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Estimation of distribution coefficient of uranium in soil by batch tests

S Manoj[1] S Parimalarenganayaki[2] and L Elango[1]*
[1]Department of Geology, Anna University, Chennai 600025, India.
[2]Deparment of Environmental and Water Resources Engineering, School of Civil and Chemical Engineering, VIT University, Vellore 632 014, India.

Email: elango34@hotmail.com

Abstract. Sorption studies were performed to estimate the soil distribution coefficient (K_d). Since soil and groundwater are major controlling factors for the K_d value, it is important to determine the site specific K_d value. In this study, special emphasis has been given to soil and groundwater parameters which control the K_d value of uranium around the mineralized zone. Based on the analysis of soil sample, the distribution coefficient of uranium around the mineralized zone varies from 7 to 369 l/kg. It is also observed that distribution coefficient of uranium in this region not only depends on the individual parameter and it varies significantly with space. Increase and decrease in K_d value was observed when the pH ranges from 4 – 7 and 7 – 8.5 respectively which indicates that the increase in pH greater than 7 will reduce the K_d value. No significant correlation was observed between the K_d value and other parameters such as soil texture, $CaCO_3$, CEC and major ion concentration in groundwater. Determination of K_d value in a uranium mineralized zone will be used to predict and model the contaminant transport.

1. Introduction

Radionuclides are naturally present in igneous and sedimentary rocks. The mobilization of radionuclides from the mineralized zone occurred either due to weathering actions or due to mining and milling of radionuclides. These radionuclides present near the mineralized zone might get transported with the rain water and contaminate both surface and groundwater. Similarly, the natural geological material has the capacity to attenuate the potential pollutants. It, therefore, becomes important to assess the capacity of the geological material to arrest or release of radionuclides to the aquatic environment. Uranium is one such radionuclide with the mixture of ^{238}U, ^{235}U and ^{234}U isotopes. The average occurrence of uranium in the earth is about 2μg. The source rocks of uranium are mostly granite of igneous origin and sedimentary deposits like lignite, phosphate etc. Predicting the migration of uranium into the environment by means of geogenic or anthropogenic disposal scenarios requires various parameters. K_d is one such key parameter in the environmental assessment for predicting the interaction and transport of radionuclide in the soil (Maity et al. 2013).

K_d of soil was determined by various experimental techniques which include batch sorption test, column experiment, and field flow test (Kumar et al. 2015). The batch adsorption technique is widely used in the laboratory by assessing the soil capacity to remove the chemical content from an experimental solution. K_d value of uranium is affected by various physicochemical parameters of soil

and groundwater such as soil texture, pH, $CaCO_3$, cation exchange capacity (CEC) and water chemistry of the study region. Sheppard et al. (1989) reported that, variations in the soil and groundwater within a specific area might the major reason to obtain K_d values with more than five orders of magnitude. Hence, it becomes important to assess the site specific K_d value. In this study, the assessment of K_d value was carried out for the soil sample collected from one feet depth and the nearby groundwater samples around uranium mineralized Gogi region, Karnataka, India. Efforts have been made to estimate K_d value through batch experiment and effects on the controlling parameter over K_d value have been evaluated.

2. Methodology

2.1. Description of the study area

Gogi is a collective term given to a combination of two areas namely Gogipeth and Gogikona. The region falls in the Shahapur taluk which is one of the 3 taluks (Shorapur, Yadgir are the other two) and lies in the middle section of the Yadgir district, Karnataka, India with an average elevation of 428m msl (Figure 1). The area experiences semi-arid type of climate and the maximum temperature shoots up to 45ºC. The southwest monsoon during June to Septemberreceives 77% of the annual rainfall. The area has dendritic to the sub-dendritic type of drainage pattern, with Krishna and Bhima rivers constituting the two major river basins of the site. Black and lateritic soil are the dominant type of soil in all the regions (Yashodhara et al. 2011). Agriculture is a major activity that covers 75% of the district area.
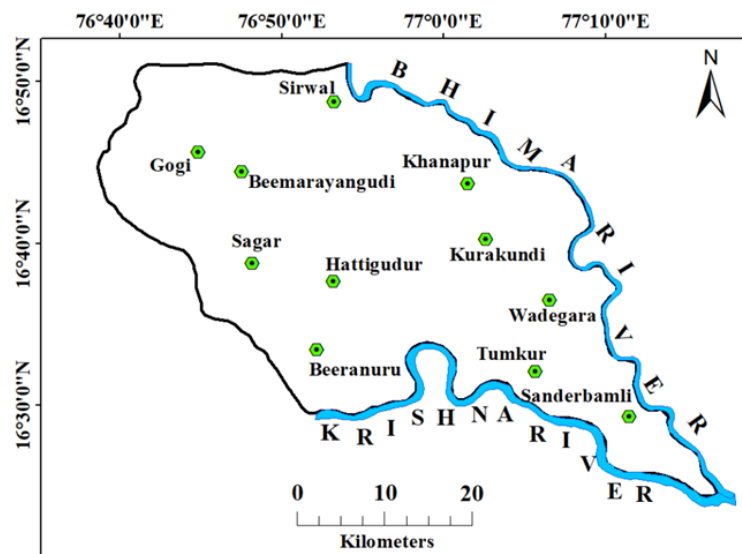

Figure 1. Study area

2.2. Soil and groundwater sampling

A total of 20 soil sample (Figure 2) were collected from one feet below the actual surface of the area and packed in a pre-treated polyethylene bags to prevent contamination. The samples were air dried and homogenized (<2mm) using sieve shaker. The Same soil sample was used for the estimation of particle size distribution, porosity, pH, electrical conductivity (EC), $CaCO_3$ and CEC. Samples that sieved to below 2mm size were selected for sorption experiment after homogenized. Percentage of sand, silt and clay present in the soil were determined by standard pipette technique. Soil bulk density

and particle density was estimated by wetting and drying of graduated cylinder method. Further, the porosity of the soil was assessed using particle density and bulk density. The pH of the soil was assessed by mixing a known weight of soil sample with water (ratio 1:1) (Kalra, 1995) and the mixture was measured using Eureka multi-parameter probe. Soil EC was determined by mixing water and soil which was allowed to stand for 30 min after the solution was measured using conductivity electrode (Rhoades, 1996). $CaCO_3$ was determined by acidimetry method by using 1N HCl and 0.5N NaOH as titrant (Bashour and Sayegh, 2007). CEC was estimated by extraction of water from the soil and analysing it for major cations. Calcium and magnesium were extracted from soil using neutral normal ammonium acetate and were determined by titration method by using phenolphthalein and methyl orange as indicator respectively (APHA, 1998). Sodium and potassium were also extracted using neutral normal ammonium acetate and then analyzed in a flame photometer (Schollenberger and Simon, 1945). CEC is determined by the summation of sodium, potassium, calcium, and magnesium ions and is represented in meq/100g of soil.

Groundwater samples were collected within a 10m distance from the soil sampling location. Groundwater level (m), pH and EC were measured using a water level indicator (Solinst 101) and portable digital meters (Eureka sub manta 2) respectively. Pre-cleaned bottles (1000ml capacity) were used to fill the groundwater samples. These bottles were soaked for 24 hours and washed a few times with distilled water. The bottles were rinsed three times with the water to be sampled. In the case of bore wells, the samples were collected after purging to collect the formation water. Collected groundwater samples were filtered using 0.45μ filter paper and analysed for major cations (sodium, potassium, calcium, and magnesium) and anions (sulphate, chloride and nitrate) using ion chromatograph (Metrohm 861 Advanced Compact IC) and uranium concentration by laser fluorimeter (Quantalase LF2a) in the laboratory. Bicarbonate and carbonate concentration of the sample was measured in the field using Alkalinity kit (Merck).
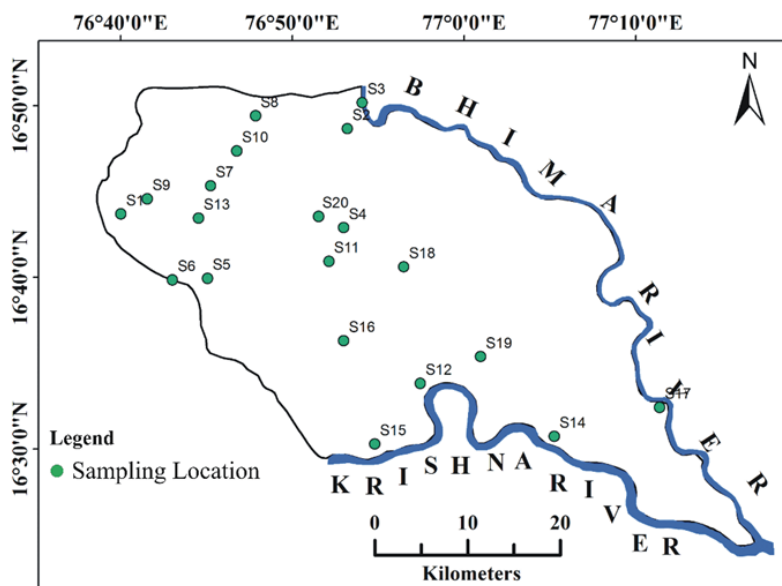

Figure 2. Sampling locations

2.3. Various methods for the determination K_d value

There are various methods to assess the K_d value including column method, field study and batch test. In the column method, groundwater containing the radionuclides is passed through the column packed with the soil and its concentration is measured. Infield based study the K_d value is measured by the

concentration of a radioactive element in soil and water. In batch technique, water containing the species of known composition and concentrations is mixed with a given mass of adsorbent for a given period of time the solution is then separated from the adsorbent and chemically analysed to determine changes in solute concentration. The solute adsorbed by the adsorbent is the difference between the initial concentration and the solute concentration after the mixing period. In this study, batch test was carried out to determine the K_d value.

3. Result and discussion

3.1. Determination of soil texture

Distribution of sand, silt and clay particles in the soil determines the soil texture. According to Wentworth scale, the size of sand (0.05 mm to 2 mm) silt (0.002 to 0.05 mm) and clay (below 0.002 mm) represent the soil particle size. Based on the soil texture, soil fertility was determined which influences the quantity of water retained in the soil. The dominant soil texture in this area is a mixture sand-silt-clay (Figure. 3).

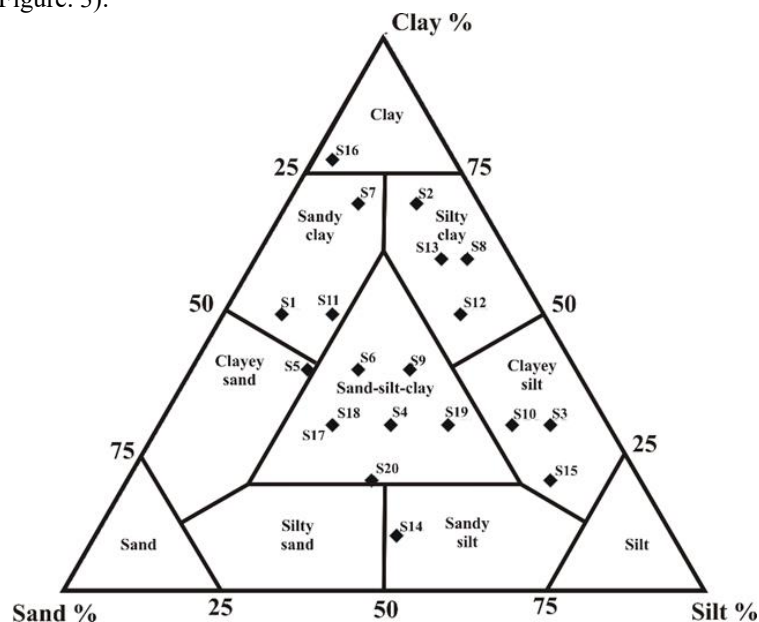Figure 3. Particle size distribution in soil

3.2. Calculation of porosity

Bulk density and particle density of the soil samples from the study area ranges from 1.03 g/cm^3 to 1.36 g/cm^3 with an average of 1.21 g/cm^3 and 1.8 to 2.7 g/cm^3 with an average of 2.3 g/cm^3 respectively (Figure 4). The porosity of the soil ranges from 36 to 53% (Table 4). The average value of the porosity of soil was 47%.
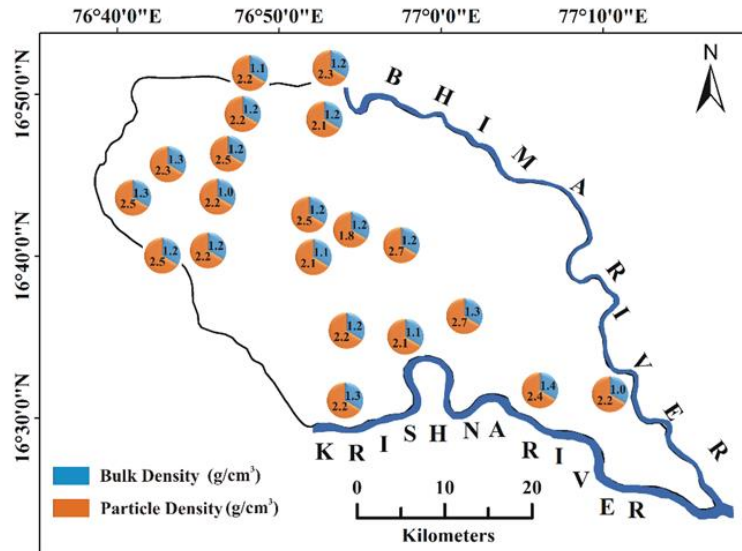
Figure 4. Spatial variation of bulk density and particle density of the soil

Table 1. Porosity of the soil sample

S. No	Location	Porosity (%)
S1	Ukkinal	50
S2	Sirwal	42
S3	Anabi	47
S4	Bevanalli	36
S5	Naganatkki	44
S6	Hoskerra	51
S7	Singhanalli	53
S8	Mudbal	51
S9	Dharshanapur	45
S10	Mudbal	44
S11	Benekalli	46
S12	Hayal	50
S13	Gogi	54
S14	Tumkur	42
S15	Kollur	40

S16	Hattigudur	47
S17	Machannor	52
S18	Tokkapur	53
S19	Aikoor	50
S20	Namdihalli	54

3.3. pH and EC of soil

pH is the measure of hydrogen ion activity in soil. The acidic or alkaline nature of soil determines the weathering of minerals. The pH of the soil can be altered due to intensive agriculture in an area. In this study region, pH varies from 4.09 to 8.63 with a mean of 7.29. Spatial variation of soil pH indicates acidic to slightly alkaline in nature (Figure 5).EC is a strong indication of the total amount of soluble salts that are present in the soil. Application of agrochemicals and intensive agriculture are the main source for the increase in salinity level in the soil. Excess evaporation and lesser rainfall will also increase the soil salinity level. These salts are essential for plant growth to some extent and may become harmful when it exceeds. The maximum EC measured in this region was 1875 µS/cm and the spatial variation of EC averages of 728 µS/cm and is non-saline.
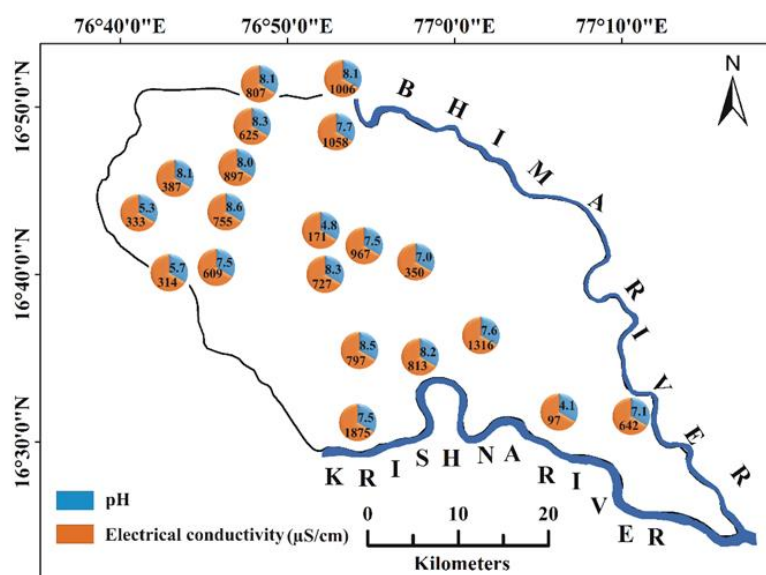
Figure 5. Spatial variation of Soil pH and electrical conductivity

3.4. Calcium carbonate

$CaCO_3$ is another important characteristic of soil which is a measure of the carbonate (calcium and magnesium) present in the soil. The quality of soil classified based on calcium carbonate percentage (Brindha and Elango, 2014) is shown in Table 2.

Table 2. Classification of soil based on $CaCO_3$ %

S. No.	Classification	Range	No. of Sample
1	Low	0 – 2.5	-

2	Moderate	2.5 – 5.0	1
3	High	5.0 - 10	9
4	Very high	>10%	10

3.5. Cation Exchange Capacity

CEC is the ability of the soil to adsorb cations in exchangeable forms (Chesworth,2008). CEC is highly depending on soil texture, increase in CEC results in retaining more nutrients than a plant would normally need in a year. The CEC of soil in the study area is categorized based on the rating (Table 3).

Table 3. Ratings for CEC of soil sample

S. No.	Rating	CEC (meq/100g)	
		Range (Brindha and Elango 2014)	No. of Sample
1.	Very Low	<6	1
2.	Low	6-12	6
3.	Moderate	12-25	2
4.	High	25-40	3
5.	Very high	>40	8

3.6. Hydrogeochemistry of groundwater

The concentration of major cations and anions in groundwater samples collected nearby to the soil sample location is shown in Table 4. Based on the hydrogeochemical analysis, the quality of groundwater is good except in few locations.

Table 4. Hydrogeochemistry of groundwater

S. No	Major ion (mg/l)	Minimum	Maximum	Average
1.	Calcium	38	380	92
2.	Magnesium	6	116	43
3.	Sodium	37	2258	386
4.	Potassium	1	13	5
5.	Bicarbonate	26	2757	444
6.	Chloride	209	799	436
7.	Sulphate	5	425	64
8.	Nitrate	9	496	120

3.7. Site specific distribution co-efficient

From the 20 soil samples, 5 g from each sample was weighed and placed in 20 conical flasks and covered with a rubber cork. In addition to the weighed soil samples, 30 mL of the nearby groundwater,

spiked with the uranium standard, was added. In addition, a blank experiment was carried out by placing diluted solutions in tubes without any soil and the soil with the spiked distilled water solution. Each tube was subsequently placed on a rotary shaker for 72 hours (3 days) at 30 rpm in room temperature to attain equilibrium. After 72 hours, the mixture (soil and groundwater) was transferred to falcon tubes and centrifuged 2000 rpm. The supernatant was transferred to new tubes and analysed for uranium concentration using Laser fluorimeter. The K_d value of uranium around Gogi uranium mineralised region varies from 7 to 369 l/kg.

3.8. Effects of soil and groundwater parameters over distribution coefficient of uranium
K_d of uranium is much dependent on soil and groundwater parameters. Hence estimation of site specific K_d is much important for migration study. The K_d increase with pH from 5 and it is very high with the pH of 8. Further, K_d decreases with increasing pH. In this region, it was observed that the decreasing trend of increase in pH of 7. The relation between the soil parameters and K_d value shows poor correlation except for clay and silt which shows moderate correlation (Table 5). Similarly, poor correlation was observed between the geochemistry of groundwater (solute) and K_d value (Table 6).

Table 5. Correlation between various soil parameters and K_d value

	pH (Soil)	EC (Soil)	U (Soil)	Porosity	Clay %	Sand %	Silt %	CaCO$_3$%	CEC	TDS (GW)	K_d
pH (Soil)	1.00										
EC (Soil)	0.60	1.00									
U (Soil)	0.59	0.44	1.00								
Porosity	-0.03	-0.32	0.14	1.00							
Clay %	0.56	0.08	0.65	0.26	1.00						
Sand %	-0.74	-0.65	-0.75	0.03	-0.49	1.00					
Silt %	-0.07	0.39	-0.16	-0.31	-0.75	-0.21	1.00				
CaCO$_3$%	0.48	0.34	0.47	0.12	0.65	-0.51	-0.34	1.00			
CEC	0.73	0.63	0.72	-0.08	0.55	-0.97	0.12	0.53	1.00		
TDS (GW)	0.42	0.37	0.35	-0.13	0.44	-0.48	-0.13	0.22	0.54	1.00	
K_d	-0.15	-0.26	-0.13	0.16	0.48	0.21	-0.70	0.22	-0.20	0.13	1.00

Table 6. Correlation between various groundwater parameters and K_d value

	Ca	Mg	Na	K	Cl	HCO_3	NO_3	SO_4	K_d
Ca	1.00								
Mg	0.82	1.00							
Na	0.93	0.84	1.00						
K	-0.04	0.18	-0.22	1.00					
Cl	0.94	0.83	1.00	-0.24	1.00				
HCO_3	0.72	0.88	0.74	0.26	0.70	1.00			
NO_3	0.98	0.76	0.89	-0.02	0.89	0.64	1.00		
SO_4	0.93	0.92	0.96	-0.05	0.95	0.86	0.88	1.00	
K_d	0.18	-0.20	0.18	-0.35	0.19	-0.27	0.28	0.05	1.00

4. Conclusion

The K_d of uranium varies from 7 to 369 l/kg in soil samples collected around Gogi mineralised region. The K_d of uranium varies depending on the soil parameters, the major ion concentration of groundwater and its distribution is highly varied with space. Increase and decrease in K_d value was observed when the pH ranges from 4 – 7 and 7 – 8.5, indicates the increase in pH greater than 7 will reduce the K_d value. No significant correlation was observed between the K_d value and other parameters such as soil texture, $CaCO_3$, CEC, concentration of major ions in groundwater. The K_d value determined in a uranium mineralized zone will be used to predict and model the contaminant transport.

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