for the selected samples shows that fluoride increases with increase in groundwater recharge date (Fantong et al., 2010).

4.6. Relationship between Tritium and pH

The plot of pH-Tritium indicated that majority of the samples fall under optimum pH range category (BIS MAC = 6.5–8.5), attributed to recharges with modern rainfalls neutralized with minerals present in soils and rocks (Fig. 5a) and have short circulation time in the ground. The samples showing acidic pH range can be attributed to dissolution of carbon dioxide in the atmosphere along with rain water forming carbonic acid (H_2CO_3), which enhances dissolving power of rainwater, devoid of minerals. Since rain water has no minerals, when rain (viz., modern recharge) falls down to the earth, its collects the environmental impurities along with minerals, dominated by alkaline components, particularly bicarbonates, carbonates and to a much lesser extent occasionally borates, sili-cates and phosphates of calcium and magnesium on its journey to the water table besides additions from geogenic origin.

4.7. Relation between tritium concentration and specific electrical conductivity (SEC)

The EC-Tritium graph (Fig. 5b) indicates the existence of groups with different origins, wherein the groups that have high EC and low tritium values represent the deep circulating waters and the groups with low EC and high tritium values are considered as shallow circulating waters. Differences appear between these two groups because the shallow circulating waters and deep circulating waters mix in different proportions (Günay, 2006) and low permeability or deep circulation, result in large residence time for groundwater. In Varahi river basin, majority of the samples were considered as shallow circulating waters, while samples from Markandeya river basin were found to be belong to both shallow and deep circulating waters. Tritium concentration had a negative correlation with salinity (viz., electrical conductivity/total dissolved solids) values at all sampling locations from Varahi (r = −0.209) and Markandeya (r = −0.159) river basins, confirming co-depen-dence between tritium and salinity values (Tonosaki et al., 2000). Increase in total dissolved solids with decreasing tritium levels reiterates that the groundwater is very young, and there is a component of the groundwater that has had more time to interact with the aquifer (i.e. relatively older). Tritium measurements in the low saline samples have shown that no quick flows occur from the recharge area and that the mean residence time of fresh ground-water is more than 50 years. All the samples from Varahi river basin had relatively low total dissolved solids (SEC < 500 μS/cm) might be due to short time for water/rock interactions to occur. In contrast, majority of the samples from Markandeya river basin had relatively higher total dissolved solids (SEC > 500 μS/cm) due to the longer time for water/rock interactions to occur (McNeill et al., 2003).

There were no samples with both high EC values and high Tritium activity (viz., no recent waters were salty).

4.8. Tritium/chloride relationship

Tritium/chloride relationship is also another method to separate shallow and deeply circulating water. In Varahi river basin, majority of samples are shallow circulating waters based on low chloride and low tritium values (Fig. 5c) while, the groundwater samples from Markandeya river basin belongs to both shallow and deep circulating waters (Çelmen and Çelik, 2009). Thus, it is evident that low permeability or deep circulation of groundwater can result in large residence time and short residence time in the ground will be due to high permeability or shallow circulation of groundwater.

5. Conclusion

In conclusion, the present study has shown the benefits of undertaking tritium analysis alongside hydrochemical analysis of groundwater samples, and has allowed for a better understanding of water quality issues affecting the important groundwater resource that lies under an area of intensive agricultural land use. Relationship between hydrochemical analyses with complemen-tary tritium analyses was attempted to understand the salinity, calcium, magnesium, fluoride, nitrate and chloride levels in terms of the relative age(s) of the groundwater contained within the study area (Ó Dochartaigh et al., 1999). High Mg/Ca ratios with decreasing tritium results suggested the influence of incongruent dissolution of a dolomite cement phase. EC-tritium and EC-chloride plots suggests that low permeability or deep circulation of groundwater can results in large residence time in ground and high permeability or shallow circulation of groundwater resulted in short residence time in the ground. There were no samples with both high EC values and high Tritium activity suggesting no recent waters were salty in nature. For groundwater resource manage-ment purposes, an indication of the age of groundwater at a particular borehole is useful for interpretation of water quality issues such as contaminations via high hardness, salinity, fluoride, nitrate, etc. Further, these data must be regarded as preliminary and further extensive studies should be done on large scale by initiating further detailed investigation of two river basins completely for tritium contamination, to increase awareness and mitigate possible hazards that are associated with exposure to tritium.

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