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the time of collection and U–Th separation. This was done using the formula

\[ A_0 = (A_i - A_0(1 - e^{-\lambda t}))e^{\lambda t} \]  

(1)

where \( A_0 \) is the inherent \(^{234}\text{Th}\) activity of the sample on the date of collection; \( A_i \), its activity measured on the date of U–Th separation; \( A_0 \) is the \(^{238}\text{U}\) activity, \( t \) is the time period between the sample collection and U-Th separation and \( \lambda \) is the \(^{234}\text{Th}\) decay constant. These corrected \(^{234}\text{Th}\) activities are given in Table 1. The uncertainties in the \(^{234}\text{Th}\) concentrations given in Table 1 include errors arising from the estimation of the slope of the best fit line, the chemical efficiency and \(^{238}\text{U}\) concentrations. Additional uncertainties due to calibration of beta detectors and the variation of its efficiency with time is less than ±10%.

The uncertainties given in the \(^{222}\text{Rn}\) concentration is sum of one sigma errors in counting statistics and calibration of detectors.

The \(^{210}\text{Pb}\) activity levels of the sample were low. None of the samples exhibited unambiguous growth of \(^{210}\text{Bi}\). Hence the \(^{210}\text{Pb}\) concentrations were calculated by assuming that the net activities of the samples (after about one month growth period) is wholly due to \(^{210}\text{Bi}\). The uncertainties given in Table 2 include those arising from the estimation of net sample counting rates and corrections for reagent and carrier blanks. In most samples the calculated \(^{210}\text{Bi}\) activity levels were nearly as same lead carrier blanks.

**DISCUSSION**

\(^{238}\text{U}\) and \(^{234}\text{U}/^{238}\text{U}\)

The \(^{238}\text{U}\) concentrations in the samples range between 2.3 and 16.2 dpm/l, with relatively higher values in the tube well samples collected near the vicinity of Ahmedabad. The high uranium concentration in these waters make them a possible source for its commercial extraction. It can be estimated from the uranium concentration (15 ppb, Table 1; see also SOMAYAJULU et al., 1979) and the consumption of groundwater (3 x 10^9 l/day, GUPTA, personal communication) that on an average it should be possible to extract 1–2 tons of uranium annually from regions adjacent to Ahmedabad city.

The \(^{234}\text{U}/^{238}\text{U}\) activity ratios do not show major variations, they range between 1.24 ± 0.05 and 1.61 ± 0.09. In the tube well samples from regions near Ahmedabad, the \(^{234}\text{U}/^{238}\text{U}\) activity ratios seem to show a decreasing trend with increasing \(^{238}\text{U}\) concentrations. COVERT and OSMOND (1974) also have observed similar inverse correlation between \(^{234}\text{U}/^{238}\text{U}\) activity ratios and \(^{238}\text{U}\) concentrations in aquifers from Southern Texas. They attributed this finding to changes in the oxidising/reducing conditions of the aquifer environment, with high \(^{238}\text{U}\) and low \(^{234}\text{U}/^{238}\text{U}\) in the oxidising zones and low \(^{238}\text{U}\) and high \(^{234}\text{U}/^{238}\text{U}\) in the reducing zone. They also suggested the source of the high \(^{234}\text{U}\) excess in

the reducing zone to be recoil injection of \(^{234}\text{Th}\). In this work, we have not made measurements of any typical diagnostic tracers which could characterise the oxidising/reducing nature of the aquifers. However, if we can infer from the relatively high \(^{234}\text{U}\) concentrations (several ppb, Table 1) then the aquifers sampled do not seem to be from reducing environments. Also, as will be discussed in a later section, \(^{234}\text{Th}\) recoil and its subsequent in situ decay does not appear to be the cause for the high \(^{234}\text{U}/^{238}\text{U}\) ratios in these aquifers. Another possible explanation for the inverse trend in the \(^{234}\text{U}/^{238}\text{U}\) vs \(^{238}\text{U}\) would be variations in the degree of weathering of subsurface soil grains; more intense weathering would result in relatively higher \(^{238}\text{U}\) concentrations in the water with \(^{234}\text{U}/^{238}\text{U}\) activity ratios closer to secular equilibrium value.

\(^{234}\text{Th}/^{238}\text{U}\) ratios

The \(^{234}\text{Th}\) concentrations in all the water samples analysed is far less than that would be expected from its in situ production in the water through the radioactive decay of dissolved \(^{238}\text{U}\). The \(^{234}\text{Th}/^{238}\text{U}\) activity ratios in the samples range between 0.00 to 0.18 (Fig. 1) with a mean of about 0.04. Our result that \(^{234}\text{Th}\) activities in the water are deficient relative to their parent \(^{238}\text{U}\) is contrary to the data of KIGOSHI (1973) who reported large excess of \(^{234}\text{Th}\) (\(^{234}\text{Th}/^{238}\text{U}\) activity ratio 3.8–39) in Tokyo groundwaters. The cause for the disagreement between the two studies is difficult to judge because of the meagre supplementary information available about them. It is unlikely that the gross deficiency of \(^{234}\text{Th}\) we have observed is due to laboratory effects since we processed unfiltered and acidified samples. Therefore we can only speculate that the water chemistry, mineralogical and particle characteristics of aquifer soils and

![Fig. 1. Histogram showing the frequency distribution of the \(^{234}\text{Th}/^{238}\text{U}\) activity ratios vs the number of samples analysed. As evident \(^{234}\text{Th}\) activity in the aqueous phase is far less than that would be expected through its production from the in situ decay of its parent \(^{238}\text{U}\).](image-url)
filtration of fine sediments by the aquifer may play a prominent role in regulating the concentration of $^{234}$Th in them.

The extremely low abundance of $^{234}$Th relative to its parent $^{238}$U in the groundwater of Gujarat is ascribable to its fast removal onto particle surfaces, a process which is common in coastal and surface sea waters for the removal of Th isotopes (Bhat et al., 1969; Broecker et al., 1973; Matsumoto, 1975). The scavenging residence time of $^{234}$Th in these aquifers can be calculated using a simple box model approach. Assuming steady state between production and removal, the equation governing the distribution of $^{234}$Th is given by

$$C_p/r_p = C_d/r_d + \psi$$  

where $C$ is the concentration (atoms/l), $r$ is the radioactive decay constant and $\psi$ is the first order scavenging rate constant. The subscripts $p$ and $d$ refer to parent ($^{238}$U) and daughter ($^{234}$Th) nuclides respectively. Rearranging eqn (2) and substituting 34.8 days for the mean life of $^{234}$Th, the scavenging residence time $\tau$ is given by:

$$\tau = 34.8 \left[ R/(1-R) \right]$$

where $R$ is the $^{234}$Th/$^{238}$U activity ratio in the groundwaters. Using a mean value of 0.04 for $R$, the value of $\tau$ is estimated to be about 1.5 days. The calculated scavenging residence time could be an upper limit since in the model we have considered only one source of injection of $^{234}$Th into the waters, viz its in situ production from dissolved $^{238}$U. Additional sources such as its ejection from surrounding soil grains through alpha recoil processes (Kigoshi, 1971; Fleischer and Raabe, 1978) if exist would also tend to decrease the calculated residence times.

The short residence time of $^{234}$Th in these Gujarat aquifers implies that almost all the $^{234}$Th introduced into the water through its in situ production (and also from other sources, such as recoil from soil grains) is removed onto particles in a very short time compared to its radioactive half life. Such as fast removal of $^{234}$Th on to particles in these ground waters rules out the possibility of the build up of $^{234}$U in solution through the in situ radioactive decay of $^{234}$Th. The natural questions which arise now are (1) what is the fate of $^{234}$U produced on the surface of the soil grains through the decay of $^{234}$Th and (2) if this $^{234}$U is leachable, then can it account for its observed excess in these aquifers? The paucity of data on soil characteristics and its uranium concentration precludes us from drawing any definite conclusions. However, model calculation (Kigoshi, 1971) using assumed values for various parameters show that in these Gujarat aquifers the 'recoil borne' $^{234}$U forms only a minor fraction (~1%) of its total abundance. Using eqn (1) of Kigoshi (1971), the rate of supply of recoil $^{234}$Th into the solution is calculated to be 1.8 atom/l water·min. for $L = 550$, $S = 40$ cm $^2$/g, $\rho = 2.5$ g/cm $^3$, 3 ppm $^{238}$U concentration in the soils and a porosity of 30%. The uncorrected $^{14}$C ages of two groundwater studies are 6000-7000 yr (Gupta, personal communication), and those of the others are also expected to be in similar range since they are all confined aquifers from nearby locations. The build up of $^{234}$U during 7000 yr (neglecting its decay) is only about 0.03 dpm/l much less than the $^{234}$U excess in the samples 0.8-6.3 dpm/l. Therefore in these aquifers the excess $^{234}$U has to be attributed to some other mechanism, a possible one being its preferential leaching (Rosholt et al., 1963). If leaching is the mechanism for the high $^{234}$U/$^{238}$U activity ratios (Table 1) then the application of this ratio to date groundwaters (Kigoshi, 1973) would be limited, since it would be difficult to substantiate the involved assumptions.

$^{222}$Rn–$^{210}$Pb ratios

The $^{222}$Rn concentrations in the samples range between 227–875 dpm/l (Table 2). In samples from PRL tube wells several repeat measurements were carried out over a period of 2–3 months; the average of these repeat measurements are given in Table 2. The $^{222}$Rn concentrations in repeat measurements were in good agreement with each other, within statistical uncertainties. This suggests that the sampling and extraction procedure for $^{222}$Rn is reproducible and that short term variations in the $^{222}$Rn concentration in these aquifers, if any, are small.

The $^{222}$Rn concentrations are about three orders of magnitude higher than the activity levels of its parent $^{220}$Ra (Table 2), a result similar to those noted earlier at many locations (Mazor, 1962; Tanner, 1964; Andrews and Wood, 1972). The large excess of $^{222}$Rn is well known to be due to its diffusion and transport through porous soil grains into the aqueous phase.

It is instructive to calculate the release of $^{222}$Rn into the atmosphere through industrial and domestic consumption of groundwaters. In Ahmedabad area, the release would correspond to $2.1 \times 10^{11}$ dpm/day (using an average $^{222}$Rn concentration of 694 dpm/l and a water consumption rate of 3 × 10$^8$ l/day) compared to the emanation rate of $7.4 \times 10^{12}$ dpm/day of $^{222}$Rn from soil layers (calculated using 0.7 atoms/cm$^2$ sec as $^{222}$Rn emanation rate and 96 km$^2$ for the area of Ahmedabad). This comparison shows that, for Ahmedabad, the industrial and domestic consumption of ground waters form only a minor auxiliary source of $^{222}$Rn to the atmosphere.

The $^{210}$Pb concentrations in the water samples range between 0.0–0.14 dpm/l (Table 2) and are very low compared to the activity levels of its parent $^{222}$Rn. The $^{210}$Pb concentrations are expected to be in radioactive secular equilibrium with its parent, $^{222}$Rn, provided (i) the aquifer behaves as a closed system for the $^{222}$Rn–$^{210}$Pb system and (ii) the waters are older than about 100 yr. As mentioned earlier, the ages of these waters are expected to be several thousands of years. In such a case, the gross deficiency of $^{210}$Pb relative to $^{222}$Rn has to be attributed to the
U-238 series radioactive disequilibrium in groundwaters: implications to the origin of excess U-234 and fate of reactive pollutants

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(Received 16 November 1979; accepted in revised form 17 April 1980)

Abstract—The concentrations of $^{238}$U, $^{234}$Th, $^{226}$Ra, $^{222}$Rn and $^{210}$Pb and $^{224}$U/$^{238}$U activity ratios have been measured in several groundwater samples from Gujarat, India. In the aqueous phase the abundances of $^{234}$Th and $^{210}$Pb are grossly deficient relative to their parents, $^{238}$U and $^{222}$Rn respectively. The deficiency is ascribable to the impact adsorption of $^{234}$Th and $^{210}$Pb atoms onto particle surfaces which are very abundant in the groundwater regimes. The scavenging residence times for both these nuclides is about a day, suggesting that irreversible removal of 'reactive' metals and pollutants in groundwaters can occur on very short time scales. The fast removal of $^{234}$Th onto particles necessitates that in these groundwaters $^{234}$U 'excess' has to originate through leaching of soil grains rather than through in situ decay of dissolved $^{234}$Th in the water.

INTRODUCTION

The existence of radioactive disequilibrium between U-238 and its granddaughter U-234 in groundwaters is well known (Osmond and Cowart, 1976). The extent of this disequilibrium has been used to trace water masses and to estimate mixing volumes between various aquifers. Recently Kigoshi (1973) using a simple model has explored the possibility of using $^{234}$U/$^{238}$U disequilibrium in groundwaters to date them. This model assumes that the U-234 excess in groundwaters arises primarily through direct transfer of recoil Th-234 atoms across the solid/liquid phase boundary. Thus through a measurement of the concentrations of U-238, Th-234 and U-234 in the water it becomes possible to deduce the flux of excess U-234 into the aquifer and hence its age. Based on this model Kigoshi (1973) obtained ages for two aquifers and the results were consistent with radiocarbon dates. Also, as expected from the model, these aquifers had large excess of Th-234 compared to its parent U-238 thereby substantiating the recoil theory (Kigoshi, 1971) for the origin of U-234 excess in groundwaters.

We have extended some of these studies to the groundwater systems in Gujarat. Our results on the distributions of $^{238}$U/$^{234}$Th/$^{224}$U isotopes differ markedly from that of Kigoshi (1973). Such a discrepancy prompted us to measure the distribution of another activie daughter-passive parent system, $^{210}$Pb/$^{222}$Rn to understand the behaviour of reactive elements in groundwaters. The results of these measurements are discussed in this paper.

SAMPLE COLLECTION AND ANALYSIS

All the samples analysed (Table 1) except those from Rakhial and Thaltej are from confined aquifers and were collected from tube wells. Samples from Rakhial and Thaltej are from open wells, however, even in these cases water was collected from tubes used to pump up water to the surface. To minimize losses due to adsorption samples were taken as close to their natural source as possible and the pump was run for 5-10 min to flush the pipe lines before collection.

For U isotopes, $^{228}$Th and $^{210}$Pb measurements about 201 of water was collected directly in polyethylene containers and acidified with HNO$_3$ to pH ~2 within minutes. From this, an aliquot of 1-2 l was removed for uranium isotope measurements. To the rest, $^{230}$Th tracer and Pb carrier (equivalent to 60 mg PbSO$_4$) was added, stirred and allowed to equilibrate for several hours. The Th and Pb isotopes were coprecipitated with Fe(OH)$_3$ and radiochemically purified using conventional ion exchange methods (Krishnaswami and Sarin, 1976). In all samples $^{230}$Th was separated from U-238 within two days of collection. Uranium isotopes were measured in the 1-2 l aliquots after adding U-232 as yield tracer. The water samples were dried and uranium isotopes were separated from the residue and purified following the procedure of Krishnaswami and Sarin (1976). The purified U and Th fractions were electrodeposited on platinum planchets and their activities assayed as follows: The beta activity of $^{234}$Th was determined by counting its daughter $^{234}$Pa in a circular 2n geometry Geiger counter. The samples were counted with an absorber of 6 mg/cm$^2$ thickness to cut off alpha activities of $^{230}$Th. The net $^{234}$Th activities on the day of first counting (within about 4 days of sample collection) ranged between 2 and 9 cpm. Most of the samples were counted at regular intervals to ascertain purity of $^{234}$Th by decay curve analysis. The alpha activities of both Th and U planchets were assayed using an alpha spectrometer.

Lead was deposited as PbSO$_4$ and its activity measured by following the ingrowth of its daughter $^{210}$Bi using a low background gas flow Geiger counter (Lal and Schink, 1960). For $^{222}$Rn measurements, about 500 ml of water sample was drawn directly into previously evacuated purging bottles. (These samples were also collected along with those used for U-Th-Pb isotope measurements) These bottles were than connected to an extraction system and radon stripped and assayed following the techniques described by Bhat et al. (1974). The radon activities were usually determined within a few hours of sample collection. The radon samples counting rates were several hundred counts per
Tables 1 and 2. The 238 U concentrations were calcu­
lated from the measured 210 Pb and 222 Rn and counted by the previously described techniques.

The concentrations (dpm/kg) of 234 Th from 226 Ra. The regenerated 222 Rn was extracted and counted by the previously described techniques.

RESULTS

The concentrations (dpm/kg) of 238 U, 234 Th, 222 Rn and 210 Pb and 234 U/238 U activity ratios are given in Tables 1 and 2. The 238 U concentrations were calculated from the measured 234 Th/238 U counting ratios and the absolute concentration of 238 U. The errors quoted in Table 1 for 238 U concentrations are one sigma uncertainties due to counting statistics. (Errors arising from uncertainties in the 234 Th absolute concentrations have not been included, the magnitude of this is determined to be ±2.5%.; SARIN, personal communication)

The 234 Th concentrations (dpm/kg) on the date of 238 U-234 Th separation were first calculated from its counting rate on that date. This counting rate was deduced from the slope of the best fit line of the gross activity of the samples (2.68)C between 0.3-0.5 cpm. In some of the samples 226 Ra measurements were also made. For this, the water samples after 211 Rn were also made. For this, the water samples after 211 Rn from 126 Ra. The regenerated 222 Rn was extracted and counted by the previously described techniques.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Location</th>
<th>(Depth, m)</th>
<th>238 U</th>
<th>234 Th</th>
<th>234 U/238 U</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW-5</td>
<td>PRL Bore-1, terrace (210)</td>
<td>14.9 ± 0.5</td>
<td>(2.68)C</td>
<td>1.42 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>GW-8</td>
<td>PRL Bore-2 Lawns (120)</td>
<td>16.2 ± 0.6</td>
<td>0.37 ± 0.12</td>
<td>1.39 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>GN-10</td>
<td>Guj. Univ. Bore-1 (190)</td>
<td>12.4 ± 0.5</td>
<td>0.57 ± 0.16</td>
<td>1.41 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>GN-12</td>
<td>Guj. Univ. Ladies Hostel (210)</td>
<td>31.8 ± 0.5</td>
<td>0.21 ± 0.1</td>
<td>1.47 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>GN-15</td>
<td>Dudheshwar N.W. Bore-3 (190)</td>
<td>10.5 ± 0.4</td>
<td>0.27 ± 0.06</td>
<td>1.52 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>GN-16</td>
<td>Dudheshwar N.W. Bore-5 (200)</td>
<td>8.8 ± 0.3</td>
<td>0.34 ± 0.05</td>
<td>1.57 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>GW-20</td>
<td>Jupiter Mills bore-1 (200)</td>
<td>9.1 ± 0.3</td>
<td>0.4 ± 0.12</td>
<td>1.49 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>GW-22</td>
<td>Jupiter Mills Bore-2 (200)</td>
<td>8.5 ± 0.3</td>
<td>0.86 ± 0.14</td>
<td>1.48 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>GW-24</td>
<td>Pallej Village (155)</td>
<td>2.6 ± 0.1</td>
<td>0.09 ± 0.03</td>
<td>1.35 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>GN-26</td>
<td>Karzan village (100)</td>
<td>2.3 ± 0.1</td>
<td>0.14 ± 0.04</td>
<td>1.61 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>GW-28</td>
<td>Madhubagh Bore-2 (200)</td>
<td>12.4 ± 0.5</td>
<td>0.9 ± 0.09</td>
<td>1.31 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>GN-30</td>
<td>Madhubagh Bore-1 (200)</td>
<td>12.5 ± 0.5</td>
<td>0.08 ± 0.15</td>
<td>1.35 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>GW-47</td>
<td>Rakhiyai (open well)</td>
<td>15.0 ± 0.5</td>
<td>0.08 ± 0.1</td>
<td>1.27 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>GW-49</td>
<td>Thaltej (open well)</td>
<td>3.4 ± 0.2</td>
<td>0.11 ± 0.04</td>
<td>1.24 ± 0.05</td>
<td></td>
</tr>
</tbody>
</table>

* All samples except those from Pallej and Karzan villages are from regions within about 10 kms of Ahmedabad city. Pallej and Karzan samples are from Broach district.

The numbers given are the maximum bore depths. Water is usually trapped below about 40 m in Broach.

This number may have large uncertainty because of poor chemical yield.

Table 2. 226 Ra, 222 Rn and 210 Pb concentrations in Gujarat ground waters

<table>
<thead>
<tr>
<th>Sample code</th>
<th>226 Ra</th>
<th>222 Rn</th>
<th>210 Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW-5</td>
<td>735 ± 28 (2)</td>
<td>0.08 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>GW-8</td>
<td>750 ± 50 (5)</td>
<td>0.01 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>GN-10</td>
<td>875 ± 19</td>
<td>0.00 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>GN-12</td>
<td>227 ± 5</td>
<td>0.01 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>GN-15</td>
<td>3.24 ± 0.31</td>
<td>660 ± 14</td>
<td>0.05 ± 0.04</td>
</tr>
<tr>
<td>GN-16</td>
<td>0.51 ± 0.13</td>
<td>569 ± 12</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td>GN-20</td>
<td>910 ± 20</td>
<td>0.05 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>GN-22</td>
<td>492 ± 11</td>
<td>0.07 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>GN-24</td>
<td>0.08 ± 0.06</td>
<td>293 ± 6</td>
<td>0.01 ± 0.03</td>
</tr>
<tr>
<td>GN-26</td>
<td>0.53 ± 0.15</td>
<td>289 ± 6</td>
<td>0.05 ± 0.03</td>
</tr>
<tr>
<td>GN-28</td>
<td>796 ± 17</td>
<td>0.02 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>GN-30</td>
<td>825 ± 18</td>
<td>0.02 ± 0.03</td>
<td></td>
</tr>
</tbody>
</table>

* Numbers in parentheses represent the number of repeat measurements. The repeat measurements were done using fresh samples collected several days apart.
removal of $^{210}\text{Pb}$ from the aqueous phase, probably on to mineral grains, a process analogous to that proposed for the removal of $^{234}\text{Th}$. The scavenging residence time for $^{210}\text{Pb}$ can be calculated using relation (3) (after replacing 34.8 days by 7 x day ratio) The average $^{210}\text{Pb}/^{222}\text{Rn}$ activity ratio of $7 \times 10^{-5}$ yield a scavenging residence time of about a day (It is implicit in this calculation that the short lived precursors of $^{210}\text{Pb}$ ($^{214}\text{Po}$, $^{214}\text{Bi}$ and $^{214}\text{Pb}$) are in equilibrium with $^{222}\text{Rn}$. It is possible that such an assumption may not be valid, and that the removal processes may be significant even for such short lived nuclides. Experiments are in progress to study the $^{214}\text{Po}$--$^{222}\text{Rn}$ distribution in these waters. The computed short residence time for $^{210}\text{Pb}$ in these groundwaters is similar to that estimated by BENNINGER et al. (1975) for well waters of Illinois based on $^{210}\text{Pb}/^{226}\text{Ra}$ ratios in them.

The deduced scavenging residence times of $^{234}\text{Th}$ and $^{210}\text{Pb}$ are very short and suggest that these isotopes are removed from solution phase to particles within a time period of few days. much less than their radioactive half lives. The behaviour of these elements in groundwaters helps us to predict that the residence time of other similarly reactive trace metals and pollutants in ground water is only of the order of days. Like in many other fields of earth sciences, these nuclides have proved to be ideal tracers to study the rates of removal processes of reactive pollutants in subsurface waters.

Acknowledgements—We thank SHRI A. H. PATEL and Dr S. K. GUPTA for providing us with depth and ages of the aquifers sampled. Permission and help provided by the various organizations for collecting the samples is thankfully acknowledged. Financial support for this work, in part, was provided by a grant from the Department of Science and Technology to the Physical Research Laboratory. The comments from three reviewers, Dr J. K. OSMOND, Dr W. M. SACKETT and Dr K. K. TUREKIAN were constructive and helpful.

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The behaviour of short-lived radiogenic lead isotopes ($^{214}$Pb and $^{212}$Pb) in groundwaters and laboratory leaching experiments

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Received October 9, 1981
Revised version received February 12, 1982

The concentrations of $^{214}$Pb (half-life = 26.4 minutes) and $^{222}$Rn (half-life = 3.84 days) have been measured in deep groundwaters of Gujarat, India. The results show that the abundance of $^{214}$Pb in the water is only ~25% of that expected from its production through the radioactive decay of dissolved $^{222}$Rn. This deficiency, if modelled in terms of a first-order removal, yields a residence time of ~10 minutes for $^{214}$Pb in these waters. The estimated residence time for $^{214}$Pb is the shortest observed for any nuclide in natural water systems and suggests that reactive nuclides like lead could be removed from aqueous phases to adjoining solid surfaces on extremely short time scales. Results of laboratory experiments using the $^{212}$Pb-$^{224}$Ra pair are compatible with the observed fast removal rate of $^{214}$Pb from groundwaters.

Re-evaluation of $^{234}$Th residence times in these waters using a model with a recoil flux of $^{234}$Th into the aqueous phase, the same as that of $^{222}$Rn, yields values in the range of 23 to <176 minutes, very similar to that of $^{214}$Pb. This “concordancy” in the residence times seems to suggest that the geochemical behaviour of $^{234}$Th and $^{214}$Pb in these waters is quite similar.

1. Introduction

During our studies on the $^{226}$Ra-$^{222}$Rn-$^{210}$Pb abundances in groundwaters of Gujarat, India, we observed [1] that the concentration of $^{210}$Pb (half-life = 22.3 years) in all the samples were considerably lower than that expected from its in-situ production from $^{222}$Rn. The $^{210}$Pb/$^{222}$Rn activity ratio yielded a residence time of ~1 day for lead relative to adsorption on solid surfaces of the aquifer.

In this paper we report measurements of $^{214}$Pb (half-life = 26.4 minutes) in some of these aquifers of Gujarat. These data permit a better understanding of the behaviour of lead and possibly other reactive species in groundwater systems. Further substantiation of these properties of lead were made through laboratory experiments using monazite and the $^{224}$Ra (half-life = 3.64 days)–$^{212}$Pb (half-life = 10.6 hours) couple.

2. Experimental techniques

2.1. Field sampling and processing for $^{214}$Pb and $^{222}$Rn

Studies on the extent of radioactive equilibrium between $^{214}$Pb and its progenitor $^{222}$Rn in groundwaters require a separation of these nuclides from each other within minutes after sample collection and rapid assay of the separated $^{214}$Pb, conditions imposed by the short half-life of $^{214}$Pb (26.4 minutes). This restricts the sampling sites to aquifers which are close to the laboratory. For the determination of in-situ $^{214}$Pb concentrations 2–5 liters of water were used. Concentrated HNO$_3$ (to bring the pH of water to <1), Pb (equivalent to ~30 mg PbCrO$_4$), and Fe carriers were added to the water samples within a minute after collection. The acidified and spiked water was stirred and helium gas bubbled through it for about 2–3
minutes to expel dissolved $^{222}$Rn. This entire operation was done at the sampling site within about 4-5 minutes of sampling and the water was brought to the laboratory for further processing. In the laboratory Pb was coprecipitated with Fe(OH)$_3$. The Fe(OH)$_3$ precipitate containing lead was dissolved in glacial acetic acid, warmed (centrifuged to separate SiO$_2$, if any), and lead was precipitated as PbCrO$_4$ for beta assay of $^{214}$Pb. $^{222}$Rn concentrations were measured by two techniques: (1) by the conventional gas stripping of $^{222}$Rn and its alpha assay [2] from ~1 liter of water, and (2) by milking its granddaughter, $^{214}$Pb, several hours after collection, followed by its ($^{214}$Pb) beta assay. For this measurement water samples of ~2 liters were drawn directly into evacuated radon purge flasks containing ~30 mg Pb carrier and ~10 ml 3-4N HNO$_3$. The samples after collection were kept sealed (without He purging step) for periods of 6-12 hours for the ingrowth of $^{214}$Pb from $^{222}$Rn. They were milked following the same procedure used for the in-situ $^{214}$Pb measurements. Details of the experimental techniques are discussed elsewhere (Hussain, thesis in preparation). The PbCrO$_4$ samples were deposited on plexiglas holders and counted in low-background (0.2 counts per minute) gas-flow Geiger counters [3]. The samples were counted with a 17 mg/cm$^2$ absorber to cut off alpha particles. The beta activities of samples ranged between 40 and 90 counts per minute at the time of first counting for the in-situ $^{214}$Pb samples and centered around 200 counts per minute for the $^{214}$Pb samples milked from $^{222}$Rn. The first counting was usually within 30-40 minutes after $^{214}$Pb/$^{222}$Rn separation. The beta activity of the samples was monitored every five minutes for 2-3 hours to ascertain the purity of $^{214}$Pb through decay curve analysis.

2. Laboratory experiments with monazite: measurement of $^{212}$Pb and $^{224}$Ra

Laboratory experiments to determine the behaviour of $^{212}$Pb relative to its ancestor $^{224}$Ra (members of the $^{232}$Th decay chain) in aqueous systems were performed using monazite sand (from Florida, Wards mineral collection) and groundwater samples. Two samples of one gram each of finely powdered monazite sand was prepared. (These were prepared separately and hence may have different grain size and surface area/gram.) One was dispersed in ~100 ml of dilute HNO$_3$ (pH 2-3) and the other in ~100 ml groundwater from PRL Bore-1 (pH ~ 7.4), each for definite intervals of time. At the end of the desired time interval the nitric acid and groundwater leaches were separated from the monazite and the same monazite sand was redispersed in fresh aliquots of the respective leachants for different intervals of time. The nitric acid and groundwater leaches were analyzed for the abundances of Th isotopes, $^{224}$Ra and $^{212}$Pb. The details of the experimental procedures will appear in Hussain’s thesis (in preparation). Briefly, the leaches were split into two fractions, one for Th isotopes and the other for $^{224}$Ra and $^{212}$Pb. For the latter, Pb (~60 mg equivalent of PbSO$_4$) and Fe carriers were added and allowed to equilibrate for about 15 minutes. The $^{212}$Pb was separated from $^{224}$Ra by coprecipitation with Fe(OH)$_3$, within about 40 minutes of separation of the leaches from monazite sand. The filtrate containing $^{224}$Ra was acidified immediately and its concentration was determined by milking its progeny, $^{212}$Pb. The milking was done after a growth period of about 20 hours. The lead samples were purified by ion-exchange chromatography, deposited as PbSO$_4$ and assayed for its beta activity in a low-background gas-glow Geiger counter [3]. The beta activity of the samples was monitored at hourly intervals for about 20 hours. The sample counting rates after four hours after $^{212}$Pb-$^{212}$Bi separation ranged between 1.5 and 25 cpm, the low count rates being typical of in-situ $^{212}$Pb samples. The Th isotopes were separated from the leach and assayed following the procedure of Krishnaswami and Sarin [4]. The Th isotopes were measured to determine the production rate of $^{224}$Ra from dissolved $^{228}$Th and to assess the role of dissolution of monazite.

3. Results

3.1. Groundwater $^{214}$Pb/$^{222}$Rn data

The $^{214}$Pb and $^{222}$Rn concentrations in the groundwater samples analyzed along with their
major cation and anion compositions are given in Table I. For calculating the $^{214}$Pb concentrations, we first computed the $^{214}$Pb activity at the time of $^{214}$Pb-$^{214}$Bi separation. This was done by correcting the beta counting data of the PbCrO$_4$ samples for contributions from $^{214}$Bi (growing in from $^{214}$Pb) using the relation:

$$A(t) = \lambda_1 N_1^0 \left[ e^{-\lambda_1 t} \frac{\lambda_2}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \right]$$  (1)

where $A(t)$ is the beta activity of the PbCrO$_4$ samples at time $t$ after $^{214}$Pb-$^{214}$Bi separation, $\lambda_1$ and $\lambda_2$ are the radioactive decay constants of $^{214}$Pb and $^{214}$Bi and $\lambda_1 N_1^0$ is the $^{214}$Pb activity at the time of $^{214}$Pb-$^{214}$Bi separation. In our experiments we have assumed that the PbCrO$_4$ at the time of precipitation is free of $^{214}$Bi and hence the $\lambda_1 N_1^0$ corresponds to the $^{214}$Pb activity at the PbCrO$_4$ precipitation. Since the beta activities of PbCrO$_4$ samples were monitored every five minutes over a period of 2-3 hours, several $A(t)$ data points are available for each sample. For each of these $A(t)$ data, a $\lambda_1 N_1^0$ value was calculated separately and from these $\lambda_1 N_1^0$ values, a weighted mean $\lambda_1 N_1^0$ for the sample and an error on the mean was computed using standard statistical methods [5, equations (5-6) and (5-10)]. (The weighting factor used was $1/\sigma^2$, $\sigma^2$ being the variance due to counting statistics). From the weighted mean $\lambda_1 N_1^0$ and a knowledge of the parameters such as the decay of $^{214}$Pb between the time of He bubbling and PbCrO$_4$ precipitation and chemical and counting efficiencies, the $^{214}$Pb concentrations (Table I) in the samples were calculated. A similar procedure was followed to compute the $^{222}$Rn concentrations from the observed $^{214}$Pb counting rates. Details of these calculations are discussed elsewhere (Hussain, thesis in preparation). The errors in the $^{214}$Pb and $^{222}$Rn concentrations given in Table I include uncertainties arising from the estimation of the mean $\lambda_1 N_1^0$ and the determinations of chemical ($\pm 3\%$) and counting ($\pm 3\%$) efficiencies.

In Table I, the concentrations of $^{222}$Rn measured by the conventional gas stripping and alpha assay are also given. Comparison of the $^{222}$Rn concentrations measured by the two methods (Table I) show that the $^{222}$Rn concentrations measured by alpha assay are about 20% higher than those obtained by the $^{214}$Pb method. This trend is expected since the $^{222}$Rn concentrations derived from $^{214}$Pb measurements are uncorrected for self and external absorption of $^{214}$Pb and $^{214}$Bi beta particles. The relative concentrations of $^{214}$Pb and $^{222}$Rn which are of major importance in the interpretation of the results are not expected to be affected by this correction, since both these isotopes were measured using identical techniques and had very similar chemical yields. The satisfactory agreement in the $^{214}$Pb/$^{222}$Rn activity ratio for a repeat measurement of PRL-Bore I (Table I) lends further credence to the above contention.

In addition to the errors discussed above, the estimates of $\lambda_1 N_1^0$ (equation (1)) are susceptible to two other sources of uncertainties. These are (1) in the in situ $^{214}$Pb samples the $^{222}$Rn expulsion may not be quantitative due to the short bubbling period, and (2) the assumption that the $^{214}$Pb was free of $^{214}$Bi at the time of PbCrO$_4$ precipitation may not be valid. Both these effects would result in an overestimation of the $\lambda_1 N_1^0$ values. It is difficult to speculate on the significance of these uncertainties on the $^{214}$Pb and $^{222}$Rn (measured via $^{214}$Pb) concentrations given in Table I. However, the observations that for each sample the calculated $\lambda_1 N_1^0$ values for the various $A(t)$ data points are very similar and that the $^{222}$Rn concentrations measured by $^{214}$Pb and alpha-scintillation methods are in satisfactory agreement seem to indicate that the magnitude of these uncertainties, if any, is small.

The results of leaching experiments are given in Table 2 and Figs. 1 and 2. The $^{232}$Th concentration in the leach is significantly lower than that of $^{224}$Ra, suggesting that the source of $^{224}$Ra to leach is not due to congruent dissolution of the monazite grains. The nature of $^{224}$Ra activity vs.-time curve (Fig. 1) resembles a typical radioactive growth curve with a constant flux of $^{224}$Ra to the aqueous phase and its radioactive decay. A similar trend is also apparent for the groundwater leach (Table 2). However, in this case two of our data points (GWM-4 and GWM-7; Table 2) deviate considerably from the trend set by the rest of the measurements. The cause for the low $^{224}$Ra activity in these two samples is unknown. The $^{212}$Pb con-
### TABLE I

$^{214}$Pb, $^{222}$Rn concentrations and chemical composition of Gujarat groundwaters

<table>
<thead>
<tr>
<th>Code</th>
<th>Location</th>
<th>Well depth (m)</th>
<th>Activity (dpm/kg)</th>
<th>$^{214}$Pb</th>
<th>$^{222}$Rn a</th>
<th>$^{222}$Rn b</th>
<th>$^{214}$Pb/$^{222}$Rn activity ratio c</th>
<th>Chemical composition (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$^{222}$Rn b</td>
<td>$^{222}$Rn b</td>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>GW(50–53)</td>
<td>PRL Bore-1</td>
<td>210</td>
<td>167 ± 8</td>
<td>719 ± 31</td>
<td>668 ± 29</td>
<td>790 ± 18</td>
<td>0.24 ± 0.02</td>
<td>-</td>
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<tr>
<td></td>
<td></td>
<td>mean</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>694 ± 31</td>
</tr>
<tr>
<td>GW(54–59)</td>
<td>PRL Bore-1</td>
<td>210</td>
<td>124 ± 6</td>
<td>617 ± 27</td>
<td>736 ± 32</td>
<td>-</td>
<td>0.18 ± 0.02</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>mean</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>677 ± 60</td>
</tr>
<tr>
<td>GW(64–69)</td>
<td>PRL Bore-2</td>
<td>120</td>
<td>82.3 ± 4</td>
<td>598 ± 26</td>
<td>547 ± 24</td>
<td>711 ± 16</td>
<td>0.15 ± 0.01</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>mean</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>568 ± 26</td>
</tr>
<tr>
<td>GW(70–74)</td>
<td>IIM Bore-1</td>
<td>220</td>
<td>135 ± 7</td>
<td>524 ± 23</td>
<td>604 ± 18</td>
<td>604 ± 18</td>
<td>0.26 ± 0.02</td>
<td>58</td>
</tr>
<tr>
<td>GW(75–80)</td>
<td>Guj Univ Bore-1</td>
<td>190</td>
<td>187 ± 8</td>
<td>625 ± 27</td>
<td>781 ± 22</td>
<td>781 ± 22</td>
<td>0.30 ± 0.02</td>
<td>58</td>
</tr>
<tr>
<td>GW(81–85)</td>
<td>ATIRA Bore-1</td>
<td>210</td>
<td>217 ± 10</td>
<td>796 ± 34</td>
<td>1005 ± 24</td>
<td>1005 ± 24</td>
<td>0.27 ± 0.02</td>
<td>65</td>
</tr>
</tbody>
</table>

* Measured by beta counting. In samples GW(50–53), (54–59) and (64–69) $^{222}$Rn concentrations were measured in duplicate. These values and their mean are given.

b Measured by stripping and alpha assay of $^{222}$Rn.

c Calculated using the $^{214}$Pb and $^{222}$Rn measured by the beta counting method.
TABLE 2
Results of monazite leaching experiments

<table>
<thead>
<tr>
<th>Code</th>
<th>Period of contact (hours)</th>
<th>Activity in solution phase (dpm)</th>
<th>Activity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>212Pb</td>
<td>224Ra</td>
</tr>
<tr>
<td>Dilute HNO3 (pH~2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ME-8</td>
<td>12.8</td>
<td>14.7±1.4</td>
<td>15.8±1.6</td>
</tr>
<tr>
<td>ME-9</td>
<td>28.2</td>
<td>17.7±0.8</td>
<td>24.5±1.3</td>
</tr>
<tr>
<td>ME-10</td>
<td>48.0</td>
<td>26.2±1.1</td>
<td>36.5±1.8</td>
</tr>
<tr>
<td>ME-11</td>
<td>92.0</td>
<td>39.6±1.6</td>
<td>57.2±2.3</td>
</tr>
<tr>
<td>ME-12</td>
<td>143.0</td>
<td>50.9±2.2</td>
<td>66.7±2.8</td>
</tr>
<tr>
<td>ME-13</td>
<td>258.8</td>
<td>60.1±3.1</td>
<td>93.3±3.6</td>
</tr>
<tr>
<td>PRL groundwater (pH~7.4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GWM-1</td>
<td>20.3</td>
<td>2.1±0.19</td>
<td>5.0±0.67</td>
</tr>
<tr>
<td>GWM-2</td>
<td>45.3</td>
<td>3.5±0.46</td>
<td>15.5±0.61</td>
</tr>
<tr>
<td>GWM-3</td>
<td>96.2</td>
<td>4.3±0.46</td>
<td>22.4±1.7</td>
</tr>
<tr>
<td>GWM-4</td>
<td>142.7</td>
<td>3.0±0.29</td>
<td>21.5±1.0</td>
</tr>
<tr>
<td>GWM-6</td>
<td>168.5</td>
<td>4.5±0.42</td>
<td>38.7±1.6</td>
</tr>
<tr>
<td>GWM-5</td>
<td>257.2</td>
<td>5.0±0.32</td>
<td>44.7±2.1</td>
</tr>
<tr>
<td>GWM-7</td>
<td>480.3</td>
<td>3.5±0.45</td>
<td>18.2±1.0</td>
</tr>
</tbody>
</table>

* The 212Pb and 224Ra activity levels given are calculated from the total beta activity of the lead sulphate deposits after appropriate corrections for contributions from 212Bi, 208Tl betas and 212Po and 212Bi alphas (Hussain, thesis in preparation). Thorium activities are based on the alpha spectrometric analysis.

Fig. 1. The 224Ra activity in the monazite leaches plotted against $[1-e^{-\lambda_{224}}]$. The straight line trend of the data suggests that the 224Ra activity in the solution phase is consistent with a model of constant supply and removal through radioactive decay. GWM-4 and GWM-7 are not plotted.

Fig. 2. The 212Pb/224Ra activity ratios in the monazite leaches as a function of the period of contact. The activity ratio in the groundwater leach is significantly lower than that in the nitric acid leach. This reinforces the hypothesis that lead isotopes are removed from solution phase to solid surfaces in groundwater media in very short time scales.
centrations in the dilute HNO₃ leach approaches that of ²²⁴Ra, with ²¹²Pb/²²⁴Ra activity ratios 0.65–0.93. The ²¹²Pb concentration in the groundwater leach is far less than that of ²²⁴Ra, and is closer to that of ²³²Th (Table 2).

4. Discussion

4.1. The residence time of ²¹⁴Pb in groundwaters

The ²¹⁴Pb concentrations in all samples analyzed are significantly lower than that expected from its in-situ production in the water through the decay of ²²²Rn. The ²¹⁴Pb/²²²Rn activity ratios in the samples (Table 1) range between 0.15 and 0.30 with a mean of 0.23. It is unlikely that the observed ²¹⁴Pb deficiencies are due to laboratory effects (e.g. adsorption on filters, sampling bottles) since we processed unfiltered and acidified samples for both ²¹⁴Pb and ²²²Rn and followed identical chemical and counting procedures for the determination of each nuclide. A more serious concern is the possibility of adsorption loss of ²¹⁴Pb on the metal pipes of the tube wells. It is difficult to assess the significance of adsorption on metal pipes on the measured ²¹⁴Pb deficiencies in the waters sampled, but we believe the effect would be small since prior to each sample collection the pumps were run for several minutes to flush the tubes. These considerations lead us to believe that in these waters the ²¹⁴Pb deficiency most likely is the result of adsorption on to the surfaces composing the aquifer.

The residence time of ²¹⁴Pb in these waters relative to adsorption can be calculated from the relationship:

\[ P + \lambda_p N_p = (\lambda_d + \psi) N_d \] (2)

where \( \lambda_p N_p \) is the in-situ production rate of ²¹⁴Pb in the water through the radioactive decay of its parent ²¹⁸Po, \( \lambda_d \) and \( \psi \) are the radioactive decay constant of ²¹⁴Pb and its removal rate constant from the aqueous phase. Since ²¹⁴Pb is an alpha decay product a finite recoil flux of ²¹⁴Pb into the aqueous phase from the aquifer rocks would be expected. This flux is termed as \( P \) in equation (2).

In this work we have not measured the distribution of ²¹⁸Po in these waters and hence we have used the concentration of its parent, ²²²Rn for \( \lambda_p N_p \) in equation (2). Implicit in this substitution is the assumption of radioactive equilibrium between ²²²Rn and ²¹⁸Po in the waters. The validity of this assumption is uncertain, however, the very short half-life of ²¹⁸Po (3 minutes) leads us to believe that the assumption most likely would be valid. Rearranging equation (2) yields for the residence time, \( \tau_P \):

\[ \tau_P = \frac{R \tau_\lambda}{[(P/\lambda_p N_p) + 1 - R]} \] (3)

where \( R \) is the activity ratio \( \lambda_d N_d / \lambda_p N_p \) (i.e. ²¹⁴Pb/²²²Rn) in the water, \( \tau_\lambda \) is the radioactive mean-life of ²¹⁴Pb (38.1 minutes). Calculation of \( \tau_P \) requires a knowledge of \( P \), the recoil flux of ²¹⁴Pb. We have considered two cases for the calculation of \( \tau_P \) from the ²¹⁴Pb/²²²Rn results: (1) \( P = 0 \), i.e. no recoil flux of ²¹⁴Pb to the groundwater, and (2) \( P = \lambda_{Rn} N_{Rn} \). This case is based on the assumption that ²²²Rn in subsurface waters is predominantly of recoil origin [6,7]. In waters which are older than a few weeks, the ²²²Rn concentration would be in steady state with respect to its supply and radioactive decay and hence its activity in the waters would be a direct measure of the recoil flux. From the recoil flux of ²²²Rn, it is possible to calculate the flux of ²¹⁴Pb if information on the behavior of ²¹⁸Po is available [7]. Since data on these parameters are lacking, we have assumed as a first approximation the recoil flux of ²¹⁴Pb to be the same as that of ²²²Rn [7]. For ²¹⁴Pb/²²²Rn activity ratios in the range of 0.15–0.30 (Table 1) the \( \tau_P \) values range between 7 and 16 for case (1) and between 3 and 7 minutes for case (2). These residence times are the shortest observed for any nuclide in natural waters.

It is instructive to compare the ²¹⁴Pb residence times with those of ²¹⁰Pb and ²³⁴Th measured in the same aquifers. Of the five wells analyzed for ²¹⁴Pb, we had measured ²¹⁰Pb and ²³⁴Th in three of them (PRL Bore-1 and -2 and Guj Univ Bore-1, Table 1) in our earlier work [1]. In Table 3 we present the comparison of the residence times for ²¹⁴Pb, ²¹⁰Pb and ²³⁴Th (for \( P = 0 \) and \( P = \lambda_{Rn} N_{Rn} \)) in these three aquifers. Although the residence times
time of lead based on $^{210}\text{Pb}/^{222}\text{Rn}$ ratios is higher than the values based on $^{214}\text{Pb}/^{222}\text{Rn}$ ratios (Table 3), the large experimental uncertainties associated with $^{210}\text{Pb}$ measurements do not allow any distinction to be made with any significance. The extremely short residence time of lead based on $^{214}\text{Pb}$ would require $^{210}\text{Pb}/^{222}\text{Rn}$ activity ratios to be $<10^{-6}$ in groundwaters if the lead isotopes are adsorbed onto particles irreversibly. More precise data on $^{210}\text{Pb}$ would be required to check whether the adsorption of lead is reversible and thereby predict the behaviour of lead in groundwaters on longer time scales.

Benninger et al. [8] calculated the residence time of lead in deep groundwaters of Illinois to be of the order of a month based on the $^{210}\text{Pb}$ data of Holtzman [9]. This value is most likely an upper limit because it has been calculated based on $^{210}\text{Pb}/^{226}\text{Ra}$ ratios rather than $^{210}\text{Pb}/^{222}\text{Rn}$ ratios. As the $^{222}\text{Rn}$ concentrations in groundwaters are 100–1000 times greater than $^{226}\text{Ra}$, the lead residence time based on $^{210}\text{Pb}/^{222}\text{Rn}$ ratios would be 100–1000 times shorter than that derived from $^{210}\text{Pb}/^{226}\text{Ra}$ ratios. Further, in these samples, the measured $^{210}\text{Pb}$ concentrations are probably an overestimation of in-situ $^{210}\text{Pb}$ [9]. In these samples $^{210}\text{Pb}$ measurements were made two or more weeks after sample collection [9], which could yield much higher $^{210}\text{Pb}$ concentrations than its in-situ values because of the decay of dissolved $^{222}\text{Rn}$ to $^{210}\text{Pb}$ during storage if the $^{222}\text{Rn}$ concentrations are as high as implied above. The magnitude of increase in the $^{210}\text{Pb}$ concentrations would depend upon the initial $^{222}\text{Rn}$ concentration, time delay between sample collection and analysis and the $^{222}\text{Rn}$ retentivity of the storage bottles.

The residence time of $^{234}\text{Th}$ in these three aquifers would be several orders of magnitude larger than that of $^{214}\text{Pb}$ (Table 3) if the supply of $^{234}\text{Th}$ to the waters is only through the in-situ radioactive decay of $^{238}\text{U}$ in the waters. This seems unlikely since $^{234}\text{Th}$ is an alpha decay product, and a major fraction of its flux to waters is expected to be through its recoil across the solid-liquid boundary [10]. If we assume that the recoil flux of $^{234}\text{Th}$ is the same as that of $^{222}\text{Rn}$ [7], then the residence of both $^{234}\text{Th}$ and $^{214}\text{Pb}$ seem to converge to values close to each other, of the order of a few minutes (Table 3). Major uncertainty in obtaining reliable values of residence times of these nuclides in groundwaters is that associated with the estimation of their input fluxes. Hence better estimates of the nuclide residence times await a detailed study of the mechanism of injection of U-Th series nuclides in groundwaters and their relative fluxes.

The near "concordancy" in the residence times of these two nuclides, if established, would suggest the rate constants for their removal from the aqueous phase is quite similar. It is likely that in subsurface aquifers, because of their very high solid/solution ratio, the removal process of

---

**TABLE 3**

Residence times of $^{214}\text{Pb}$, $^{210}\text{Pb}$ and $^{234}\text{Th}$ in Gujarat groundwaters

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Isotope ratios</th>
<th>Residence time (minutes) $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{214}\text{Pb}/^{222}\text{Rn}$ $^b$</td>
<td>$^{210}\text{Pb}/^{222}\text{Rn}$ $^c$</td>
</tr>
<tr>
<td>PRL Bore-1</td>
<td>0.24±0.02</td>
<td>(1.07±0.54)×10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>(5±0.4)</td>
<td>(905±450)</td>
</tr>
<tr>
<td>PRL Bore-2</td>
<td>0.15±0.01</td>
<td>(0.13±0.52)×10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>(3±0.2)</td>
<td>(110±440)</td>
</tr>
<tr>
<td>Guj Univ Bore-1</td>
<td>0.30±0.02</td>
<td>(0.0±0.34)×10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>(7±0.5)</td>
<td>(0.0±285)</td>
</tr>
</tbody>
</table>

$^a$ Two numbers are given: the top number for $P=0$ (no recoil flux) and the number in parenthesis for $P=\lambda_{\text{Rn}}/N_{\text{Rn}}$.  
$^b$ From Table 1.  
$^c$ From Hussain and Krishnaswami [1].
nuclides like Pb and Th, to a first approximation is independent of their chemistry. Further, if the recoil flux of $^{234}\text{Th}$ is similar to that of $^{222}\text{Rn}$, then this flux can constitute a significant source of $^{234}\text{U}$ to these waters. The magnitude of this source would depend upon the behaviour of $^{234}\text{Th}$ in the waters and the mobility of $^{234}\text{U}$ produced from adsorbed $^{234}\text{Th}$ on aquifer solid surfaces.

4.2. The behaviour of $^{212}\text{Pb}$ in the laboratory replication of groundwater processes

The results in Table 2 and Fig. 2 permit us to derive information on the relative behaviour of $^{212}\text{Pb}$ in dilute $\text{HN0}_3$ and groundwater media. The acidic environment would most closely resemble a low adsorption system. For all growth periods, the $^{212}\text{Pb}/^{224}\text{Ra}$ activity ratio in the groundwater leach is far less than the corresponding values in the dilute $\text{HN0}_3$ leach, a result consistent with the known behaviour of Pb isotopes in natural waters. The $^{212}\text{Pb}/^{224}\text{Ra}$ activity ratios of $0.11 \pm 0.01$ and $0.2 \pm 0.03$ for growth periods 258 and 480 hours, respectively (Table 2) yield box-model residence times (equation (3), $P = 0$) in the range of about 2–4 hours for $^{212}\text{Pb}$ in the groundwater leach for our laboratory experiment. These results suggest that $^{212}\text{Pb}$ is removed from aqueous phases to monazite sand grains on short time scales, analogous to the observed behaviour of $^{214}\text{Pb}$ in Gujarat groundwaters. However, the calculated residence times for $^{212}\text{Pb}$ in the laboratory experiments are about an order of magnitude higher than those estimated for $^{214}\text{Pb}$ in groundwaters. This discrepancy can result if the surface to volume ratio available in natural aquifers is considerably larger than that in the monazite beaker experiment.

5. Conclusions

Our results on the $^{214}\text{Pb},^{222}\text{Rn}$ disequilibria in Gujarat groundwaters and $^{212}\text{Pb}/^{224}\text{Ra}$ ratios in laboratory simulation experiments seem to suggest that lead isotopes are removed from the aqueous domain of natural waters to particle surfaces in extremely short time scales, of the order of minutes. The deduced removal rates for these nuclides are much faster than previously envisaged and suggest that any particle-seeking nuclide introduced into groundwater aquifers will be removed onto particle surfaces very close to their point of injection. In the absence of advection the mean distance travelled by such “reactive” nuclides before being adsorbed on to particle surfaces can be approximated as $\sqrt{Di}$, where $D$ is the diffusion coefficient of the nuclide in the aqueous phase. For $D = 10^{-6}$ cm$^2$/s and $t = 600$ seconds (typical residence time of $^{214}\text{Pb}$) the distance travelled would be $\sim 250$ μm. The presently available data on the Pb and Th isotopes in groundwaters are inadequate to determine whether their adsorption on the aquifer surfaces are reversible. More detailed and systematic measurements of the radioactive isotopes of these elements would be required to predict their long term fate in groundwater systems.

Acknowledgements

We thank Drs. K.K. Turekian and W.C. Graustein for discussions and critical review of the manuscript. Permission and help provided by various organizations for sample collection is thankfully acknowledged. Financial support for this work in part was provided by a grant from the Department of Science and Technology to the Physical Research Laboratory. Mr. M.M. Sarin's help in the atomic absorption measurements of water samples is thankfully acknowledged.

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