Radionuclides in groundwaters: contaminants and tracers

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Abstract As groundwaters serve for drinking-water purposes, radionuclides in groundwater are generally considered as contaminants. Some of the radionuclides contributing to natural radioactivity in groundwater and some of the manmade atmospheric radionuclides, however, have become good tracers for the assessment of residence times (groundwater age) and mixing. Controlled experiments with artificial radionuclides, on the other hand, are restricted to a few special cases, e.g. the single-borehole dilution method, or two-borehole injection-withdrawal experiments.

INTRODUCTION

Radioactive wastes, which have been produced since the Second World War, include some of the most toxic groundwater contaminants. Because of their toxicity and their behaviour and fate in groundwaters, they have been subject to considerable research (e.g. Lyon & Patterson, 1984; Jackson & Inch, 1989). Much of what we know concerning the transport and the attenuation of radionuclide contaminants in aquifers is based on investigations of accidents and hydrogeological research with radioactive tracers. Few dissolved radionuclides are mobile in groundwaters, among them simple anions (e.g. $^{131}$I (Pickens et al., 1981), $^{36}$Cl), inorganic and organic complexes (e.g. $^{60}$Co in organic ligands (Killey et al., 1984)), or neutral compounds such as tritium. While tritium is of relatively low toxicity but very mobile in aquifers, many other dissolved radioactive contaminants (e.g. $^{134,137}$Cs, $^{85,90}$Sr), are more toxic but not particularly mobile. This is because of geochemical interactions between the radionuclides and aquifer material, in particular sorption phenomena on mineral surfaces (e.g. ion exchange) and on organic matter (e.g. Gee et al., 1983; Bradbury, 1989).

In most countries of central Europe, a relevant fraction of the drinking water originates from groundwater resources. The protection of the groundwater from contamination and its management requires knowledge about residence times and the mixing of the various waters, and about the interactions between the solid aquifer material and dissolved compounds. While the processes at solid surfaces are mostly studied in the laboratory, with static and dynamic experiments, tracer methods in the field give valuable information about physical transport processes and scale-up (e.g. Jackson & Hoehn, 1987). Radioactive tracers are obviously not in the foreground for the exploration and monitoring of groundwater. This paper gives some examples of the successful application of radioactivity as a tracer in groundwater hydrology.
NATURAL RADIOACTIVITY IN GROUNDWATER

Natural groundwaters contain radionuclides in trace concentrations. The most important contributors to natural radioactivity in groundwaters are $^{40}$K and the members of the natural $^{238}$U decay chain. Minor contributors are tritium ($^3$H), $^{14}$C, $^{87}$Rb, and the members of the other two natural decay series, $^{235}$U and $^{232}$Th. Natural radionuclides are released to the groundwater from rocks by dissolution and desorption, or by diffusion or atomic recoil, during radioactive decay. The concentration and distribution of uranium and thorium radionuclides and their daughter products of the naturally occurring decay chains in rock-water systems are important tracers of processes of mobilization, transport and fixation (Pearson et al., 1991; Ivanovich & Harmon, 1982). A rock mass which has remained undisturbed for about $10^7$ years may be considered as a closed system, and the decay series nuclides of the long-lived parents are in secular radioactive equilibrium. Secular equilibrium means that the parent nuclide and all successive members of its decay chain are present with the same activity. In such closed systems, all activity ratios (AR) are equal to one. Opening the rock-mass system by a geologic disturbance such as interaction with flowing groundwater will, in general, lead to radioactive disequilibria (AR ≠ 1), by two processes: (a) fractionation induced by recoil; (b) fractionation caused by differences in the physical and chemical behaviour of the various elements in a decay series (e.g. von Gunten, 1995). Chemical fractionation will always occur between different elements in a decay series, independent of any preceding recoil fractionation.

Example: the use of $^{222}$Rn as a groundwater tracer

Within the $^{238}$U decay series, the decay of $^{226}$Ra and its short-lived daughters is of interest in groundwater hydrology because it allows one to observe processes of a short duration. In rocks such as aquifer materials, the α-particle decay of the radioactive isotope $^{226}$Ra (radium: half-life 1600 years) produces $^{222}$Rn (an isotope of the noble gas radon, half-life: 3.8 days) as a daughter product. When $^{226}$Ra decays, which is present near the surface of aquifer grains, radon emanates continuously from minerals to the fluid phases groundwater (in the saturated zone) or soil gas (in the unsaturated zone) of aquifers by recoil and diffusion (emanation). Surface waters usually contain little $^{222}$Rn (about 1 Bq l$^{-1}$), since $^{222}$Rn gases are emitted to the atmosphere. When waters infiltrate from the surface to the saturated subsurface, the $^{222}$Rn activity can accumulate in the groundwater and increase to reach a steady state between ingrowth and radioactive decay. According to the law of radioactive ingrowth, the time necessary to establish steady state is about 20 days. Upon infiltration and movement in the ground, the radon concentrations increase by up to two orders of magnitude. Radon concentrations in fluid phases reach a steady state between ingrowth and decay, after about four half lives of $^{222}$Rn, i.e. about 20 days.

We assumed that the ingrowth of radon can be described by the growth law of radioactivity. This may be the case, if the progenitors of radon ($^{226}$Ra, $^{238}$U) are homogeneously distributed in the aquifer, and if the freshly infiltrated water is not mixed significantly with older groundwater (equation (1); e.g. Hoehn & von Gunten, 1989; Hoehn et al., 1992):
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\[ A_t = A_e[1 - \exp(-\lambda t)] \] (1)

where \( A_t \) is the activity of the daughter nuclide at time \( t \) (here assumed to be residence time (Bq l\(^{-1}\))), \( A_e \) is the activity of daughter nuclide at secular equilibrium with parent nuclide, (Bq l\(^{-1}\)), and \( \lambda \) is the radioactive decay constant of daughter (\( \lambda = T_{1/2}/\ln2; T_{1/2} = \) half life) (t\(^{-1}\)).

We used the ingrowth of radon in a system of river infiltration to groundwater of a glaciofluvial aquifer in central Switzerland (River Töss Site) to assess mixing and to estimate groundwater residence times. Tubes which were percussion-drilled into the river bed, allowed the detection of a mixing zone in the interstitial domain, between river water and underlying groundwater, with radon measurements. Mixing was assessed from the end-member activities (<1 Bq l\(^{-1}\) for river water; about 30 Bq l\(^{-1}\) for groundwater older than 20 days). A sharp boundary with almost no mixing was found at depths varying from 0.5 to 1.5 m (see Table 1).

In aquifers contaminated with nonaqueous-phase liquids (NAPLs) such as mineral oil, radon partitions preferentially from the aqueous phase into the organic phase. We studied the impact of a mineral-oil contamination on the \(^{222}\)Rn activities in the groundwater, in laboratory experiments and at a field site (Hunkeler et al., 1997). A mineral oil–water partition coefficient of \(^{222}\)Rn was calculated (\( K_p = 44 \pm 4 \) ml g\(^{-1}\) at 12°C) and used to estimate the \(^{222}\)Rn activity in the contaminated aquifer. The assessment was based on a mass balance of \(^{222}\)Rn which takes into account advective and dispersive \(^{222}\)Rn transport, emanation from mineral surfaces into the aqueous phase, decay and partitioning of \(^{222}\)Rn into the NAPL phase. The \(^{222}\)Rn partitioning among water and NAPL is linear and at equilibrium; the partition coefficient is independent of the NAPL saturation. \(^{222}\)Rn activities were used to detect and quantify contamination with diesel fuel in the glaciofluvial aquifer of Menziken, Switzerland. Upgradient of the contaminated zone, the \(^{222}\)Rn activity was about 9 Bq l\(^{-1}\) and decreased to about 5 Bq l\(^{-1}\) within the contaminated zone. In wells with a reduced \(^{222}\)Rn activity, dissolved hydrocarbons were detected (Fig. 1). This makes us assume that the decrease of the \(^{222}\)Rn activity is due to the presence of mineral oil, and can be used to detect mineral-oil contamination. Laboratory experiments showed that at steady state the ratio of the \(^{222}\)Rn activity in uncontaminated aquifer material to the \(^{222}\)Rn activity in contaminated aquifer material is a linear function of the volumetric mineral-oil content (Hunkeler et al., 1997).

**ANTHROPOGENIC RADIONUCLIDES**

An important type of radionuclide originates from the emission to the atmosphere, e.g. nuclear explosions (\(^{3}\)H) or reactor operations (\(^{85}\)Kr). Subsequent fallout of

<table>
<thead>
<tr>
<th>Depth in riverbed (m)</th>
<th>Radon activity (Bq l(^{-1}))</th>
<th>Mixing ratio</th>
<th>Age (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1.5</td>
<td>0.05</td>
<td>&lt;2</td>
</tr>
<tr>
<td>0.5</td>
<td>8.1</td>
<td>0.27</td>
<td>2-20</td>
</tr>
<tr>
<td>1</td>
<td>28.3</td>
<td>0.94</td>
<td>&gt;20</td>
</tr>
<tr>
<td>1.5</td>
<td>29.6</td>
<td>1.0</td>
<td>&gt;20</td>
</tr>
</tbody>
</table>

**Table 1** Radon activities and mixing ratios in riverbed interstitial waters (radon activity in the River Töss: 1 Bq l\(^{-1}\); steady-state radon activity in groundwater: 30 Bq l\(^{-1}\)).
radionuclides with precipitation and infiltration to the groundwater makes useful tracers for detecting the age of groundwaters: The groundwater system of interest is often assumed to be a black box, and the residence time function of the radionuclide in this box to decrease exponentially with time. The input function of $^3$H and $^{85}$Kr is sufficiently well documented worldwide. The dispersion throughout the hydrological cycle of tritium from the post-war atmospheric nuclear tests in the 1960s is so widespread that the presence or absence of tritium is used to identify the approximate age of the groundwater. A convolution to measured concentrations in groundwaters of springs or wells leads to robust values for the mean age (e.g. Siegenthaler et al., 1983). The present $^3$H concentration in precipitation is, however, several orders of magnitude lower than its peak during the period of atmospheric weapon testing and it continues to decrease. To overcome the problem of the low tritium concentrations, a method relates the radioactive decay of tritium to $^3$He ($T_{1/2} = 12.4$ years; e.g. Schlosser et al., 1988). In a closed system in which all isotopic changes only...
result from radioactive decay, the ratio of the stable daughter ($^3$He) to the radioactive mother ($^3$H) is a direct measure of the time elapsed since the water was last in contact with the atmosphere. The $^3$H-$^3$He method does not require knowledge of the atmospheric tritium input function, since it relies on the radioactive decay only. At the River Töss Site, shallow groundwaters revealed mixed ages of about 100 days in summer and of about 430 days in winter. We concluded from this that the river water infiltrates into the aquifer preferably in summer (Hofer et al., 1997).

In the catchment of the River Glatt, northern Switzerland, an accidental pulse release of about 20 TBq of tritiated water from an industrial plant in northern Switzerland moved from sewers to a sewage treatment plant, and from there to the River Glatt which loses water to the groundwater. Tritium contaminated the groundwater near the river with up to 6 kBq l$^{-1}$. Mass balance assessments indicated that 2–10% of the tritium infiltrated to the groundwater of the River Glatt Site, and that about 0.6% of the total activity reached eight public drinking water wells near the river. Large-scale longitudinal macrodispersivity of the glaciofluvial aquifer was evaluated from the mode of increase of the temporal variance of the tritium concentration distribution (Hoehn & Santschi, 1987).

CONTROLLED GROUNDWATER EXPERIMENTS WITH RADIONUCLIDE TRACERS

Very few conservative radioactive tracers are used for controlled experiments in groundwaters. Since groundwater is widely used for drinking-water purposes, long-lived radionuclides are out of the question for controlled experiments in open systems. Consensus established that radionuclides with half lives longer than two days should, in general, not be considered. Provided good methods for detection exist, experiments with the following radionuclides can last for a period of 4–5 times their half lives, i.e. a maximum of about 7 days (Table 2).

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Half-life (h)</th>
<th>Chemical compound</th>
<th>Chemical species</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{82}$Br</td>
<td>35.3</td>
<td>NaBr</td>
<td>Br$^-$</td>
</tr>
<tr>
<td>$^{123}$I</td>
<td>13.2</td>
<td>NaI</td>
<td>I$^*$</td>
</tr>
<tr>
<td>$^{99m}$Tc</td>
<td>6.0</td>
<td>†</td>
<td>†</td>
</tr>
</tbody>
</table>

* In most oxic groundwaters (e.g. von Gunten, 1995).
† Complexed in most groundwater Eh/pH fields (e.g. von Gunten, 1995).

The single-borehole dilution method with $^{82}$Br$^-$ as a conservative tracer allows the estimation of the specific discharge of groundwater through a borehole and the groundwater flow direction (e.g. Drost, 1986). The half life of $^{82}$Br$^-$ and the easy production of this $\gamma$-ray emitting radionuclide in a nuclear reactor makes it the most widely used in groundwater systems. The specific discharge is estimated as follows:

$$ q = (\pi r/2\alpha t) \ln(C_0/C) $$

where $q$ is the specific discharge (m day$^{-1}$), $r$ is the radius of screened tube in well
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(m), \( \alpha \) is the correction factor for distortion of flow lines (-), and \( C, C_0 \) is the actual and the initial activity concentration of \(^{82}\text{Br}\), respectively (Bq l\(^{-1}\)). At the River Glatt Site, values for \( q \) and the hydraulic conductivity, measured with pump tests and flowmeters (Drost & Hoehn, 1989), showed distributions of a similar statistical variance.

Example: two-borehole injection–withdrawal experiments (Grimsel Test Site, Switzerland)

To evaluate the barrier function of the geosphere at potential sites for deep disposal of radioactive wastes and to test models of radionuclide migration in the field, the breakthrough of weakly to strongly sorbing cationic alkaline and earth-alkaline radionuclides (\(^{22,24}\text{Na}\), \(^{85}\text{Sr}\), \(^{86}\text{Rb}\), and \(^{137}\text{Cs}\)) was studied in a shear zone (set of fractures filled with a fine-grained porous fault gouge) of granodioritic rock (Migration Experiment, NAGRA Grimsel Test Site, Switzerland: Frick et al., 1992). Two linear flow distances were extensively investigated, one of 1.7 m and one of 4.9 m. Among the various \( \gamma \)-emitting radionuclides used, \(^{137}\text{Cs}\) and the conservative tracer \(^{123}\text{I}\) (as a substitute for \(^{129}\text{I}\)) are of relevance to safety assessments. Reactive and non-reactive tracers were compared in two-borehole injection–withdrawal arrangements. Figure 2 shows patterns of an early breakthrough and of tailing. These patterns points to a double-porosity nature of the heterogeneous flow path, and to matrix diffusion in the investigated fracture zone (Hoehn et al., in press; Hadermann & Heer, 1996).

![Figure 2: Tracer concentration–time distribution as breakthrough curve (BTC) of uranium, \(^{22}\text{Na}\), \(^{85}\text{Sr}\), and \(^{137}\text{Cs}\), in double-logarithmic scale; tracer concentration, \( C \), normalized to injected uranine mass or radionuclide activity, \( M_0 \) (i.e. \( C/M_0 \); units: mg ml\(^{-1}\) per mg; Bq ml\(^{-1}\) per Bq), and corrected for radioactive decay; flow distance, 4.9 m; recovery curves shown at linear vertical axis, at right-hand side. Apparent second peak in Cs BTC, due to malfunction of pumps maintaining dipole flow field.](image-url)
CONCLUSIONS

In our effort to make good use of all possible tracer signals, natural as well as artificial, radioactivity must be taken into consideration in hydrogeological work. While natural radioactivity lends itself as a good groundwater tracer, the use of artificial radionuclides in groundwater tracer studies is restricted to a few special cases.

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