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The Behavior of U- and Th-series Nuclides in Groundwater

Donald Porcelli

*Department of Earth Sciences
University of Oxford
Parks Rd.
Oxford, OX1 3PR, United Kingdom
don.porcelli@earth.ox.ac.uk*

Peter W. Swarzenski

*Coastal Marine Geology Program
US Geological Survey
St. Petersburg, Florida, 33701, USA
pswarzen@usgs.gov*

1. INTRODUCTION

Groundwater has long been an active area of research driven by its importance both as a societal resource and as a component in the global hydrological cycle. Key issues in groundwater research include inferring rates of transport of chemical constituents, determining the ages of groundwater, and tracing water masses using chemical fingerprints. While information on the trace elements pertinent to these topics can be obtained from aquifer tests using experimentally introduced tracers, and from laboratory experiments on aquifer materials, these studies are necessarily limited in time and space. Regional studies of aquifers can focus on greater scales and time periods, but must contend with greater complexities and variations. In this regard, the isotopic systematics of the naturally occurring radionuclides in the U- and Th- decay series have been invaluable in investigating aquifer behavior of U, Th, and Ra. These nuclides are present in all groundwaters and are each represented by several isotopes with very different half-lives, so that processes occurring over a range of time-scales can be studied (Table 1). Within the host aquifer minerals, the radionuclides in each decay series are generally expected to be in secular equilibrium and so have equal activities (see Bourdon et al. 2003). In contrast, these nuclides exhibit strong relative fractionations within the surrounding groundwaters that reflect contrasting behavior during release into the water and during interaction with the surrounding host aquifer rocks. Radionuclide data can be used, within the framework of models of the processes involved, to obtain quantitative assessments of radionuclide release from aquifer rocks and groundwater migration rates. The isotopic variations that are generated also have the potential for providing fingerprints for groundwaters from specific aquifer environments, and have even been explored as a means for calculating groundwater ages.

The highly fractionated nature of the ^{238}U and ^{232}Th series nuclides is illustrated by the measured activities in some representative waters in Figure 1. The highest activities are typically observed for ^{222}Rn , reflecting the lack of reactivity of this noble gas. Groundwater ^{222}Rn activities are controlled only by rapid *in situ* decay (Table 1) and supply from host rocks, without the complications of removal by adsorption or precipitation. The actinide U, which is soluble in oxidizing waters, is present in intermediate activities that are moderated by removal onto aquifer rocks. The long-lived parent of a decay series, ^{238}U , does not have a radioactive supplier, while ^{234}U is a radiogenic nuclide; both of these nuclides have half-lives that are long compared to

Table 1. Radionuclides important in groundwater studies.

<i>Nuclide</i>	<i>Half-life¹</i>	<i>Atoms/dpm²</i>	<i>Factors Controlling Groundwater Concentrations</i>
²³⁸ U	4.47 × 10 ⁹ a	2.35 × 10 ¹⁵	weathering, adsorption
²³⁴ Th	24.1d	3.47 × 10 ⁴	recoil, strong adsorption, decay
²³⁴ U	2.45 × 10 ⁵ a	1.29 × 10 ¹¹	weathering, adsorption
²³⁰ Th	7.57 × 10 ⁴ a	3.98 × 10 ¹⁰	recoil, weathering, strong adsorption
²²⁶ Ra	1.60 × 10 ³ a	8.42 × 10 ⁸	recoil, strong adsorption, decay, surface production
²²² Rn	3.83d	5.52 × 10 ³	recoil, decay, surface production
²¹⁰ Pb	22a	1.2 × 10 ⁷	recoil, strong adsorption, decay
²³² Th	1.39 × 10 ¹⁰ a	7.31 × 10 ¹⁵	weathering, strong adsorption
²²⁸ Ra	5.75a	3.02 × 10 ⁶	recoil, strong adsorption, decay, surface production
²²⁴ Th	1.91a	1.00 × 10 ⁶	recoil, strong adsorption, decay, surface production
²²⁴ Ra	3.64d	5.24 × 10 ³	strong adsorption, decay, surface production
²³⁵ U	7.13 × 10 ⁸ a	3.75 × 10 ¹⁴	weathering, adsorption
²²³ Ra	11.7d	1.68 × 10 ⁴	recoil, strong adsorption, decay, surface production

1. From compilation by Bourdon et al. (2003).

2. dpm is decays per minute, and so is 60 Bq.

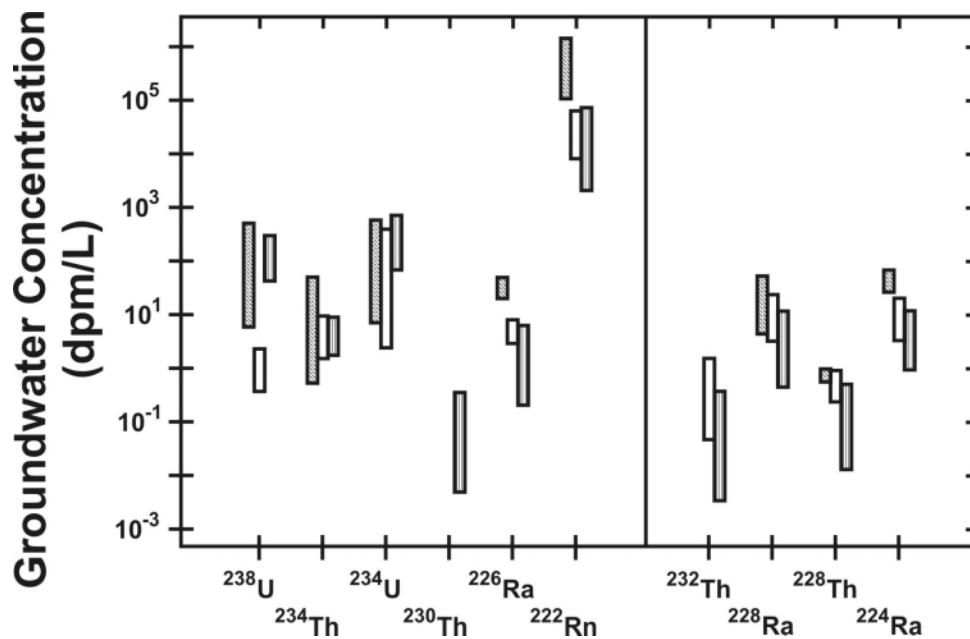


Figure 1. Comparison of ²³⁸U and ²³²Th series nuclide activities in some representative waters. The highest concentrations are typically observed for ²²²Rn. The isotopes of Th and Ra are strongly depleted due to interaction with the host rock, while somewhat higher activities of U are generally maintained. Data from Krishnaswami et al. (1982) on the left, Tricca et al. (2001) in the center, and Luo et al. (2000) on the right.

groundwater ages and so are generally not substantially affected by decay within aquifer systems. The alkaline earth Ra, and to a greater extent the less soluble actinide Th, are readily removed from groundwater by water-rock interactions, and so are strongly depleted. Both of these elements have very short-lived as well as longer-lived isotopes, and so their isotope compositions reflect processes over a range of time scales. Overall, since the set of nuclides in each decay series are tied by decay systematics, with daughter nuclide productions and distributions dependent upon parent distributions, combined studies of these elements can generate considerable information regarding radionuclide water-rock interactions and weathering release rates.

Many studies have evaluated the behavior of these elements in the hydrosphere, and have been reviewed earlier (Gascoyne 1992; Osmond and Cowart 1992). A large body of data has been gathered using widely practiced counting techniques, although this cannot provide precise data on the longer lived nuclides. The development of high precision mass spectrometric techniques (Chen et al. 1986; Goldstein and Stirling 2003) have made it possible for more subtle variations in U isotopes to be explored, and also provide the potential for doing so with long-lived Th isotopes. However, these techniques have yet to be fully exploited in this field and data remain limited.

Research into the behavior of radionuclides continues to be active, greatly motivated by the necessities of understanding and predicting migration of contaminant actinides and related species. The focus of this review is on the use of the isotope systematics of the U- and Th-decay series in understanding natural radionuclide migration. In general, quantifying aquifer parameters that control trace element behavior are difficult at many sites by direct measurements, since the host rocks typically cannot be as readily sampled as groundwater, and average values for host rocks recovered from boreholes are difficult to obtain. However, decay series systematics of nuclides in groundwater provide the potential for quantifying some chemical parameters of water-rock interaction from direct measurements of waters alone. Various studies have attempted to model the transport of the range of U, Th, Ra, Rn, and Pb radioisotopes in groundwaters by combining the systematics of the nuclides within the decay chains, and so providing a framework for calculating such critical parameters as retardation factors. These particular elements have the additional appeal of providing natural analogues for radioactive wastes, so that evaluations of the transport behavior of U and Th series nuclides can have predictive power for assessing the possible migration of low level anthropogenic waste nuclides in any environment. A key difference is in the supply functions; where the effects of the supply rate of naturally occurring nuclides within the aquifer can be distinguished, the controls on nuclides introduced only at the aquifer recharge boundary can be quantified. Many of the earlier advances in modeling naturally occurring nuclides have been summarized by Osmond and Cowart (1992), Ku et al. (1992), and Ivanovich et al. (1992a). While there are many different approaches that have been used to infer radionuclide behavior, these are all based on the fundamental connections between nuclides by radioactive decay, and simple modeling of known processes of input by weathering and recoil into groundwater as well as interaction with aquifer host rock surfaces by sorption and precipitation.

In this review, the general principles incorporated in most modeling approaches will be outlined. While the principles of the models are relatively straightforward, the derivations of the equations involved are involved. The intention here is not to derive the specific equations used by the various studies to obtain quantitative results. These are considered in detail by Ku et al. (1992) and the studies referenced here. Rather, the emphasis is on the qualitative understanding of how the important conclusions are

derived as well as identifying and evaluating the underlying assumptions. The detailed discussion of individual processes and parameters are intended to demonstrate where assumptions that underpin model calculations are fully justified, whether additional work is required to support these assumptions, and when experimental or theoretical considerations indicate that alternative parameter values are possible. Overall, it should become clearer where qualitative conclusions regarding radionuclide behavior are firm and to what extent quantitative evaluations might be questioned. Such a systematic evaluation of the controlling processes has not been compiled recently, and is needed for future progress in this field.

Considerable recent attention also has focused on the discharge of groundwaters into surface water. Earlier water budget studies often regarded these inputs as negligible in the absence of methods for their quantification. However, distinct isotopic characteristics of groundwater, imparted by close interaction with aquifer rocks where daughter nuclides are supported by continuing supply from host minerals, can be used to trace these inputs. This is particularly true of Rn and the short-lived isotopes of Ra, which have concentrations that diminish in the absence of direct supply from host rocks, and so can be used to fingerprint patterns of groundwater inflow into highly depleted surface waters. These studies are also reviewed here.

2. NUCLIDE TRANSPORT IN AQUIFERS

A key parameter in understanding the controls on groundwater concentrations and radionuclide transport is the retardation factor R_I . The rate of transport of a groundwater constituent I is decreased by the factor R_I relative to the groundwater flow rate due to interaction with aquifer host rock surfaces. The retardation factor is $R_I = 1 + K_I$, where K_I is the ratio of the inventory atoms adsorbed on surfaces to the inventory in the surrounding groundwater. Thus if 90% of a species is on surfaces, then it will migrate at a rate of 1/10 that of groundwater, while if there is none on the surfaces so that it is behaving conservatively, it will keep pace of groundwater flow. Therefore, a major goal of groundwater models is to obtain values of K_I . A bulk value is used for large-scale transport modeling, although comparison with laboratory experiments is required to determine the specific mechanisms that define this value and are responsible for any changes across an aquifer. Mathematical treatments of simple aquifer models have been used to calculate retardation factors, as well as the rates of weathering, recoil, and adsorption/desorption, and have been extensively developed by Krisnaswami et al. (1982), Davidson and Dickson (1986), Ku et al. (1992), Luo et al. (2000), and Tricca et al. (2000, 2001). These approach the determination of various parameters using somewhat different perspectives and underlying assumptions. The modeling equations for most models are generally subsets of the same general set of equations, as shown by Ku et al. (1992), with different studies utilizing different assumptions regarding parameter inputs or neglecting as insignificant different processes. The details of specific processes, and alternatives, are discussed according to element in subsequent sections. Note that the ratios and concentrations in parentheses refer to activities; others refer to molar concentrations.

2.1. General modeling considerations

The general modeling approach is described here to provide a context for understanding recent observations and identifying which processes, whether generally explicitly considered or neglected, are important. Individual studies generally incorporate further simplifying assumptions. Ku et al. (1992) provide a discussion of the general equations.

Model components. Models generally consider 3 populations of radionuclides:

- *Groundwater*, where concentrations are obtained by direct sampling. Since transport of radionuclides is being considered without regard for the mobile form these are in, bulk activities per unit mass are used. Speciation does not change the calculation of the bulk transport properties of each nuclide, although this is certainly an underlying control on observed behavior and so becomes important only when calculated transport and water/rock interaction rates are being interpreted. Operationally, most samples are filtered to remove particles less than $\sim 0.5 \mu\text{m}$ to remove material presumably mobilized by pumping. Of particular concern is the inclusion in samples of colloid-bound species, which may not readily exchange with dissolved nuclides and may have different transport properties. Unfortunately, this generally is not considered in isotope models.
- *Host aquifer rock*, which can include inventories in primary minerals and secondary phases generated prior to establishment of the present environment, or actively precipitating phases. For modeling calculations, this strictly represents all radionuclides not actively exchanging with the groundwater, although the distribution of radionuclides is important for interpreting the pattern of releases to groundwater.
- *Atoms adsorbed on host rock surfaces*. This pool is assumed to readily exchange with atoms in groundwater. Bulk abundances are sought in the models, while specific mechanisms that explain these values must be sought separately in laboratory experiments.

It is sometimes useful to consider the abundances in the groundwater and sorbed together as the “mobile” population, in contrast to those fixed within the host rock.

Processes controlling nuclide distributions. The general equations for one-dimensional advective transport along a groundwater flow path of groundwater constituents, and the incorporation of water/rock interactions, are given in such texts as Freeze and Cherry (1979). The equations can be applied to the distribution in groundwater of each isotope I with a molar concentration I_W and parent with P_W to obtain

$$\frac{\partial I_W}{\partial t} + \frac{v \partial I_W}{\partial x} = b w_I I_R + b \varepsilon_I \lambda_P P_R + I_{\text{ADS}} k_{-1} + f_I \lambda_P P_{\text{ADS}} + \lambda_P P_W - Q_I - \lambda_I I_W - k_I I_W \quad (1)$$

which includes the groundwater flow velocity (v), weathering rate constant (w_I), recoil release fraction ε_I , adsorbed molar concentrations of species I (I_{ADS}) and parent P (P_{ADS}), host rock molar concentrations for the species (I_R) and parent (P_R), desorption (k_{-1}) and adsorption (k_{-1}) rate constants, fraction produced by sorbed parent atoms that are directly released to groundwater (f_I), the nuclide and parent decay constants λ_I and λ_P , and precipitation rate (Q_I). The parameter b converts concentrations of weathered rock to those in water. In porous rocks, $b = (1 - n)\rho_R/\rho_W$ is the mass ratio of rock to water with densities ρ_R and ρ_W , where n is the porosity. Equation (1) can be cast in terms of the activity (I_W) per unit mass by multiplying all terms by the decay constant for I (λ_I). The convention of using parentheses to denote activities per unit mass or activity ratios will be used here. It is worth bearing in mind that unfortunately notation for many of the parameters is not consistent between published studies; the notation used here is summarized in Table 2.

The terms on the left side represent the change of I_W with time and the change of

Table 2. Parameters used in groundwater models.

$I_W, (I)_W$	Groundwater nuclide I molar and activity concentration
$P_W, (P)_W$	Groundwater parent P molar and activity concentration
$I_R, (I)_R$	Host rock nuclide I molar and activity concentration
$P_R, (P)_R$	Host rock parent P molar and activity concentration
$I_{ADS}, (I)_{ADS}$	Adsorbed nuclide I molar and activity concentration (per mass of rock)
$P_{ADS}, (P)_{ADS}$	Adsorbed parent P molar and activity concentration (per mass of rock)
v	Groundwater flow velocity
x	Distance along a groundwater flow line
w_I	First order constant for weathering release of nuclide I
ϵ_I	Recoil release fraction for nuclide I
λ_I, λ_P	Decay constants of nuclide I and parent P
k_I	First order bulk adsorption rate constant
k_{-I}	First order bulk desorption rate constant
Q_I	Rate of precipitation of nuclide I
f_i	Fraction of nuclide I produced by adsorbed parents and recoiled into water
b	Mass ratio of rock to water, where $b = (1 - n) \rho_R / n \rho_W$
ρ_W, ρ_R	Densities of groundwater and host rock
n	Porosity of the host rock
R_I	Retardation factor of nuclide I, where $R_I = 1 + K_I$
K_I	Partition coefficient between dissolved and adsorbed atoms

I_W with distance x along a groundwater flow path. The terms on the right side represent the input and removal terms (see Fig. 2a), which in order are:

- *Input by weathering.* Minerals with molar concentrations I_R release nuclides according to rate constant w_I by simple breakdown of mineral structures. Weathering is depicted here as a first-order rate constant for convenience (Tricca et al. 2000), but is constant for small degrees of weathering, and conversion to more familiar rates per unit area can be done by determining the ratio of the mass to the surface area of the weathering minerals. Note that the weathering constant for U- and Th-bearing minerals may be different from that of the bulk rock, and release of nuclide I by w_I may be different than dissolution of the bulk mineral due to e.g., leaching or incongruent breakdown (Eyal and Olander 1990; Read et al. 2002). However, it is generally assumed that all the nuclides in each series are released together, and that U and Th are similarly sited so nuclides from the different series are not separated due to different release rates.
- *Input by recoil.* The parent nuclide population, with molar concentration P_R , releases a fraction ϵ_I of the daughter by direct recoil or related losses (e.g., rapid migration along its recoil track). Direct recoil of nuclides into groundwater (Kigoshi 1971; Fleischer and Raabe 1978) occurs when daughter nuclides that are generated with high kinetic energies are propelled across the mineral surface and are stopped within the aqueous phase. The direction of recoil is random for each decay, and the rate of ejection into groundwater is determined only by the fraction of parent nuclides within recoil distance of mineral surfaces or channels

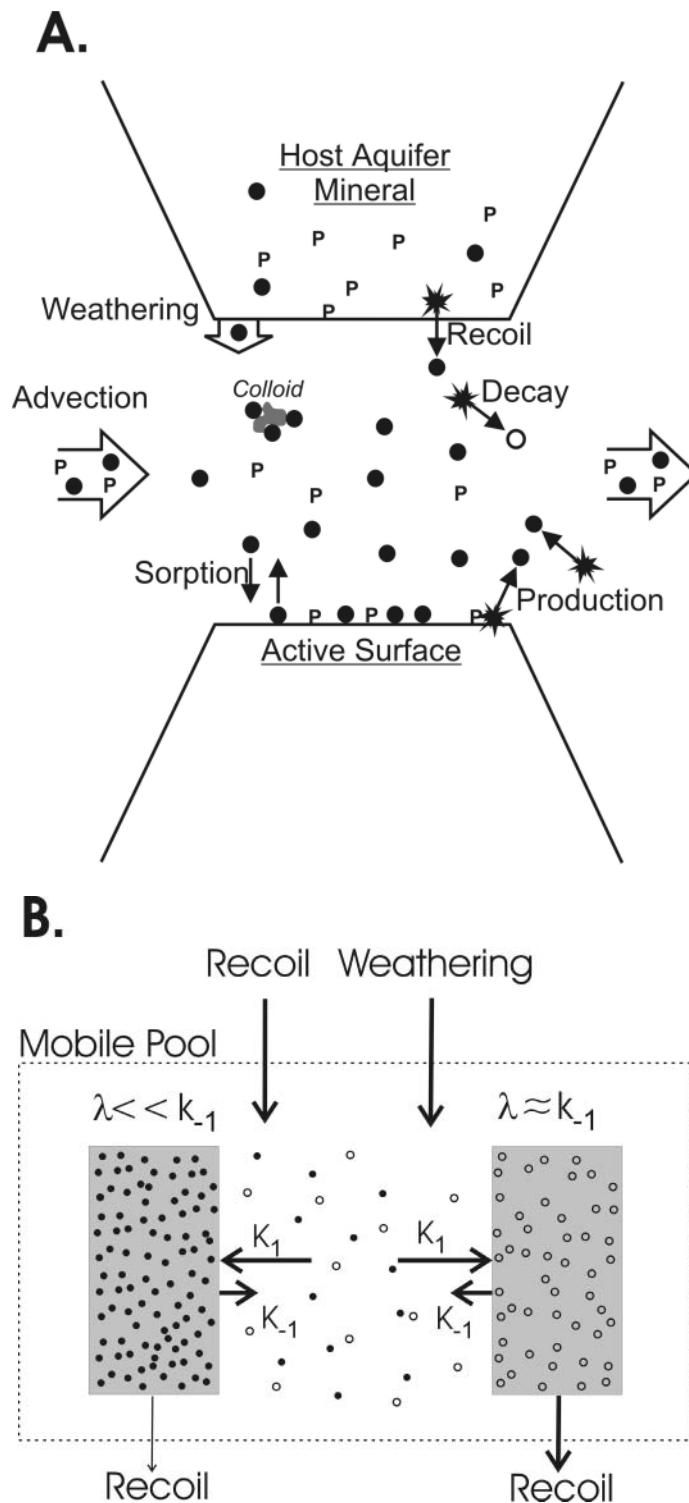


Figure 2. (A.) The radionuclides in an aquifer are divided into three reservoirs; groundwater, the host aquifer minerals, and adsorbed onto active surfaces. Also shown are the processes adding to a daughter nuclide (closed circles) in the groundwater of weathering, advection, recoil from decay of parent atoms (“P”) in the aquifer minerals, and production by parent decay, the processes of losses of a radionuclide of advection and decay, and exchange between dissolved and adsorbed atoms.

(B.) In steady state, the mobile pool of nuclides is constant. For a long-lived nuclide (solid circles), the adsorbed abundances are determined by exchange with the groundwater. For a short-lived isotope that has a decay constant that is comparable to the desorption rate constant k_{-1} , decay of sorbed atoms is a significant flux, and so the steady state sorbed abundance is lower (see Eqn. 3).

to the surface, and so can be readily calculated given the distribution of parent nuclides. Recoil of nuclides is the most clearly defined physical supply process, and has been considered to be most amenable to quantification, and so has been the focus of considerable research. This is discussed further in Section 2.2.

- *Input by desorption according to first order rate constant k_{-1} .* Note that this represents the association of atoms on surfaces that are free to exchange with the groundwater. The alternative formulation of specifying a volume and density of a layer containing species with defined migrations velocities (Tricca et al. 2001) is only a mathematical construct and is not consistent with established absorption processes involving association of species directly with surfaces.
- *Input by production from sorbed parent atoms.* Daughter atoms recoiled during α decay are unlikely to come to rest on the surfaces, and are ejected either into the surrounding groundwater or into the mineral. The fraction released, f_i , may be 0.5 if half the daughter atoms are recoiled into the underlying mineral (Tricca et al. 2000), or 1 (Luo et al. 2000) if these atoms are rapidly released by migration back along the recoil track, or a value in between. Unfortunately, there is no experimental evidence to establish which value is appropriate. In contrast, if a daughter atom is produced by low energy β decay, it may remain on the surface, and so the fraction released is zero. However, in this case, this production must be considered when calculating the budget of adsorbed atoms (see below).
- *Input by decay* in solution of parent with molar concentration P_w .
- *Removal by precipitation.* This is represented here by some function Q_i , with the exact form depending upon the controlling parameters. U may precipitate as uraninite where reducing conditions are encountered, and Th may reach the thorium solubility limit under some conditions (see Tricca et al. 2001). In these cases, precipitation will balance supply by weathering of the major isotope. Alexander and McKinley (1994) noted that precipitation of such minerals is not necessarily a first-order process, and it is related to the difference between concentration and solubility limit rather than to absolute concentrations. Note, however, that during precipitation of low concentration species by partitioning into phases defined by other elements, removal may be proportional to groundwater radionuclide concentrations and so may be governed by a first order rate constant (Ku et al. 1998).
- *Removal by decay* of I in the water.
- *Removal by sorption.* It is generally assumed that adsorption is reversible. Irreversible removal directly from groundwater would be included in the term for precipitation, although slow irreversible incorporation of sorbed atoms is not considered in Equation (1).

Note that the models aim to define general descriptive bulk parameters for an aquifer. Values for bulk adsorption or weathering will reflect the weighted range for a variety of phases present in complex, natural systems, and provide an overall measure of the behavior of the aquifer. In contrast, individual phases can be examined in the laboratory to determine the specific processes involved.

An important consideration is the relative importance of the two processes that supply radionuclides to the dissolved and adsorbed inventories from within the host rock minerals. The recoil term in Equation (1), $b_{e_i} \lambda_p P_R$, can be compared to the weathering

term, bw_1I_R , most clearly when these are expressed using activity concentrations rather than atom concentrations by multiplying each by λ_I to obtain $b\lambda_I\varepsilon_I(P)_R$ and $bw_1(I)_R$. Then noting that in minerals the radionuclides are expected to be approximately in secular equilibrium so that $(P)_R = (I)_R$, it can be seen that weathering is more important when w_1 ($\equiv 1/\tau_W$, where τ_W is the mean time required for completely weathering host minerals) is greater than $\lambda_I\varepsilon_I$ ($\equiv \varepsilon_I \ln 2 / t_{1/2}$, where $t_{1/2}$ is the half life of nuclide I). Values of $\sim 10^{-2}$ have often been inferred for ε_I (see Section 2.2), so that if aquifers were being removed by chemical weathering with a mean time of 10^7 years, any nuclide with a half life of $< 10^5$ years will be supplied largely by recoil. This includes all daughter nuclides except ^{234}U . Where ε_I is much smaller, weathering may become important for the supply of ^{230}Th or even ^{226}Ra . However, for the shorter-lived nuclides, it is unlikely that weathering can be important.

Adsorbed nuclides. Obtaining a solution to Equation (1) requires knowledge of the absorbed abundance of the nuclide of interest (I_{ADS}). Assuming that steady state abundances have been achieved at each location, supply by adsorption is balanced by desorption and decay. No supply is expected to occur by decay of adsorbed parent atoms in the cases where α recoil drives daughters instead into solution or into the underlying mineral (although modification may be made in the case of β decay). Then,

$$I_W k_1 = I_{\text{ADS}} k_{-1} + \lambda_I I_{\text{ADS}} \quad (2)$$

The dimensionless partition coefficient K_I is defined as the ratio of atoms adsorbed to atoms in solution. Rearranging Equation (2) (Krishnaswami et al. 1982),

$$K_I \equiv \frac{I_{\text{ADS}}}{I_W} = \frac{k_1}{k_{-1} + \lambda_I} \quad (3)$$

It should be emphasized that where this value is calculated from field data, it simply represents the distribution of the radionuclides, and makes no assumptions about whether thermodynamic equilibrium has been achieved, about the precise mechanisms of adsorption, or about the form of the isotherm describing adsorption as a function of concentration. Alexander and McKinley (1994) have objected to this modeling approach by arguing that *in situ* values are valid only if the mechanism responsible can be shown to distribute a species between water and solid so that the equilibrium phase concentration is directly and linearly related to that in the aqueous phase. Also, it was pointed out that where substantial changes in water chemistry are encountered, competition with other species might change the distribution values. However, a linear relationship between the partition coefficient and the water concentration is an issue only where the distribution between water and solid is assumed to remain constant during large changes in total abundances. This is not an issue in describing the present aquifer system, but is a factor when predicting radionuclide behavior under changed conditions. Note that in most cases, the actual number of atoms involved is exceedingly small. Miller and Benson (1983), using numerical models, point out that when species concentrations are sufficiently small relative to the supporting electrolytes in solution and the capacity of the sorbing material, the distribution coefficient is constant. Where the relationship is nonlinear, empirical data must be used to define applicable isotherms. While this may not affect the modeling of naturally occurring nuclides, it complicates extrapolation to high radionuclide concentrations. In that case, the number of sites for sorption on a solid phase may be limited, and beyond this there is no direct relationship between aqueous and dissolved concentrations. Overall, these considerations do not compromise the calculations generally performed in studies of the distribution of naturally occurring radionuclides, but do become critical where conclusions are extrapolated to make predictions involving grossly different concentrations.

The migration rate of a groundwater constituent, relative to the groundwater flow rate, is controlled by the retardation factor, where $R_I \equiv 1 + K_I$. Where $K_I \gg 1$ (e.g., for Th and Ra), $R_I \approx K_I$, and $I_{ADS} + I_W = I_W R_I$. Note that k_1 and k_{-1} are element-specific but not isotope-specific. All isotopes that decay slower than desorption, so that $k_{-1} \gg \lambda_I$, have a value of K_I that is equal to that of a stable isotope (Eqn. 3). The value of K_I may be lower for the shortest-lived nuclides (see Fig. 2b), and so a series of equations derived from Equation (3) applied to different isotopes of the same element may be used to obtain absolute values for the separate rate constants.

Obtaining solutions to the model equations. The general modeling approach has been discussed in considerable detail in Ku et al. (1992). Detailed application of these models to a wide range of nuclides have been performed by Krishnaswami et al. (1982) and Copenhaver et al. (1992, 1993) to single wells, by Tricca et al. (2000, 2001) to data from across a shallow, unconfined, unconsolidated sandy aquifer, and by Luo et al. (2000) to a regional basalt aquifer. Each of these studies, as well as many others, treat radionuclide transport in fundamentally the same way, although the full derivation of the equations is not always presented; rather, subsets of the full equations are often obtained directly by applying simplifying assumptions or implicitly neglecting some processes as inconsequential.

More complete treatment of the derivation of the equations governing radionuclide distributions along a single groundwater flow path are given by Ku et al. (1992) and Tricca et al. (2000). The general strategy has been to combine Equations (1) to (3) for various nuclides. It is possible to fully integrate the equations for each radionuclide and so obtain analytical solutions for the distribution and migration rates. However, the task becomes progressively more difficult along each decay series (see Figs. 3 and 4), since the production rates of each nuclide depend upon the distribution of the parent element (see Tricca et al. 2000). Therefore, all studies have focussed on particular special cases that allow simplifying assumptions. The most common is to assume that the radionuclide distributions are in steady state. In this case, at each location along a flow line the concentrations of all radionuclides in groundwater, surfaces, and host minerals are constant with time. The first term on the left of Equation (1) (the time dependence of the concentration of a nuclide) then can be set to zero. The assumption requires that all controlling processes have been operating steadily over sufficient time to have allowed the accumulation of adsorbed inventories that are in exchange with the groundwater inventories, and that there are no processes such as irreversible removal of adsorbed nuclides that have not allowed this to occur. These conditions, however, do not mean that concentrations are the same along a flow line, and should be carefully distinguished from the assumption that the concentrations in a flowing groundwater do not change. This further assumption is often also made, so that the second term on the left side of Equation (1), which is the effect of advection of nuclides where there are concentration gradients, can also be set to zero.

Where there is an abrupt change in conditions, e.g., where water interacting with the vadose zone enters into the groundwater, strong concentration gradients may occur along groundwater flow lines as concentrations change from initial to steady state values. Groundwater profiles were calculated by Tricca et al. (2000) and it was shown that steady state concentrations are achieved over distances that are inversely proportional to the nuclide decay constant and the partition coefficient. Therefore, while ^{238}U , ^{234}U , and ^{232}Th do not reach constant concentrations over any reasonable distances, ^{226}Ra does over several hundred meters, and all the other radionuclides require less than a few meters. Constant concentrations are achieved when the inventories of a radionuclide in both groundwater and adsorbed on surfaces decay at the same rate at which this radionuclide is

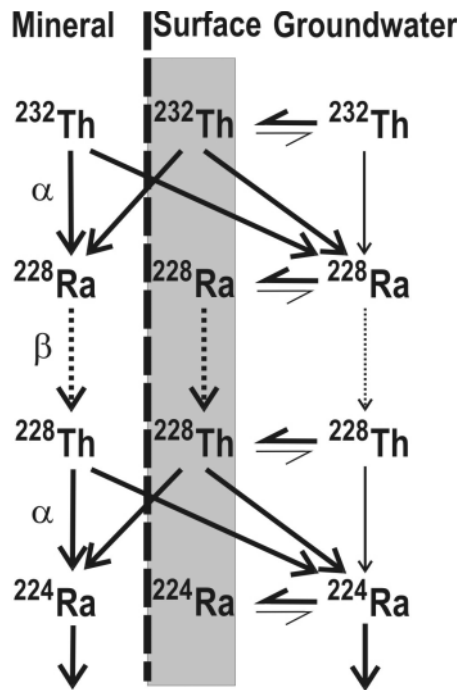


Figure 3. Systematics of radionuclides along the ^{232}Th series. The major and minor fluxes to each nuclide can be readily seen from the arrows shown. The behavior of each nuclide can be evaluated by considering the surface and groundwater populations individually, or together as the “mobile” pool. Nuclides in the decay series within the host rock minerals supply atoms at the surface and in the groundwater by recoil during α decay, so that there are greater abundances in the mobile pool of nuclides progressively along the series. α decay of nuclides at the surface injects atoms back into the minerals as well as into groundwater.

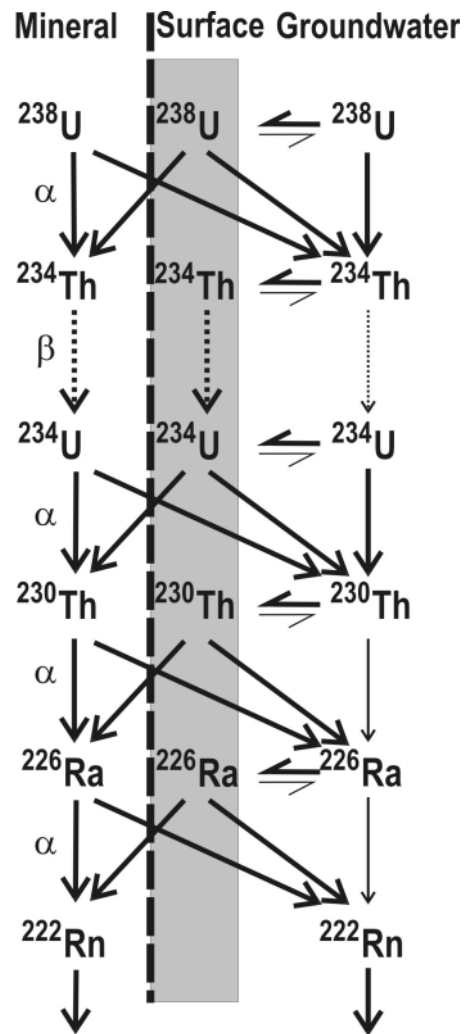


Figure 4. Systematics of radionuclides along the ^{238}U series. The major and minor fluxes to each nuclide can be readily seen from the arrows shown. The behavior of each nuclide can be evaluated by considering the surface and groundwater populations individually, or together as the “mobile” pool. As with the ^{232}Th series (Fig. 3), there is addition to the mobile pool of nuclides produced by α decay along the series. Note, however, that steady state abundances may not be achieved for ^{234}U , which is long-lived and may also be sufficiently mobile in the groundwater for advection to be important.

supplied by recoil as well as adsorbed and dissolved parent inventories. Where recoil is not the dominant supply term, groundwater concentrations will change along with those of the parent nuclide, although if parent concentration gradients are not steep, a quasi-steady state will be reached. Overall, for all but the most long-lived nuclides (^{238}U , ^{234}U , ^{232}Th), constant activities per unit mass are generally reached over short distances (Tricca et al. 2000). Unfortunately, there have not been detailed studies comparing model calculations of the approach to constant groundwater concentrations with field data.

An important assumption in solving Equations (1) to (3) is that the values of all parameters are constant both at each location and along the flow line. Where there are changes within the aquifer, these must be incorporated into the equations. The simplest cases are where all the changes occur abruptly, so that segments of the aquifer can be treated as separate, uniform systems. In many cases, field studies have found that the concentrations and isotopic ratios of short-lived nuclides vary across an aquifer (see sections of specific elements below); this is taken to reflect variations in some of the controlling parameters over a limited area, so that values representing local steady state conditions can be calculated. Such calculations generally ignore the possibility that strong radionuclide concentration gradients are present at the sampling locations.

It is worth emphasizing that these are one-dimensional models and track concentrations in groundwater along a single flow path, neglecting the effects due to such factors as lateral heterogeneities and dispersion. Also, where there is groundwater flow along fractures or preferential pathways, waters moving more slowly may develop distinctive characteristics before joining the main flow paths (e.g., Nitzsche and Merkel 1999), and averages calculated from waters drawn from these flow paths will not adequately represent the relationships of the short-lived nuclides across the aquifer. This may be most pronounced in fractured rock aquifer systems. Therefore, care must be taken in defining the flow regime being modeled.

The model equations can of course be modified to include different processes or more complex descriptions of water/rock interaction within the general approach described here. However, further complexity can only be fruitfully added where independent information can provide additional constraints and limit the range of solutions. An important application of radionuclide transport models is the calculation of the transport of anthropogenic nuclides. In this case, several modifications must be made, including nonsteady state concentrations as the contaminant plume migrates and possible nonlinear adsorption behavior at higher concentrations. Similarly, changes in weathering in the vadose zone due to changes in climate could change the input at the water table and require consideration of time-dependent concentrations where there has been insufficient time to re-establish steady state conditions.

Relative recoil input rates. As discussed above, for all the short-lived nuclides, recoil is the dominant input. Many nuclides are supplied to groundwater by the same physical process of recoil during α decay production, and so their supplies can be related to one another. For simplicity, the recoil rates of the different nuclides are often assumed to be equal within each chain, and proportional to the bulk rock $^{238}\text{U}/^{232}\text{Th}$ and $^{238}\text{U}/^{235}\text{U}$ ratios between chains. However, there are several factors that will affect individual recoil release rates.

- *Different locations of parent elements.* ^{238}U and ^{232}Th are generally located in minor phases within host rocks. Due to different U/Th ratios in these phases, recoil from the two chains may be affected by different surrounding matrix characteristics or mineral sizes. Not only might the primary distribution of U and Th be different, but earlier weathering or alteration may also have redistributed U and Th. This is discussed further below.
- *Different recoil lengths.* The distance that a daughter nuclide is recoiled depends upon the recoil energy as well as the host matrix. There are some uncertainties in the precise recoil distances. Kigoshi (1971) gave an average recoil distance of 550 Å for ^{234}Th , although this appears to be too high, since subsequent experiments suggest values of ~200 Å (Fleischer 1980; Sheng and Kuroda 1986). Recoil distances have been calculated for a range of recoil energies and

matrices (Hashimoto et al. 1985; Roessler 1989). There are some differences between isotopes where similar matrices were examined, on the order of up to ~10%, but there are greater differences between matrices. For example, while the recoil energies of ^{230}Th (83 keV) and ^{234}Th (72 keV) are similar and so losses are similar from the same matrix, recoil distances for ^{230}Th varies between 160 Å for uraninite, to 413 Å for autunite, to 270 Å for muscovite (Hashimoto et al. 1985). Therefore, different mineral locations between parents or between aquifer rocks can account for over a factor of 2 variation.

- *Different depletions of parents.* Recoil of daughter atoms from a mineral structure results in the depletion near the surface of parent atoms for the next nuclide in the decay chain. This effect advances progressively along each chain. Krishnaswami et al. (1982) calculated that the recoil supply of ^{222}Rn , the result of the fourth α recoil product in the ^{238}U chain, is 48% that of ^{234}Th , the first product. However, if the daughters are adsorbed onto the mineral surfaces, then there is the progressive migration of parents toward the surface either by accumulation on adsorbed sites or by injection from the surface back into the mineral; if all the Ra and Th are adsorbed, then ^{222}Rn supply from ^{226}Ra that is both within the mineral and adsorbed is 30% greater than that of ^{234}Th . Note that selection of the proper value for this process must be consistent with the value of f_1 that defines the supply of daughters from adsorbed atoms into the groundwater.
- *Differential losses due to differences in chemistry.* While the physical process of recoil makes no distinctions due to the contrasting chemistries of the nuclides involved, subsequent further release by leaching of daughter nuclides along recoil tracks (Fleisher 1980) may depend upon nuclide chemistry. Such a process is generally considered to be part of the recoil process in modeling treatments, since the other supply term from aquifer solids, weathering, is assumed to be non-fractionating between all parents and daughters. However, in this case differences in behavior must be reflected by differences in recoil release fractions (ϵ_1). Leaching is considered in more detail below under the treatment of individual elements. However, it is worth noting here that such leaching will only occur when the recoil track crosses the mineral surface or a fast pathway to the surface, even though the daughter has not been directly lost. This can occur if daughters cross mineral boundaries and are implanted into adjacent minerals (e.g., Suksi and Rasilainen 1996), or if a process such as fracturing creates a new mineral face. Nuclides within recoil tracks may also be released if weathering moves the mineral boundary inwards by bulk dissolution of the mineral or by incongruent dissolution that releases those constituents that are incompatible with the secondary phase. However, in many circumstances, the recoil track will not cross a mineral surface unless the daughter is also directly ejected. It has been argued that ^{222}Rn is a special case, and as an unreactive noble gas is preferentially released. This is discussed in detail in Section 2.2.

Distributions in host rock minerals. A key issue in determining the recoil supply of ^{222}Rn and other daughter nuclides, as well as the weathering supply of the long-lived isotopes, is the distribution of ^{238}U and ^{232}Th within host rocks. During the initial formation of igneous rocks, U and Th are incompatible with many major rock-forming minerals and are largely incorporated into various minor phases, but also may be on grain boundaries. For example, analyses of the Göttemar Granite in SW Sweden found zircon and monazite to be dominant sources of U and Th, while there were secondary amounts in sphene and magnetite (Smellie and Stuckless 1985). Weathering and secondary processes may redistribute U and Th (see Chabaux et al. 2003). In a granodiorite weathering profile, U in

weathered rocks was largely in primary resistates and Th was in fine-grained material such as clays and Fe phases; selective leaching experiments found that U was fractionated from Th by up to 30% (Pliler and Adams 1962). Studies of monazite weathering by Read et al. (2002) found that preferential loss of U occurred, while Th was also leached from primary phases but was incorporated in nearby sites within the host rock in microcrystalline silicate and oxide alteration products. Redistribution between mineral phases may also occur by hydrothermal alteration during initial cooling of igneous rocks, weathering, and during transport of minerals before incorporation into sedimentary deposits. Overall, it is generally difficult to predict the distributions of U and Th in host rocks without direct detailed study of the host aquifer rocks, and any modeling of a particular past process of secondary radionuclide redistribution from groundwater data (e.g., Tricca et al. 2001) has been only hypothetical and essentially unconstrained. Once an aquifer regime has been established, further U and Th redistribution can result from precipitation under presently observed aquifer conditions. In this case, there are often mass balance constraints on the fraction of aquifer U and Th could have been released by *in situ* weathering and the associated removal of major elements. This is particularly true of less soluble elements such as Th, which are not readily mobilized and so often have not been transported far from weathering zones (see Section 2.4).

From the diversity of potential sites for U and Th, it is clear that the weathering release of ^{238}U and ^{232}Th , as well as of the recoil and leaching release of daughter nuclides, must be determined for each site. Nonetheless, most studies assume that ^{238}U and ^{232}Th have similar distributions, so that the values for ε_1 (the fraction released by recoil) and w_1 (the weathering release constant) is assumed to be approximately equal for all nuclides I.

Colloids. As discussed above, in most models groundwater concentrations are characterized by bulk measurement of all species. One particular component in groundwater that has received particular attention is colloids, which have the potential of increasing the proportion of radionuclides in the groundwater rather than on surfaces, and so in some circumstances may provide an explanation for enhanced migration rates. In general, colloids are a common component of groundwaters. The composition, structure, and size distribution of colloids vary widely and so the population in each aquifer must be characterized separately. Inorganic constituents include weathering products such as Fe or Mn oxyhydroxides and clays as well as precipitates. Organic colloids include humic and fulvic acids, along with microorganisms. Small fragments of primary host rock mineral phases may also be included. Colloids have large surface areas for complexation and ion exchange reactions, and have been shown to effectively transport a variety of constituents. Colloids are often characterized operationally, especially when separation from large volumes is required for trace element analyses, and may contain a mixture of different active components, although bulk characteristics can be used to determine their overall importance to trace element transport. There are now various ultrafiltration separation techniques for separating sufficient quantities of colloids for trace element analyses from large volume samples (Buffle et al. 1992). Unfortunately, different techniques may separate different colloid populations due to differences in exclusion by size, shape, charge, or other characteristics, and a direct comparison between available methods using seawater samples (Buessler et al. 1996) found a significant range of results that cannot be clearly interpreted. Nonetheless, available data provide qualitative information on the importance of colloid transport in groundwaters.

A general review of actinide transport on colloids, and how this may relate to radionuclide transport studies, is provided by Ivanovich (1991). It has been found that colloids can carry a large fraction of U (Dearlove et al. 1991). Due to the greater reactivity,

Th is likely to be more efficiently carried by colloids, and it has indeed been found on colloids (Short and Lowson 1988). Porcelli et al. (1997, 2001) found that in an organic-rich river a significant fraction of U, and a greater fraction of Th, in colloids that likely included humic acids. Ra is not expected to be so strongly associated with humic acids, but may be readily attached to other colloids due to its strong affinity to surfaces. Overall, these associations of radionuclides with colloids can increase groundwater concentrations above those possible in the presence of smaller, dissolved ligands, or compete with host rock surface adsorption sites. In these cases, a controlling parameter in nuclide transport is the migration rate of the colloids (see review by Ryan and Elimelech 1996).

An important issue is whether there is continuing rapid and complete isotopic equilibration between colloids and other groundwater species, so that no isotopic differences are maintained. If this does not occur, and the colloidal species respond differently than dissolved components to processes such as adsorption, then the net effect is that the nuclides in groundwater cannot be described as a single population, violating a basic assumption of most models. In this case, colloid-bound nuclides must be considered separately and assigned exchange rates with other components. Some studies have found that low fractions of U were on colloids, with no isotopic difference from dissolved U, suggesting isotopic equilibrium occurs (see Osmond and Ivanovich 1992). No U isotopic differences were found in riverine U that was likely associated with humic acids, even as changes occurred along the river (Porcelli et al. (1997, 2001). Laboratory experiments also found that actinides uptake by humic groundwater colloids was reversible with changes in pH (Kim et al. 1992). In contrast, Dearlove et al. (1991) found that U on colloids in organic-rich groundwaters was not in isotopic equilibrium. Substantial differences were found in some samples from a sandy aquifer (Tricca et al. 2001), with higher $^{234}\text{U}/^{238}\text{U}$ ratios found in the colloids, indicating that the difference was not due to the presence of colloid-sized primary mineral fragments, which do not contain ^{234}U excesses. Since Th and Ra may be more closely associated with colloids than U, it is possible that isotopic differences between groundwater species may be found for these elements, although there is insufficient data available to quantify this.

Models of the systematics of the decay series nuclides generally have not considered the effects of colloid transport. If radionuclides associated with colloids are fully exchangeable with dissolved atoms, then the modeling of groundwater as a single component is valid, and colloids then may provide an explanation for observed increased groundwater concentrations and faster transport. Where rapid isotopic exchange does not occur, a separate component must be considered to account for isotopic variations in the groundwater. However, there is little data quantifying the isotopic composition of colloid-bound radionuclides, and so little basis for modeling isotopic exchange rates between colloids and dissolved species. This is clearly an area for future research.

2.2. Radon and the recoil rate of U-series nuclides

As a noble gas, ^{222}Rn in groundwater does not react with host aquifer surfaces and is present as uncharged single atoms. The radionuclide ^{222}Rn typically has the highest activities in groundwater (Fig. 1). Krishnaswami et al. (1982) argued that ^{222}Rn and all of the other isotopes produced by α decay are supplied at similar rates by recoil, so that the differences in concentrations are related to the more reactive nature of the other nuclides. Therefore, the concentration of ^{222}Rn could be used to calculate the recoil rate for all U-series nuclides produced by α recoil. The only output of ^{222}Rn is by decay, and with a 3.8 day half-life it is expected to readily reach steady state concentrations at each location. Each measured activity (i.e., the decay or removal rate) can therefore be equated with the input rate. In this case, the fraction released, or emanation efficiency, can be calculated from the bulk rock ^{226}Ra activity per unit mass;

$$b\varepsilon_{222}({}^{226}\text{Ra})_{\text{R}} = ({}^{222}\text{Rn})_{\text{W}} \quad (4)$$

where ε_{222} is the fraction of ${}^{222}\text{Rn}$ produced within the host rock that is released by recoil into groundwater, and b is the conversion factor to account for the ratio between the masses of host rock and groundwater (see Eqn. 1). Since $({}^{226}\text{Ra})_{\text{R}}$ generally can be measured or estimated (from an estimated ${}^{238}\text{U}$ concentration), a measurement of $({}^{222}\text{Rn})_{\text{W}}$ leads directly to a value for ε_{222} . The measured ${}^{222}\text{Rn}$ groundwater activities per unit mass that are obtained can correspond to ${}^{222}\text{Rn}$ release rates of up to $\sim 10\%$ of the amount being produced in the aquifer rock (Krishnaswami et al. 1982). This requires that $\sim 20\%$ of the ${}^{226}\text{Ra}$ in the host rock is within recoil distance of the surface. Such surprisingly high rates generally cannot be reached by recoil from typical size aquifer grains with uniform parent Ra concentrations. There are various possible causes for the high release rates, with different implications for the recoil of other nuclides. These include:

- *A dominant proportion of the ${}^{226}\text{Ra}$ is in small grains.* The size of the grains required to produce emanation rates of up to $\sim 10\%$ are several microns in diameter. This is generally below the typical size of U-bearing minerals in aquifers, although it is possible locally. In this case, the recoil into groundwater of other nuclides in the chain will be similarly high, subject to the scaling parameters discussed in Section 2.1.
- *A dominant proportion of the Ra is in secondary phases.* The concentration of parent ${}^{226}\text{Ra}$ in surface coatings and secondary phases is often considered the main cause of high emanation rates. For an emanation rate of $\sim 10\%$, up to 20% of the ${}^{226}\text{Ra}$ in the rock must be located in such sites. For many environments, there is no evidence for weathering of as much as 20% of a sedimentary aquifer to release the Ra and reprecipitate it onto remaining grains within the present geological environment. The redistribution is likely to have occurred during evolution of the source rocks, weathering, transport of sediment, or final deposition. Clearly, if this occurred at an age much greater than 10^3 years (and so much greater than the 1600 a half life of ${}^{226}\text{Ra}$), then the ${}^{226}\text{Ra}$ must be supported by ${}^{230}\text{Th}$, and if much greater than 10^5 years, then the ${}^{230}\text{Th}$ must be supported by ${}^{234}\text{U}$ and possibly also ${}^{238}\text{U}$. Therefore, the recoil rate of ${}^{222}\text{Rn}$ is related to the activity of other nuclides further up along the supported chain within the secondary phases. In order to determine how much of the chain is supported in these sites, and so which other radionuclides are similarly subject to the high recoil rates recorded by ${}^{222}\text{Rn}$, the time period for the development of these phases must be explicitly considered.
- *${}^{226}\text{Ra}$ adsorbed on surfaces can also supply ${}^{222}\text{Rn}$.* As described above, this would require weathering of a considerable fraction of the host rock. However, there may be circumstances where changing conditions can cause adsorption from Ra-rich waters that have transported ${}^{226}\text{Ra}$ into the aquifer from elsewhere, for example where brines that readily dissolve Ra mix with fresh groundwaters, resulting in a large increase in Ra partition coefficient and so extensive adsorption of the Ra from the brine (Moise et al. 2000; see below). In this case, the high ${}^{222}\text{Rn}$ recoil rates do not apply to other nuclides. However, this does not provide a general explanation for high ${}^{222}\text{Rn}$ recoil rates.
- *Leaching of nuclides implanted into adjacent minerals* has been suggested for the supply of ${}^{222}\text{Rn}$ into the vadose zone. Where there are intermittent undersaturated conditions, i.e., in soils or rocks where the water table lowers seasonally, the low stopping power of air allows atoms ejected from minerals to be implanted across pore spaces. These atoms will then be available for leaching

subsequently (Fleischer and Raabe 1978) and this has consequences for the seasonal supply of ^{222}Rn from soils and at the water table. This surface accumulation can also occur in minerals within low permeability rocks (Suksi and Rasilainen 1996). This raises the possibility that there are available pools of other nuclides in minerals from such rocks that have been eroded and incorporated into aquifer rocks within time periods comparable with the half-life of some nuclides. For example, sediments from the last glaciation may have an implanted near-surface pool of ^{226}Ra , ^{230}Th and ^{234}U that not only can provide high supply rates into surrounding groundwater of recoiled daughters, but can also be leached at a rate unrelated to present ^{222}Rn fluxes. However, this remains to be documented.

- *U and Th may be heterogeneously distributed within the aquifer.* In particular, these may be enriched in fine-grained clay layers or other aquicludes with very low hydraulic conductivities that are not part of the main water-bearing deposits considered in model calculations. If these materials are interspersed within the aquifer rocks, then there is the potential for ^{222}Rn to diffuse out into the main groundwater flow, while other radionuclides are retained by adsorption in the aquiclude. However, such a process may have restricted application due to the short half-life of ^{222}Rn , which limits the distance that may be travelled. Tadolini and Spizzico (1998) found that ^{222}Rn concentrations in an Italian limestone were also much higher than could be supplied by the host rock, and found that it was supplied by ^{226}Ra (presumably supported by ^{238}U) concentrated in nearby layers of detrital material. The migration from such deposits of ^{222}Rn and other radionuclides with high retardation factors but longer half lives has neither been modeled.
- *Diffusive transport in a hypothesized network of nanopores* has been suggested by Rama and Moore (1984) as a mechanism for transporting ^{222}Rn from across a large volume of a mineral to grain boundaries. The result is a high ^{222}Rn release rate that does not apply to other nuclides. High release rates of ^{220}Rn ($t_{1/2} = 1$ minute) have also been reported (Rama and Moore 1984; Howard et al. 1995) that would require even faster diffusive transport, although it is in the ^{232}Th chain, and so may be produced at different sites. Rama and Moore (1990a) found that high emanation rates were observed even from individual crystals that did not exhibit evidence for surface concentrations of parent nuclides. Further, Rama and Moore (1990b) showed that ^{220}Rn diffusion through mineral slabs was uneven, and suggested that this reflected nanopore geometry. Similarly, Andrews and Wood (1972) suggested that ^{222}Rn migrates along dislocation planes and grain boundaries in wall rocks. However, other experiments have not found evidence for such nanopores. Hussain (1995) found in experiments that the activity of ^{212}Pb in water surrounding monazite and zircon grains was not enhanced by rapid escape of its parent ^{220}Rn compared to that of its precursor ^{224}Ra in the ^{232}Th chain. Copenhagen et al. (1993) measured similar recoil rates of ^{222}Rn and ^{224}Ra from core samples. Krishnaswami and Seidemann (1988) found that Ar isotopes produced throughout sample grains during irradiation did not leak out along with ^{222}Rn , suggesting that ^{222}Rn was not released by interconnected pores available to both Ar and Rn. Overall, more direct evidence of the widespread presence of nanopores is required to substantiate this mechanism.

Mathematical treatments of ^{222}Rn release from minerals have been developed (Semkow 1990; Morawska and Phillips 1992), although these are only useful once the

issues listed above are resolved. Clearly, additional work is required before a more definitive statement is made about the existence of nanopores. However, it is likely that different features will control the recoil flux of the nuclides for different lithologies and local geological histories, and it will be necessary to investigate the various possibilities at each study site. As discussed above, the ^{222}Rn release rate cannot be simply extrapolated to all other parent nuclides. It should be emphasized that, as discussed further in subsequent sections, ^{222}Rn measurements are often used for obtaining the emanation efficiencies of other radionuclides, which in turn are critical for deriving key parameters for the behavior of these species. Where the ^{222}Rn emanation efficiency obtained from ^{222}Rn measurements can be shown to be compatible with that deduced from the geometry of U- and Th-bearing mineral grains, then a generalized recoil rate obtained from ^{222}Rn may be justified. However, this information necessary to confirm this is often not available. Also, high ^{222}Rn release rates due to preferential siting of ^{226}Ra in secondary sites seems most plausible at present, although this does not always necessarily imply that ^{230}Th , ^{238}U , or ^{232}Th are also in such locations, and the possibility that ^{222}Rn is preferentially released from mineral phases relative to all other radionuclides by diffusion in nanopores or by some other mechanism remains. Where the assumption that all radionuclides are recoiled at the same rate is not correct the model equations are not invalidated, but rather require different input values for ϵ_i . Some calculated results do not depend upon radionuclide recoil rates relative to that of ^{222}Rn and so are unaffected by these considerations.

2.3. Ra isotopes

There are four naturally occurring isotopes of Ra; ^{228}Ra ($t_{1/2} = 5.8$ a) and ^{224}Ra (3.7 d) in the ^{232}Th series, ^{226}Ra (1600 a) in the ^{238}U series, and ^{223}Ra (11.7 d) in the ^{235}U series (Table 1). The data for ^{223}Ra are more limited, since it is generally present in low concentrations due to the low abundance of ^{235}U . The differences in half lives and the connections across the different decay series have been used to infer a variety of groundwater and water-rock interaction features. For the short-lived Ra isotopes, the dominant input term to groundwater is recoil, rather than weathering, and steady state concentrations are often achieved (see Section 2.2).

Behavior of Ra in groundwater. The general behavior of Ra has been examined under laboratory conditions and in various environments (see Osmond and Cowart 1992). A major goal of field studies of Ra isotopes have aimed at obtaining bulk, *in situ* values of adsorption rates and so the retardation factors. Note that Ba serves as a very close chemical analogue to Ra but is typically 10^7 times more abundant, and so its behavior is related to that of Ra.

The speciation of Ra is reviewed by Dickson (1990). In low salinity solutions, Ra occurs as uncomplexed Ra^{2+} , while significant complexing as RaSO_4 , RaCO_3 , and RaCl^+ will only occur in brines with high concentrations of the respective inorganic ligand. Organic complexing has not been considered to be significant in groundwaters (Dickson 1990). It is possible that colloid and particulate transport on clays and iron hydroxides may have a role in Ra transport, although this has not been widely documented. The solubility limit of Ra compounds is generally not reached, but Ra can be precipitated in solid solution within Ca and Ba minerals. For example, in deep brines of the Palo Duro Basin, saturation of sulfate minerals such as barite and gypsum controls dissolved Ra concentrations (Langmuir and Melchior 1985), and Langmuir and Riese (1985) found Ra is incorporated into barite without substantial Ra/Ba fractionation from the groundwater ratio. While Andrews et al. (1989) suggested that calcite precipitation controls dissolved Ra in the Stripa granite based on a correlation between Ra and Ca, Gnanapragasam and Lewis (1991) found that the Ra/Ca ratio in precipitated calcites is $\sim 10^{-2}$ times the value

for the source solution, and so calcite is less likely to be a common control on Ra concentrations.

Adsorption exerts a strong control on Ra in dilute groundwater. Adsorption constants are strongly dependent upon the type of substrate, solution composition (e.g., Eh, pH, and other cations), and temperature (see Benes 1990). Decreases in adsorption have been observed due to increases in salinity (e.g., Zuckin et al. 1987; Krishnaswami et al. 1991; Sturchio et al. 2001). Reasons suggested for this include competition by other, abundant cations for available adsorption sites, increases in mineral surface charge (Mahoney and Langmuir 1991), increases in the stability of inorganic complexes (Hammond et al. 1988), and the presence of strong organic complexes (Langmuir and Riese 1985; Molinari and Snodgrass 1990). Where there are strong changes in groundwater salinity, e.g., by mixing, Ra may be deposited on aquifer surfaces and so may be a local source of ^{222}Rn (Moise et al. 2000).

Initial inputs to groundwater can occur due to weathering in the vadose zone. There are few data for Ra in natural soils (e.g., not impacted by mining wastes) and Frissel and Köster (1990) have reviewed what is known of the mobility in soils of Ra. Partitioning onto soil solids is quite strong, but it is not uniform and is hard to predict due to the effects of precipitation reactions, bioturbation, and varying distributions of organic matter and clays. Groundwater characteristics will reflect vadose zone inputs for some distance below the water table depending upon the half-life of the isotopes (Tricca et al. 2000).

Isotope systematics. There are two Ra isotopes in the ^{232}Th series, which is shown in Figure 3, and determining the behavior of these Ra isotopes requires consideration of the closely related Th isotopes as well. The factors affecting the groundwater concentrations of each relevant nuclide in the series are:

- ^{232}Th . The ^{232}Th within the mineral phases produces ^{228}Ra that is ejected by recoil. Any ^{232}Th that has been released by weathering will be largely on the surface, and will produce ^{228}Ra that will be recoiled back into the mineral or into groundwater. Note that there is generally no a priori way of determining the amount of ^{232}Th that is not in the mineral, although this might be calculated from both the amount of ^{232}Th in the water that is exchanging with the surface reservoir, and the distribution factor obtained from Th isotope systematics (Luo et al. 2000; see Section 2.4).
- ^{228}Ra . The ^{228}Ra in the water is largely supplied by the ^{232}Th in the minerals and on the surfaces, and since it is strongly adsorbed exchanges with a much larger surface reservoir.
- ^{228}Th . ^{228}Ra decays by low energy beta decay to the short-lived ^{228}Ac (with a half life of 6 hours), which rapidly decays to ^{228}Th . It is generally assumed that the behavior of ^{228}Ac , due to its short lifetime, does not affect the subsequent supply of ^{228}Th , and so ^{228}Ac is ignored. Since the decays of both ^{228}Ra and ^{228}Ac are low energy, there is no release of ^{228}Th from the mineral by recoil. Consequently, the ^{228}Th in the surface is supplied only by decay of the parent ^{228}Ra reservoir already there, and the amount in groundwater is determined by interchange with the surface. This therefore directly connects the mobile abundances of ^{228}Th and ^{228}Ra .
- ^{224}Ra . The amount in groundwater is largely supplied by recoil from ^{228}Th in the host rock minerals, as well as ^{228}Th on the mineral surfaces (which in turn was supplied by ^{228}Ra that was recoiled from the mineral as well as possibly from ^{232}Th on surfaces).

Note that surface and groundwater nuclides can be considered together as the mobile pool (see Ku et al. 1992; Luo et al. 2000), with the Th and Ra isotopes largely residing at the surface. The supply to this pool is by recoil; weathering for short-lived nuclides can be neglected (see Section 2.2), although it is the source of any ^{232}Th that is outside the host minerals.

The main factors that have been considered in calculating Ra nuclide abundances in the surface and groundwater are as follows:

- Since ^{228}Ra and ^{224}Ra are both produced by recoil from the host mineral, it might be assumed that the production rates are equal. However, the relative recoil rates can be adjusted by considering that the parent nuclides near the mineral surface may not be in secular equilibrium due to ejection losses; i.e., the activity of ^{228}Th may be lower than that of ^{232}Th due to recoil into groundwater of the intermediate nuclide ^{228}Ra . Krisnaswami et al. (1982) calculated that the recoil rate of ^{224}Ra is 70% that of ^{228}Ra if radionuclides are depleted along the decay chain in this way.
- Taking into account the decay of nuclides on the surfaces, the ^{224}Ra on both surfaces and in the groundwater is supplied by two recoil events; directly from the mineral, and indirectly through the supply of ^{228}Ra . Note that not all ^{228}Ra may lead to mobile ^{224}Ra , since some ^{228}Th is recoiled back into the mineral.
- There may be mobile ^{232}Th that supplies ^{228}Ra directly, and so also ^{224}Ra indirectly. Note that there are few ^{232}Th data available, and this flux is often assumed to be insignificant.

The Ra isotopes in the other decay series can be evaluated similarly. ^{226}Ra in the ^{238}U series (Table 1) is the product of the third α decay, and so the effects of near-surface depletion or decay of recoiled precursors must be calculated accordingly. ^{223}Ra in the ^{235}U series is also the product of the third α decay. Further processes that may be considered where circumstances warrant include nonsteady state conditions or removal by precipitation at rates that are fast compared to the decay rate of the Ra nuclides.

^{226}Ra abundances. Activities of ^{226}Ra per unit mass in groundwater vary widely. Fresh groundwaters typically have on the order of 1-2 dpm/L (e.g., King et al. 1982). Saline groundwaters, by contrast, have much higher concentrations that correlate with salinity (e.g., Krishnaswami et al. 1991). This is compatible with the much lower partitioning of Ra onto surfaces in such waters. While the shorter-lived isotopes will generally adjust to local conditions over short distances, ^{226}Ra , with a much longer half-life than the other Ra isotopes, requires a much longer distance along a flowline to achieve a steady state groundwater concentration. This is reached once the recoil rate from host minerals in a volume of aquifer is equal to the activity (i.e., decay rate) of the ^{226}Ra in both the groundwater and on the surfaces (that is, the supply rate to the mobile pool is equal to the decay rate). The distance over which this occurs depends upon the fraction adsorbed, the groundwater flow rate, and the recoil rate (Section 2.1), and may occur within a km (Tricca et al. 2000). Therefore, ^{226}Ra concentration gradients may be found over greater distances than those of the other Ra isotopes, but still close to abrupt changes in groundwater chemistry.

$(^{226}\text{Ra}/^{228}\text{Ra})$ ratios. This ratio in the groundwater is dependent upon the $(^{238}\text{U}/^{232}\text{Th})$ ratio of the host rock, and so provides information on the relative recoil rates of nuclides from the two decay series. Supply to the groundwater by recoil produces $(^{226}\text{Ra}/^{228}\text{Ra})$ ratios up to 1.75 times that of the rock due to accumulation in the mobile pool of preceding nuclides (Davidson and Dickson 1986). The average upper crust has a

($^{238}\text{U}/^{232}\text{Th}$) activity ratio of ~ 0.8 (equivalent to a Th/U weight ratio of 3.8), and this is often taken to represent that of the host rocks in the absence of direct measurements, although this can of course be substantially different in rocks such as limestones or other sedimentary deposits. If it is assumed that the groundwater profile is in steady state, that weathering and precipitation are not important for these nuclides, and that the parent nuclides ^{230}Th and ^{232}Th have similar behaviors, then the corresponding terms in Equation (1) can be ignored. Assuming further that the desorption rate is fast compared to the Ra half lives, then the ($^{226}\text{Ra}/^{228}\text{Ra}$) ratios in the groundwater and adsorbed on surfaces (and so in the mobile Ra pool) are equal. In this case, the measured groundwater ($^{226}\text{Ra}/^{228}\text{Ra}$) ratio reflects the ratio of the supply rates of ^{226}Ra and ^{228}Ra , which is equal to the ($^{238}\text{U}/^{232}\text{Th}$) rock ratio, adjusted for any differences in the distributions of ^{238}U and ^{232}Th and the depletion of ^{230}Th relative to ^{232}Th due to recoil along the ^{238}U decay chain. Luo et al (2000) found ($^{226}\text{Ra}/^{228}\text{Ra}$) ratios of 0.34 to 1.4 in a basaltic aquifer, compared to a bulk rock ($^{238}\text{U}/^{232}\text{Th}$) value of 0.9, and the variation may be due to different distributions of U and Th producing different relative recoil rates, either reflecting different amounts adsorbed onto surfaces (Luo et al. 2000) or within the host rock. The values found by Tricca et al. (2001) in a sandy aquifer of 0.3 to 0.9 are low compared to the likely (but unmeasured) ($^{238}\text{U}/^{232}\text{Th}$) ratio of the host rock and may reflect variable losses of Th in the depositing sediments relative to source rocks due for example to sorting of heavy minerals. Local variations are also possible due to changes in supply or adsorption characteristics along a groundwater flow line followed by a much slower return to steady state along the flow line by longer lived ^{226}Ra .

Sturchio et al. (2001) found ($^{226}\text{Ra}/^{228}\text{Ra}$) ratios in carbonate aquifers in the central US largely within the range of 1.3-10 (with a complete range of 0.7-17) that generally coincides with the range in the aquifer rocks. There is a strong correlation between concentrations of ^{226}Ra and total dissolved solids, as well as of Ca, Sr, and Ba, and some fluids are saturated with calcite and barite. The highest ^{226}Ra concentrations are up to 6 times that found in the host rock, and it was suggested that this is due to the supply of ^{226}Ra by ^{230}Th enrichments on surfaces. However, concentrating so much ^{230}Th by local weathering is implausible, and this Th is likely derived from layers with higher U concentrations.

($^{224}\text{Ra}/^{228}\text{Ra}$) ratios. As members of the same decay series, these Ra isotopes are the most closely related and differences in groundwater activity ratios cannot be ascribed to differences in aquifer rock distributions of ^{238}U and ^{232}Th . Within host rocks that are in secular equilibrium, ($^{224}\text{Ra}/^{228}\text{Ra}$) = 1. Reported values for fresh groundwaters fall in a narrow range, with 0.5-2.1 reported for a sandy aquifer (Tricca et al. 2001), 1.0-2.2 (and one high value of 4.2) for a basaltic aquifer (Luo et al. 2000), and 0.8-1.8 for arkose and glacial drift (Krishnaswami et al. 1982). Much higher values have also been reported (e.g., Davidson and Dickson 1986; Krishnaswami et al. 1991). Various reasons have been discussed for values that are different from the host rock production ratio. Krishnaswami et al. (1982) calculated a ratio of 0.67 due to progressive depletion along the decay series at grain boundaries, and 1.2 if ^{228}Ra and ^{228}Th are adsorbed onto surfaces and continue to supply daughters into the groundwater. Davidson and Dickson (1986) considered the recoiled ^{228}Ra , strongly adsorbed, to be a source of ^{228}Th (with 50% recoiled into solution) and so ^{224}Ra , so that steady state values in groundwater should be ($^{224}\text{Ra}/^{228}\text{Ra}$) = 1.5 (see also Luo et al. 2000). Another process is therefore required to explain the highest measured ratios, and some variations may be due to redistribution of ^{228}Th . There are also several effects to be considered due to the much shorter half-life of ^{224}Ra . Along a flowline, ^{224}Ra will reach a steady state concentration more rapidly than ^{226}Ra , and so higher values of ($^{224}\text{Ra}/^{228}\text{Ra}$) will be observed in recently recharged waters (Davidson and Dickson 1986; Tricca et al. 2000), or immediately downgradient of Ra

precipitation (Sturchio et al. 1993). Also, ^{224}Ra may decay within the surface layer at a rate comparable to the desorption rate, resulting in a lower effective partitioning value for ^{224}Ra over ^{228}Ra (Eqn. 3; Krishnaswami et al. 1982). In general, it appears that unusually high values are due to circumstances where steady state conditions have not been reached, while smaller variations are due either to the recoil loss and redistribution of ^{228}Th or decay of ^{224}Ra on surfaces where desorption rates are relatively long.

($^{224}\text{Ra}/^{222}\text{Rn}$) ratios. A comparison between Ra and Rn isotopes can be made when the recoil supply rates are related to one another. Notwithstanding the range of possible mechanisms for Rn release (see Section 2.2), if it is assumed that measured ^{222}Rn concentrations provide values for the emanation efficiency of all radionuclides, with the adjustment for the rock ($^{238}\text{U}/^{232}\text{Th}$) ratio, then the ($^{224}\text{Ra}/^{222}\text{Rn}$) ratio can be used to obtain a value for the partition coefficient of Ra. The concentrations of ^{224}Ra , along with ^{222}Rn , are generally expected to be in steady state due to their short half lives. In this case, the total activity of mobile ^{224}Ra in a volume of aquifer (that is, ^{224}Ra in solution and adsorbed, which is equal to $(1 + K_{226\text{Ra}})(^{226}\text{Ra})_w$) and so is equal to the recoil supply rate of ^{224}Ra , and the total activity of ^{222}Rn in solution (with none adsorbed) is equal to the recoil supply rate of ^{222}Rn . While the ($^{224}\text{Ra}/^{222}\text{Rn}$) ratio for the mobile pool is then equal to the ratio of the emanation rates, which is then equal to $(^{224}\text{Ra}/^{222}\text{Rn})/K_{224\text{Ra}}$. Although typical bulk rock ($^{238}\text{U}/^{232}\text{Th}$) activity ratios are close to one, so that the recoil rates of ^{224}Ra and ^{222}Rn are similar, the ratio of the recoil supplies of ^{222}Rn and ^{224}Ra might be somewhat different due to different distributions between ^{238}U and ^{232}Th , and this can be confirmed using the ($^{226}\text{Ra}/^{228}\text{Ra}$) ratios (see above). Also, ^{222}Rn is further down its decay series and is preceded by 4 α decays, while ^{224}Ra is preceded by 2, and so ^{222}Rn production may be 50% higher due to precursors accumulated on surfaces. Measured ranges of $^{224}\text{Ra}/^{222}\text{Rn}$ ratios in fresh groundwaters of $(0.5-2.2) \times 10^{-4}$ (Tricca et al. 2001), $(0.8-1) \times 10^{-4}$ (Luo et al. 2000), and $(0.2-4.4) \times 10^{-4}$ (Krishnaswami et al. 1982) somewhat surprisingly coincide, indicating that the partitioning of Ra onto host surfaces are similar despite the contrasting lithologies. The corresponding partition coefficients are 10^3-10^4 . Some variation may be due to desorption rates that are comparable to the decay constant of ^{224}Ra . By comparing ($^{224}\text{Ra}/^{228}\text{Ra}$) and ($^{224}\text{Ra}/^{222}\text{Rn}$) ratios, Krishnaswami et al. (1982) calculated sorption rates of $3-20 \text{ min}^{-1}$ using Equation (3), and clearly similar values can be obtained for each of the other datasets. Higher $^{224}\text{Ra}/^{222}\text{Rn}$ ratios have been found in saline groundwaters (Krishnaswami et al. 1991), consistent with the reduced absorption in these waters.

Luo et al. (2000) used a somewhat different method for determining the partitioning of Ra by noting that ^{222}Rn is produced by the total amount of ^{226}Ra both in solution and on surfaces (and so equal to $(1 + K_{226\text{Ra}})(^{226}\text{Ra})_w$) as well as by recoil. ^{224}Ra is produced similarly by ^{228}Ra (through the beta decay of ^{228}Th) from within the minerals and from the surface. Combining the respective equations (by assuming that the recoil rates for ^{238}U series nuclides and ^{232}Th series nuclides are proportional to the ($^{238}\text{U}/^{232}\text{Th}$) ratio of the bulk rock), values for the recoil of ^{224}Ra that are 0.1-0.2 that of the ^{222}Rn flux were calculated, compared to a value of 0.3 expected by assuming that there was no ^{238}U and ^{232}Th (and associated daughters) on surface sites. This difference does not significantly change the calculated Ra partition coefficients that can then be obtained from ^{226}Ra or ^{224}Ra , but it implies that there is a significant production of radionuclides above that from recoil from ^{238}U in the host mineral alone, and requires a substantial budget of U on mineral surfaces (see Section 2.5).

($^{223}\text{Ra}/^{226}\text{Ra}$) ratios. Since ^{235}U and ^{238}U are present in constant proportions everywhere and so are located in the same locations, there are no fractionations between their decay series due to siting in the host rock. ^{223}Ra and ^{226}Ra are both generated after 3

α decays, and so waters should have a ratio similar to the rock ($^{235}\text{U}/^{238}\text{U}$) activity ratio of 0.046. Where ^{226}Ra has not reached a steady state concentration in a flowing groundwater after recharge or precipitation due to its longer half-life, higher ratios may be found locally (Davidson and Dickson 1986; Martin and Akber 1999).

Martin and Akber (1999) looked at a confined aquifer of weathered and fresh bedrock below the Ranger U mine in Australia that apparently has not been significantly impacted by mine tailings. ($^{223}\text{Ra}/^{226}\text{Ra}$) ratios substantially above the rock value of 0.046 were found in samples that were saturated in barite and suggested this was due to precipitation of both Ra isotopes, followed by more rapid return to steady state of the shorter-lived isotope, creating higher ($^{223}\text{Ra}/^{226}\text{Ra}$) ratios near the sites of precipitation that progressively drop off as ^{226}Ra is added. This data therefore could be used to calculate how much ^{226}Ra was precipitated. An interesting observation at the site was the presence of some low ($^{223}\text{Ra}/^{226}\text{Ra}$), as well as ($^{224}\text{Ra}/^{228}\text{Ra}$), ratios that might be explained by the transport to the site of a substantial fraction of the longer lived Ra on colloids and without rapid exchange with dissolved Ra. This allowed a greater concentration of ^{226}Ra and ^{228}Ra to be maintained against more efficient removal of dissolved Ra that contained a greater proportion of the ^{223}Ra and ^{224}Ra .

Summary. Ra isotopes can provide information regarding the supply of ^{238}U series nuclides relative to those of ^{232}Th series, and indicate where significant changes in adsorption or parent element distribution occur along groundwater flow paths. Values for Ra partitioning coefficients, and so retardation factors, can be obtained, but only by assuming that ^{222}Rn provides a reasonable measure of recoil supply of Ra isotopes. In this way, values of 10^3 - 10^4 for K_{Ra} have been calculated for a range of aquifer lithologies. This is an important result, as it suggests that under natural conditions, low concentrations of Ra will migrate at rates of 10^{-3} - 10^{-4} times that of the groundwater, and so is significantly retarded by adsorption. Different studies have used different methods to calculate precise values, based on assumptions regarding the relationship between recoil supplies of the different isotopes. The simplest approach for calculating retardation factors is based on ($^{222}\text{Rn}/^{224}\text{Ra}$) ratios, although ^{224}Ra data is not always available and more complex calculations can be used with further assumptions. An important issue is how high can Ra concentrations be elevated without changing adsorption rate constants, and how variations in other factors that may accompany releases of anthropogenic nuclides (e.g., pH, or concentrations of other solutes and colloids) affect Ra adsorption. In regions where saline waters occur, mixing and precipitation processes may result in waters that do not have steady state concentrations, and Ra evolutions become more complicated (e.g., Moise et al. 2000). Detailed profile data in these areas can potentially provide more Ra transport information, although care must be taken that changes in values for all input parameters (such as adsorption rates due to changes in adsorbing surface area) is considered. It should be emphasized that while the conclusion that Ra is strongly adsorbed is compatible with laboratory data (e.g., Ames et al. 1983), the values obtained in radionuclide transport models are based on the assumption that measured ^{222}Rn concentrations provide a reasonable measure of the recoil rate of other nuclides in the decay series. While this is plausible (see Section 2.2), the thorough investigation of other possibilities that might lead to significant changes in these values (up to a factor of 10) is still required, although the conclusion that Ra is strongly adsorbed at the freshwater locations studied will likely not be affected.

2.4. Th isotopes

The isotopes of Th certainly have the widest range of half-lives, from the decay series parent ^{232}Th (1.39×10^{10} a half life) and the relatively long lived ^{230}Th (7.52×10^4 yrs) to a short-lived isotope in each of the decay series: ^{234}Th (24 days), ^{227}Th (18 days),

and ^{228}Th (1.9 years). Unfortunately, there are few data for ^{227}Th , which is a part of the less abundant ^{235}U chain, and the long-lived Th isotopes have not been explored as much as the others due to lower activities, and so difficulties in obtaining precise measurements.

Behavior of ^{232}Th in groundwater. ^{232}Th can only be released from aquifer minerals by weathering, and the presence of ^{232}Th in groundwaters throughout aquifers despite strong removal processes indicates that continuous release occurs. Th concentrations in waters are generally very low due to the low solubility of thorianite (ThO_2) and strong sorption properties. While very little data has been available, it is clear that Th is highly reactive with mineral surfaces, and is much more strongly sorbed than U. In natural waters, it is present only in the tetravalent form. Langmuir and Herman (1980) have calculated the solubility and speciation of Th in groundwaters. Above a pH of 5, the dominant species is $\text{Th}(\text{OH})_4$ in pure water, but is $\text{Th}(\text{HPO}_4)_3$ between 5 and 7 where phosphate is available. Data for EDTA suggests that complexing with organic ligands can increase Th solubility. Solubilities calculated by Langmuir and Herman (1980) for possible groundwater compositions are shown in Figure 5. Available ^{232}Th data include those for saline groundwaters from Missouri carbonates and sandstones of (0.1-9.1) pg/g (Banner et al. 1990) and a similar range for a basaltic Idaho aquifer in the Snake River plain of (0.1-11.5) pg/g (Luo et al. 2000). An unconsolidated unconfined sandy Long Island aquifer in New York has comparable values of (0.01-11.5) pg/g but one sample from the underlying, oxygen-poor (but still oxic) sandy Magothy aquifer has a much higher concentration of 90 pg/g (Tricca et al. 2001). Values from a bedrock spring (7 pg/g) and from within overlying tills (8-27 pg/g) from Sweden are comparable

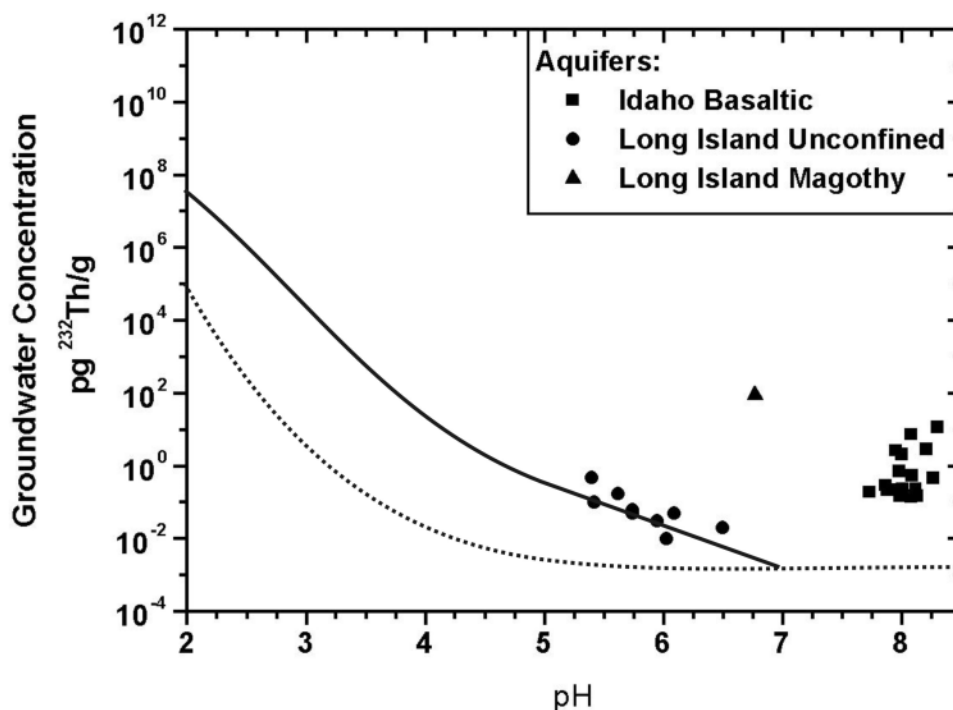


Figure 5. Concentrations of ^{232}Th and pH are shown for groundwaters from a basaltic aquifer (■ Luo et al. 2000), a sandy unconfined (●) and underlying confined (▲) aquifer (Tricca et al. 2001). The dotted line is the solubility of thorianite in pure water, and the solid line is for the presence of typical inorganic ligands (Langmuir and Herman 1980). In the pH range for the samples, phosphates are the dominant inorganic ligands, although there is no phosphate data available for the samples to calculate actual solubility limits. Groundwater concentrations above the solubilities shown can be attained in the presence of organic compounds or colloids.

(Porcelli et al. 2001). All of these data are above the solubility of thorianite in pure water. The unconfined Long Island aquifer data are inversely correlated with pH and fall along the solubility curve for inorganic ligands in a model groundwater composition in Fig. 5 (Langmuir and Herman 1980). However, the phosphate concentrations are not available for these samples, and so actual saturation indices for these samples cannot be calculated. Therefore, it is possible that there are other pH-dependent controlling factors, such as adsorption. Also, a significant proportion of the U in these unconfined Long Island waters is associated with colloids (of unidentified nature), and while there are no colloid data available for Th, it is likely that an even greater proportion of Th is associated with the colloids (Ivanovich et al. 1992a) and so present in the groundwater above inorganic solubility limits. While the high concentrations found in both the Magothy and basaltic aquifers might be ascribed to organic complexing, the samples in all of these studies have been filtered only for particles ($\sim 0.5 \mu\text{m}$), and so the effect of colloids cannot be evaluated. It should be noted that the Magothy also has elevated Fe concentrations, and where this aquifer has been sampled elsewhere, such high Fe concentrations were present as suspended Fe(III) oxyhydroxides (Langmuir 1969), so that these may be important colloid carriers of actinides. The Th/U ratio of this water is similar to that estimated for the host rock (Tricca et al. 2001), suggesting that any transporting colloids did not substantially fractionate the two actinides. The uptake of Th on colloids has been studied in the laboratory by Lieser and Hill (1992).

Modeling the concentrations of ^{232}Th in groundwater involves considering the influx by weathering and the interactions with the host aquifer by sorption and precipitation. If concentrations are indeed limited by thorianite solubility, then since Th is also strongly adsorbed, sufficient Th has been released by weathering to have also reached steady state sorbed concentrations as well. This implies that the rate of any irreversible incorporation of sorbed Th (e.g., by recrystallization of sorbing Fe phases) is slow compared to the supply by weathering so that the groundwater concentrations are maintained at the solubility limit. However, in regions where changing conditions create lower solubility limits, removal by precipitation can occur. In modeling of ^{232}Th concentrations by considering only weathering and adsorption, steady state concentration profiles are achieved that increase linearly along a flow line, regardless of the distribution coefficient between water and surfaces (Tricca et al. 2001). A consequence of this is that groundwater ($^{232}\text{Th}/^{238}\text{U}$) ratios then reflect the relative weathering input rates rather than differences in chemistry; in this case, the ^{232}Th weathering supply is typically orders of magnitude lower than that of ^{238}U . This of course implies very different siting of these elements. However, these profiles presuppose that steady state concentrations have been reached at each location, weathering and adsorption parameter values are constant along the flow path, Th solubility limits have not been reached, Th and U are not irreversibly bound on colloids, and Th and U are not removed by irreversible adsorption (see Section 2.5). Since such linear profiles of either ^{232}Th or ^{238}U are generally not observed, these assumptions commonly are not applicable.

The distribution of ^{232}Th is not controlled by decay processes that can be used to constrain its supply rate, but the ^{232}Th - ^{228}Ra pair can be used to provide some constraints on Th adsorption. In an area where ^{228}Ra concentrations are constant, mobile ^{228}Ra is supplied by only recoil and decay of mobile ^{232}Th . The amount of ^{232}Th that is adsorbed on surfaces can be obtained if the amount of mobile ^{228}Ra is constrained (i.e., the Ra partition coefficient and the groundwater concentration are known) and can be compared to an estimate of the recoil rate of ^{228}Ra (using the measured ^{222}Rn activity in the groundwater) from the host rock. In this way, Luo et al. (2000) calculated that recoil from the host rock was insufficient to explain the amount of mobile ^{228}Ra , and argued that adsorbed ^{232}Th provided much of the mobile ^{228}Ra ; then ^{232}Th partition coefficients can

be obtained from the amount of measured groundwater ^{232}Th and the amount adsorbed, and these partition coefficients can be compared with those of other Th isotopes (see below). Note that this assumes not only that ^{222}Rn represents the recoil flux of ^{232}Th series nuclides (adjusted for the rock Th/U ratio), but also that the additional fluxes of ^{228}Ra are due to mobile ^{232}Th that freely exchanges with groundwater ^{232}Th .

^{228}Th and Th retardation factors. ^{228}Th is distinctive in being produced by low energy β decay, from ^{228}Ra . As can be seen in Figure 3, where advection is not important the steady state activity per unit aquifer mass of mobile ^{228}Ra and that of ^{228}Th should be equivalent. In this case, $(^{228}\text{Th})_{\text{w}}R_{228\text{Th}} = (^{228}\text{Ra})_{\text{w}}R_{228\text{Ra}}$ (where $R_{\text{I}} = K_{\text{I}} + 1$). Therefore, the value of the ratio of the retardation factors $R_{228\text{Ra}}/R_{228\text{Th}}$ is the inverse of the measured groundwater $(^{228}\text{Th}/^{228}\text{Ra})$ ratio (Luo et al. 2000). Groundwater values of $(^{228}\text{Th}/^{228}\text{Ra}) = (0.6-8) \times 10^{-2}$ (Luo et al. 2000), $(2-5) \times 10^{-2}$ (Ivanovich et al. 1992b), and $(5-20) \times 10^{-2}$ (Tricca et al. 2001) indicate that Th is generally adsorbed 10^1 - 10^2 times more efficiently than Ra, with the largest difference in the basaltic aquifer of Luo et al (2000). Note that this is based largely on the assumption that ^{228}Th is not supplied from the host minerals, and although this has not been confirmed experimentally it appears to be a reasonable assumption. In this case, these relative adsorption values are reasonably well constrained. Where the value for Ra can be obtained (based on the assumption that ^{222}Rn provides a measure of the recoil input of Ra isotopes), a value for Th can be obtained. If the retardation factor of Ra is 10^4 (see Section 2.3), then that of Th appears to be typically $\sim 10^6$.

It should be noted that the ^{232}Th data raises questions about whether Th is saturated or colloid-bound. Saturation will be dictated by the concentration of ^{232}Th . The other, shorter-lived Th isotopes are present in molar concentrations that are typically over 10^5 times lower than that of ^{232}Th , and so separate additions of these nuclides will likely be absorbed through isotopic exchange with the surfaces, rather than by triggering increased precipitation. Therefore, except under the unusual circumstance of large additions of ^{232}Th , the precipitation rate is unlikely to be a dominant flux for the other isotopes. Colloids will only be a factor where nuclides are rapidly irreversibly incorporated and so exhibit different exchange behavior with the host rock than dissolved species. Where colloids are composed of secondary phases from the wall rock that reversibly adsorb nuclides, or include organic compounds that allow continuous exchange with dissolved species, the presence of colloids will not affect modeling calculations. However, as discussed in Section 2.1, colloids may control the value of the calculated partition coefficients.

^{234}Th and sorption rate constants. The concentrations of ^{234}Th are highly variable with respect to those of parent ^{238}U , with $(^{234}\text{Th}/^{238}\text{U}) = (0.7-7) \times 10^{-2}$ where U contents are high (Luo et al. 2000) to 0.1-14 where U concentrations are generally much lower (Copenhaver et al. 1993; Tricca et al. 2001). This range reflects the very different controls on U and Th chemistry. The ^{234}Th concentrations have been used to calculate Th sorption coefficients. Krisnaswami et al. (1982) calculated adsorption rates by neglecting the desorption rate; while the $(^{234}\text{Th}/^{238}\text{U})$ ratio would be greater than 1 in the absence of adsorption due to not only *in situ* decay of ^{238}U but also by recoil, the much lower measured ratios reflect the rapid adsorption of ^{234}Th relative to the ^{234}Th decay constant (which controls how the ^{234}Th activity would reach steady state without adsorption). In this case, adsorption rates of minutes were obtained. With a partition coefficient of 10^6 , this corresponds to a desorption rate of \sim month. Partition coefficients can be calculated from Equation (3) when the Th desorption coefficient is comparable to at least one half-life. Values of $(^{234}\text{Th}/^{228}\text{Th})$, both of which are supplied by one α recoil, should be equal to the $(^{238}\text{U}/^{232}\text{Th})$ ratio of the rock and generally close to one if desorption were very fast. Higher values of 6-230 (Luo et al. 2000) and 2-7 (Tricca et al. 2001) are plausibly

due to sorption rate constants comparable to the half-life of the shorter-lived ^{234}Th . Note that the alternative explanation, that ^{232}Th is distributed near surfaces preferentially to ^{238}U , is contrary to the ($^{226}\text{Ra}/^{228}\text{Ra}$) ratios, which suggest that U series nuclides are more readily supplied (see Section 2.3). Luo et al. (2000) used model equations to calculate progressively smaller partition coefficients for ^{232}Th , ^{228}Th , and ^{234}Th . Note that the ^{232}Th values were calculated from ^{228}Ra groundwater concentrations and using ^{222}Rn from the recoil flux, and assuming that the ^{232}Th in the groundwater was not bound irreversibly in colloids (see above). In this case, ^{232}Th provides the Th partition coefficient when sorption dominates over decay. By combining values for K_1 for the other Th isotopes, adsorption coefficients of $0.1\text{--}4.1\text{ min}^{-1}$, and desorption coefficients of $0.8\text{--}2.5\text{ yr}^{-1}$ were obtained (Luo et al. 2000). Copenhaver et al. (1993) found adsorption coefficients of $0.01\text{--}4.6\text{ min}^{-1}$, with the lowest values for sandy deposits. Tricca et al. (2001) assumed that the desorption rate constant was much less than the decay constant of ^{228}Th , and that the total recoil supply of ^{234}Th is known from ^{222}Rn concentrations, and obtained substantially lower values for the partition coefficient of $\sim 10^3$. Tricca et al. (2001) also considered that while ^{234}Th is supplied by recoil into groundwater and then sorbed, ^{228}Th is formed largely on the surface and then desorbs. This provides a desorption value of 1 yr^{-1} for the sandy aquifer data.

^{230}Th . Groundwater concentrations of ^{230}Th , with a 75ka half-life, can have significant contributions from both recoil and weathering. Distinguishing different ($^{230}\text{Th}/^{232}\text{Th}$) ratios due to weathering of minerals with different Th/U ratios from those due to ^{230}Th additions by recoil is difficult. This is due to the analytical difficulties in obtaining precise counting data for such a low concentration element, and in obtaining mass spectrometric data from such low $^{230}\text{Th}/^{232}\text{Th}$ atomic ratios of $10^{-6}\text{--}10^{-5}$ (see Goldstein and Stirling 2003). Luo et al. (2000) found ($^{230}\text{Th}/^{232}\text{Th}$) activity ratios of 1.0–1.9, somewhat higher than the value for the host rock. Other studies have found similar ratios of ($^{230}\text{Th}/^{232}\text{Th}$) (Ivanovich et al. 1992b). These values may be due to either excess ^{230}Th added by recoil or differences between the rates of weathering of minerals bearing ^{238}U (and so ^{230}Th) and those bearing ^{232}Th . Note that the activity of excess ^{230}Th is $(0.3\text{--}4) \times 10^{-3}$ that of ^{234}Th , and so there is clearly a deficiency in recoiled ^{230}Th . This may be because adsorbed Th is irreversibly incorporated into the solid phase, perhaps by recrystallization of host Fe phases, on timescales that are long relative to the half life of ^{234}Th but short relative to that of ^{230}Th .

Summary. Further studies of the longer-lived isotopes of Th are essential for understanding the roles of colloids and weathering in the transport of Th. While it is clear that short-lived Th isotopes are strongly absorbed on aquifer materials and have retardation factors that are orders of magnitude greater than Ra, more detailed analysis is more model dependent and so requires further constraints on the processes involved. Modeling the behavior of long-lived Th isotopes appears to require further understanding regarding the irreversible retention of Th onto host rock surfaces. As with Ra, the absolute value for retardation factors remains dependent upon using ^{222}Rn concentrations to obtain rates of recoil supply into the groundwater, and so is subject to the same uncertainties as those discussed in Sections 2.2 and 2.4. While the conclusion that Th is strongly adsorbed will not change, retardation factors could conceivably be substantially lower.

2.5. U isotopes

The ubiquity of groundwater ($^{234}\text{U}/^{238}\text{U}$) ratios above the equilibrium value attests to the widespread operation of preferential ^{234}U release processes in aquifers. Since the U isotopes are long-lived, the concentrations cannot be assumed to be in steady state, adding difficulties to unravelling the causes of U isotopic variations. However, U

isotopes provide the greatest potential for tracing groundwater flow and studying the migration of the more mobile anthropogenic nuclides.

Behavior of U in groundwater. The general behavior of U was reviewed by Gascoyne (1992). Under oxidizing conditions, U is highly mobile in the hexavalent form, forming soluble complexes primarily with carbonate and phosphate under near-neutral conditions, and with sulphate and fluorides at lower pHs. In saline groundwaters, solubilities are higher, where chloride and sulphate complexes are important. Concentrations are typically close to 1ppb, and values over 1ppm are generally only found in mineralised areas (Osmond and Cowart 1992). Under reducing conditions, U is in the tetravalent state and stable as $U(OH)_4$, and the solubility limit of uraninite, UO_2 , sets the maximum U concentration to ~ 0.06 ppb (Gascoyne 1992). Groundwaters crossing a redox front therefore can precipitate U, which then serves as a source of ^{234}U to the passing groundwaters that can exhibit high ($^{234}U/^{238}U$) ratios (Osmond and Cowart 1992).

^{238}U is released from the host aquifer by weathering. Primary minerals that contain U, as well as Th, are often considered insoluble (e.g., Tole 1985). While enhanced weathering may occur in the vadose zone, the presence of U throughout aquifers, despite removal processes, indicates that U release continues to occur in the saturated zones. Recoil damage may enhance loss of radionuclides (Fleischer 1982, 1988), and the dissolution of actinide-rich minerals also may be enhanced due to accumulated recoil damage (Petit et al. 1985a). The release of radionuclides from secondary minerals and grain boundaries also may be important.

A substantial amount of experimental work has been published on the sorption behavior of U. The ability of clays, carbonates, and surfaces of other minerals to adsorb substantial amounts of U has been well documented. While these data are critical for explaining calculated bulk adsorption parameters and predicting migration behavior under changing conditions, these studies are not directly part of models of decay series isotopic systematics, and so are not discussed here. The goal of the field studies using decay series nuclides is to obtain bulk values for the fraction of radionuclides adsorbed without specifying specific processes and which are likely to be due to reactions involving a mixture of sites. A study by Payne et al. (2001) found that laboratory partitioning data were comparable to the distribution of U in groundwater and adsorbed or incorporated in readily soluble sites in cored materials. Models assume that adsorption is reversible, and Sims et al. (1996) found that most of the U that was passed through a sandstone core was readily recoverable by changing water conditions, although a small fraction was released more slowly, suggesting that adsorbed U becomes progressively more strongly bound within periods of a few months.

Secondary iron minerals are widespread and have highly reactive surface areas, and are important in controlling radionuclide migration. Ferrihydrite was found to sorb greater amounts of U than crystalline forms such as hematite and goethite (Payne et al. 1994). Structural changes in host Fe phases may further bind adsorbed species. U adsorbed by amorphous Fe hydroxides was found to be incorporated into more stable sites during crystallization of Fe minerals (Payne et al. 1994; Ohnuki et al. 1997). Giammar and Hering (2001) found that U sorption onto goethite was initially reversible, but during aging over months a portion of the U was no longer readily exchangeable. The long-term precipitation of Fe minerals therefore may transfer a significant fraction of U and other adsorbed radionuclides more permanently into surface coatings. While these processes may not affect the systematics of very short-lived nuclides, calculations of the evolution of longer lived nuclides over greater distances will be altered, since long-term accumulation on sorption sites will not occur. Rather, there will be a continuing process of irreversible removal. This may make it impossible to achieve a stable profile for longer-lived isotopes,

since the exchangeable adsorbed pool is constantly being irreversibly incorporated. This process has not been incorporated into radionuclide models.

Several field and modeling studies have sought to obtain U partitioning information. It is difficult to obtain partitioning data for U from Equation (1). Due to the long half life of ^{234}U , steady state concentrations along a flow line are not expected to be reached, and so the advection term is significant. Further, it is unlikely that the various controlling parameters are constant over the long distances over which U isotope compositions are expected to vary. Steady state concentrations at each location also requires that significant reversibly adsorbed abundances have accumulated, although as discussed above this may not be possible. Tricca et al. (2000) showed that under constant conditions and reversible adsorption behavior, U concentrations are expected to increase linearly with groundwater age, while U isotope compositions will vary due only to mixing between U provided at the water table and that added in the aquifer by weathering and recoil. These characteristics have not been observed. Alternatively, Luo et al. (2000) calculated the distribution of ^{238}U by noting that the mobile ^{234}Th (i.e., $(1 + K_{234\text{Th}})(^{234}\text{Th})_w$, representing groundwater and adsorbed species) is the result of recoil from host rock minerals and decay of mobile ^{238}U . Therefore, by using values for the partition coefficient of Th to calculate the total production rate of mobile ^{234}Th , and the recoil rate from within aquifer minerals by assuming the recoil rate of ^{234}Th can be obtained from that for ^{222}Rn , the amount of ^{234}Th supplied by dissolved and adsorbed ^{238}U was obtained; this corresponds to values for the partition coefficient of U (K_U) of $\sim 10^3$. Clearly, these calculations are sensitive to the uncertainties in calculating the relevant ^{234}Th partitioning and recoil parameters. A laboratory study of aquifer rocks in this area by Fjeld et al. (2001) found a U retardation factor of 30, and the difference with the field study values reflects either the difficulties of using laboratory data as an average for the larger scales of the aquifer or the limitations of the mathematical model that was applied to the field data. Using similar modeling assumptions, Ivanovich et al. (1992b) deduced U retardation factors of $(0.8-7) \times 10^3$ for a sandstone aquifer. In contrast, as discussed below, some aquifers have U concentrations that appear to fall on conservative mixing trends, suggesting that adsorption is less important there. Overall, since the data does not consistently point to strong retardation of U under all circumstances, it is important to characterize U behavior at each location of interest.

Generation of U isotope variations. Both ^{234}U and ^{238}U are provided in secular equilibrium to the groundwater by simple weathering release. In addition, “excess” ^{234}U is released by recoil from host minerals of ^{234}Th , followed by decay to ^{234}Pa (with a 1 minute half life) and then to ^{234}U . Further release of ^{234}U is often assumed to occur by leaching of ^{234}U along recoil tracks, although in practice this is not readily distinguished from direct recoil and is only plausible where new surfaces are exposed or dry periods occur that allow implantation of recoiled radionuclides into adjacent phases. In sum, the ratio of supply rates of “excess” ^{234}U to ^{238}U in groundwater is equal to the ratio of ^{234}Th (and so ^{234}U) recoil release rate to weathering rate. Where removal processes are not fractionating, this ratio will be retained in groundwater. In this case, the measured ratio of the excess ^{234}U to ^{238}U (that is, $(^{234}\text{U}/^{238}\text{U})_w - 1$) is equal to the ratio of recoil supply to weathering (Petit et al. 1985b; Tricca et al. 2001). Note that both recoil and weathering are proportional to the surface area of U-bearing phases; therefore, changes in grain size or the abundances of these phases within the rock will not change the ratio of these supply rates, but changes in water chemistry or in the nature of the U host phases will alter only the weathering rate and so will produce a change in groundwater isotopic composition. Note that preferential losses of ^{234}U will result in a $(^{234}\text{U}/^{238}\text{U})$ activity ratio in the weathering mineral that is lower than 1, and so release of this U by weathering will partly balance the recoiled ^{234}U . Therefore, there are limits on the ratio that can be

generated by the combined effects of recoil and weathering from a single phase (Petit et al. 1985a,b; Hussain and Lal 1986).

High ratios in groundwaters can be generated where U is concentrated in secondary phases and weathering is limited. For example, U can be precipitated when groundwaters become anoxic since reduced U^{+4} is much more insoluble. Therefore, concentrations are greatly lowered, and ($^{234}U/^{238}U$) ratios increase due to efficient recoil from precipitated phases (Osmond and Cowart 1992). In such cases, the generation of high ($^{234}U/^{238}U$) values in groundwater depends upon limited isotopic exchange with the larger reservoir of precipitated U.

Isotopic variations can also occur due to changes in groundwater chemistry or host rock characteristics. The most obvious change occurs at the water table. Distinctive U characteristics can be generated in waters travelling through more rapidly weathering, organic-rich deposits in the unsaturated zone. Once water with this U reaches the water table, conditions are encountered which often are dramatically different. U will then evolve along a flow line following a mixing trajectory between vadose zone U and that provided by the host aquifer rocks from the combined processes of weathering and recoil (see Tricca et al. 2000). Any adsorbed U will have the same isotopic composition as the groundwater and the concentration will follow that of the groundwater, assuming that the partitioning between surfaces and groundwater remains constant. Where regular groundwater patterns are found, U isotopes might be used to date groundwaters. Using short-lived nuclides to identify the recoil inputs, the accumulation of excess ^{234}U can be tracked. For example, studies of the Milk River aquifer in Canada found that reasonable ages could be determined from changes in $^{234}U/^{238}U$ ratios along a flowline, as long as significant retardation of U in the aquifer was included in the calculations (Ivanovich et al. 1991). Henderson et al. (1999) similarly used U isotope variations to determine pore water flow rates. Overall, this raises the hope that a reliable dating method could be found using U isotopes, but also indicated that independent controls on U behavior are required. Dating of groundwaters using these methods has not yet been applied widely.

Some of the complications involved in multi-scale porosities and evolutionary paths within fractured rock systems have been explored. For example, in the Palmottu site of gneisses in Finland U, as well as Th, was found to be redistributed into fracture coatings of carbonates and Fe oxides (Suksi et al. 1991). Suksi and Rasilainen (1996) have demonstrated how U concentrated in these fracture fillings can implant daughters in the surrounding phases, generating large fractionations between $^{234}U/^{238}U$ and $^{230}Th/^{234}U$. This suggests that phases that may weather at different rates later through changing conditions, new fracturing, or transport to a sedimentary aquifer and can become sources of highly fractionated nuclides into groundwater by leaching or weathering. Different migration patterns could also be discerned in the ($^{234}U/^{238}U$) signatures found in the groundwater-derived U in the coatings (Suksi et al. 2001). Matrix diffusion, where dissolved species can diffuse into rock pores and microfractures away from the main groundwater flow, can greatly affect water-rock interaction processes and migration rates of radionuclides (Neretnieks 1980; Suksi et al. 1992). Variations in ($^{230}Th/^{234}U$) and ($^{234}U/^{238}U$) indicated that leaching of ^{238}U , and to a greater extent of ^{234}U , occurred over a scale of centimeters from fractures (Suksi et al. 2001), so that under these conditions U could be used to map migration paths of different groundwaters.

Preferential leaching of oxidized U. Unlike Th or Ra, U has two oxidation states with very different solubilities. U in minerals is generally present as U^{4+} . However, separation of U from various minerals and rocks by oxidation state has found that there is hexavalent U present with substantially higher $^{234}U/^{238}U$ ratios (Chalov and Merkulova 1968; Kolodny and Kaplan 1970; Suksi et al. 2001). It was suggested that some ^{234}U

atoms are oxidized during α decay due to stripping of electrons (Rosholt et al. 1963), or an increase in positive charge during the two β decays from tetravalent ^{234}Th and pentavalent ^{234}Pa ($t_{1/2} = 1$ minute) (Kolodny and Kaplan 1970). Alternatively, it has been suggested that since ^{234}U is resident in damaged lattice locations, it is more vulnerable to oxidation by fluids (Kolodny and Kaplan 1970; Cherdyntsev 1971) and so is due to external conditions. A detailed model of ^{234}U oxidation during recoil has been formulated (Ordonez Regil et al. 1989; Adloff and Roessler 1991; Roessler 1983, 1989). Using computer simulations of the recoil process, it was shown that recoiling ^{234}Th atoms push lighter oxygen atoms in front of it, enriching the final resting location in oxidizing species that are responsible for subsequent oxidation of ^{234}U after decay of the ^{234}Th . Note that this does not occur in minerals where U or Th is a major element, since the final resting place is not enriched in oxidizing species, and reactions with surrounding actinide atoms may occur which hinder oxidation. Therefore, in this model, the composition of the phase hosting ^{238}U is a controlling factor for the generation of disequilibrium in the groundwater.

Release of preferentially oxidized ^{234}U by subsequent leaching can only occur where the recoil path crosses the mineral-water interface and exposes the atom to leaching, but has not already led to direct injection of the daughter into solution. This may be applicable under some aquifer-specific conditions, similar to those discussed for preferential leaching. Sediments that have been deposited within the last 10^5 years may include minerals that were within nonporous rocks or under-saturated conditions so that radionuclides have been implanted in adjacent minerals. Recent fracturing may also provide water conduits exposed to such tracks. The development of a hydrated layer on some weathered silicate surfaces may allow enhanced diffusive escape of oxidized U that has been implanted there (Petit et al. 1985b). Also, weathering has the effect of moving the interface inwards to intersect new tracks, although this generally occurs too slowly to account for measured groundwater ^{234}U enrichments. In sum, this mechanism can explain the preferential release of ^{234}U where the necessary conditions for leaching exist, although data is required to confirm that this occurs under natural conditions.

Alternatively, it has been suggested (Petit et al. 1985a,b; Dran et al. 1988) that as U is released by weathering, tetravalent ^{238}U is preferentially precipitated or adsorbed, while hexavalent ^{234}U , oxidized during the recoil process, more readily remains in solution. This will increase the ($^{234}\text{U}/^{238}\text{U}$) ratio of the groundwater if isotopic equilibration does not then occur between adsorbed and dissolved U. A consequence of such preferential solution of ^{234}U is that excess ^{234}U in groundwater is not related to the amount of ^{234}Th in solution and on aquifer surfaces, and so the supply rates of the two nuclides cannot be directly linked. This process can provide an explanation for widespread enrichment of ^{234}U that is greater than that produced by direct recoil into groundwater. However, there is no data available to assess whether this generally operates in groundwater systems.

U isotope variations in groundwater. There have been several studies in the last 10 years that have reported ($^{234}\text{U}/^{238}\text{U}$) distributions in aquifers; earlier studies have been reviewed by Osmond and Cowart (1992, 2000). Kronfeld et al. (1994) measured values in a phreatic, oxidizing dolomite aquifer in South Africa. Young well waters (with measurable ^3H) had ($^{234}\text{U}/^{238}\text{U}$) = 2.2-5.8, while values up to 11 were found in springs and speleothems. The host aquifer rock had low U concentrations, and so it was hypothesized that a substantial inventory of ^{238}U resides adsorbed on the surfaces to supply ^{234}U . However, such a reservoir would isotopically exchange with U in the water, and so the high ($^{234}\text{U}/^{238}\text{U}$) ratios must be generated from ^{238}U is irreversibly bound in the host rocks. It is interesting to note that if the ^{222}Rn supply rates, calculated from the

reported ^{222}Rn concentrations, are equated to that producing excess ^{234}U , then much greater times are required to generate the measured excess ^{234}U concentrations than the possible ages of the waters. These are minimum times, based upon the assumption that there are no losses of U to the aquifer surfaces. This raises the possibility that the ^{234}U excesses were generated under different conditions, such as in the vadose zone. Bonotto and Andrews (1993) suggested that the ratios of ~ 1.5 in the Carboniferous Limestone of SW England were due to leaching of silicates such as micas that are continually exposed during carbonate dissolution.

U isotope variations in young, shallow groundwaters in a sandy unconfined aquifer were reported by Tricca et al. (2001). A considerable range of ^{234}U excess and ^{238}U concentrations were found in water table wells, with a similar range in wells less than 5km down gradient. Therefore, it is possible that the generation of much of the U characteristics that is seen in young waters occurs outside the aquifer and in the vadose zone. Unfortunately, it is generally difficult to precisely follow groundwater flow paths and account for dispersion effects, so that close to the water table it is often difficult to separate variations in groundwater chemistry due to variable water table inputs from those due to aquifer processes. At greater distances, the changes due to aquifer processes will be clearly greater than the range in water table characteristics.

Several recent studies have used U isotope compositions to trace groundwater flow patterns, and Osmond and Cowart (2000) have discussed the basic principles involved. Roback et al. (2001) combined U and Sr isotope data for the Snake River Plain aquifer to identify the flow of isotopically distinctive recharging waters as well as flow along higher conductivity flow paths. While some regions could be explained by mixing of different water masses, simple mixing trends between U concentrations, ($^{234}\text{U}/^{238}\text{U}$), and $^{87}\text{Sr}/^{86}\text{Sr}$ were not always observed, suggesting that U was not conservative during mixing. Dabous and Osmond (2001) reported that waters from the sandstone Nubian Aquifer in Egypt exhibit broad correlations between ($^{234}\text{U}/^{238}\text{U}$) and $1/\text{U}$, consistent with mixing between recharging and aquifer waters with distinct ($^{234}\text{U}/^{238}\text{U}$) ratios as well as ^{238}U and excess ^{234}U excess concentrations. While the data are not tightly constrained due to secondary processes, the systematic variations indicate that conservative mixing is the dominant process in the area sampled. Similarly, Hodge et al. (1996) found that there is a broad correlation between U and the conservative components Na, Cl, and SO_4 in spring waters from California, and argued that this indicated that U was behaving conservatively. Overall, it appears that the behavior of U varies between groundwater conditions, although a direct comparison between the different methods for deducing U behavior, including laboratory experiments of U adsorption on aquifer rocks, is necessary.

The unusual occurrence of ($^{234}\text{U}/^{238}\text{U}$) ratios less than one were observed in waters from the weathered zone around the Koongarra ore deposit (Yanase et al. 1995). While this could be due to prior leaching and depletion of ^{234}U from the U that is now released by weathering, it was suggested that this reflects implantation of recoil ^{234}U into phases more resistant to weathering during undersaturated conditions in this zone.

Summary. U isotope compositions potentially can provide an important tool for tracing groundwaters from different aquifer conditions. However, clear interpretations of ($^{234}\text{U}/^{238}\text{U}$) ratios, and quantification of the responsible processes, remain difficult. Additional work regarding the release rates of ^{234}Th and ^{234}U , and the weathering and retardation rates of U, is still required to complement site evaluations.

2.6. ^{210}Pb

Few studies have addressed the groundwater behavior of Pb. It is clear that Pb is highly surface reactive, since ^{210}Pb that is deposited onto watersheds after production in

the atmosphere from ^{222}Rn , has residence times in watersheds on the order of 10^4 years due to retention in soils. ^{222}Rn decays to ^{210}Pb (the four intermediate radionuclides have half lives less than one hour and so are unlikely to significantly affect distribution of ^{210}Pb), and so ($^{210}\text{Pb}/^{222}\text{Rn}$) ratios can be used to obtain a retardation factor in the same way that ($^{224}\text{Ra}/^{222}\text{Rn}$) ratios are used to determine Ra retardation factors, although in these case the nuclides are in the same decay series chain so that there are fewer issues regarding possible differences in parent nuclide siting. When both have steady state concentrations, the mobile ^{210}Pb is derived from both recoil and ^{222}Rn in solution. If the latter was generated only by recoil, the pool of mobile ^{210}Pb is twice that of ^{222}Rn in groundwater (see Hussain and Krishnaswami 1980), and the groundwater ($^{210}\text{Pb}/^{222}\text{Rn}$) ratio is then simply half the inverse of the Pb distribution coefficient. Measured ($^{210}\text{Pb}/^{222}\text{Rn}$) values are $(0.1-6) \times 10^{-4}$ for sandy aquifers (Copenhaver et al. 1993) and $(0.14-1.6) \times 10^{-3}$ for a schist (Yanase et al. 1995). Therefore, partition coefficients of $\sim 10^3-10^5$ are obtained, with the largest assumption being that ^{222}Rn provides a measure of the ^{210}Pb recoil flux into groundwater. Comparison with ^{224}Ra suggests that Pb is generally somewhat more surface-reactive than Ra.

3. GROUNDWATER DISCHARGE INTO ESTUARIES

As discussed in the preceding sections, interactions with host aquifer rocks, including the supply of dissolved constituents as well as removal by adsorption and precipitation, can impart radionuclide signatures to groundwaters that are distinctive from those in surface waters. In particular, the very short-lived nuclides that are present in significant concentrations due to continuous supply from host rocks become strongly depleted in surface waters. All waters flowing into rivers have interacted with rocks or soils to varying degrees. These signals are then modified by residence in the river system. Waters in larger surface bodies have even longer residence times with only limited interaction with sediments. Clearly this effect is most pronounced in the ocean basins. One issue that has received considerable attention is the magnitude of groundwater discharge into coastal and estuarine waters, and the relative inputs in these regions from rivers and groundwater. In this environment, radionuclides have the potential for tracing waters from groundwater.

Groundwater discharge to coastal waters and estuaries has been of interest for centuries (Dominica and Schwartz 1990; Seltzer et al. 1973; Seltzer and Logician 1993). Several studies have utilized U- and Th- decay series nuclides to assess groundwater inputs to the coastal ocean (e.g., ^{228}Ra , ^{226}Ra and ^{222}Rn) as well as the short-lived isotopes (^{224}Ra , ^{223}Ra) to assess coastal mixing (Moore 1996; Cable et al. 1996a,b; Toreros et al. 1996; Hussein et al. 1999; Corbett et al. 2000b,c; Moore 2000; Swarzenski et al. 2001; Top et al. 2001; Schwartz and Sharpe 2003). More recently, a renewed interest in submarine groundwater discharge has emerged from studies on coastal eutrophication and contamination (Giblin and Gaines 1990; Reay et al. 1992; Bugna et al. 1996). The ecological importance of subsurface flow to water and nutrient budgets has been repeatedly demonstrated during the last two decades (Bokuniewicz 1980; Johannes 1980; Simmons 1992).

3.1. Background

The complex interactions amongst geological, biological, and geochemical processes at the land-sea margin control the delivery and fate of radionuclides, contaminants, and other natural elements in coastal environments (Swarzenski et al. 2003). For many such constituents, there is at least a fundamental understanding of major source and sink functions and their potential estuarine transformation reactions. For example, rivers can be monitored quite easily for discharge rates into estuaries as well as for elemental

concentrations to derive estimates of the integrated fluxes that are introduced to estuaries. Continental constituents can also be delivered into estuaries by groundwaters. However, the importance of the delivery of dissolved constituents by submarine groundwater discharges directly into coastal bottom waters, such as select radionuclides and nutrient species, to coastal bottom waters has often been neglected (Harvey and Odum 1990; Valiela et al. 1990; Simmons 1992). This general omission from coastal mass balance budgets by both hydrologists and oceanographers alike is largely due to the difficulty in accurately identifying and quantifying such submarine groundwater discharges (Burnett et al. 2001b, 2002). However, this flux recently been shown to indeed play a substantial role in the overall delivery of certain radionuclides and other elements to the coastal sea (Moore 1996; Cable et al. 1996a,b; Swarzenski et al. 2001).

Hydrologists and oceanographers do not necessarily share the same vocabulary to define processes, so a few comments on definitions is warranted. Groundwater is most commonly defined as water within the saturated zone of geologic material (Freeze and Cherry 1979). The bottom sediments of an estuary are obviously saturated, so water within submerged sediments (i.e., pore waters or interstitial waters) can be defined as groundwater. Therefore, submarine groundwater discharge includes any upward fluid transfer across the sediment-water interface, regardless of its age, origin and salinity. Exchange across this interface is bi-directional (discharge and recharge), although a net flux is most often upward.

The rates of submarine groundwater discharge within “leaky coastal margins” are controlled by inland recharge rates and the underlying geologic framework. Figure 6 shows the dominant characteristics of a generalized coastal groundwater system influenced by submarine groundwater discharge. Fresh water that flows down gradient from the water table towards the sea may discharge either as diffuse seepage close to

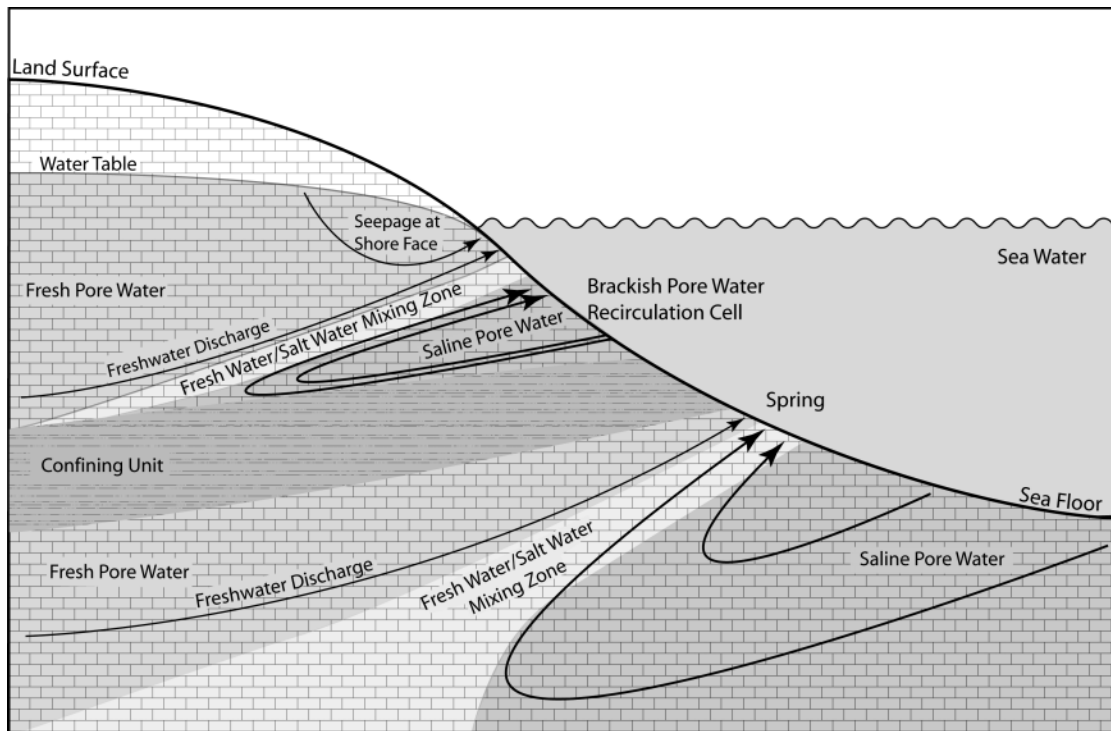


Figure 6. Fluid exchange at the land-sea margins and schematic illustration of processes associated with submarine groundwater discharge.

shore, or directly into the sea either as submarine springs (Swarzenski et al. 2001) or wide scale seepage. The hydraulic gradient that drives freshwater towards the sea can also drive seawater that has intruded into underlying deposits back to the ocean, creating a saltwater circulation cell. Wherever multiple aquifers and confining units co-exist, each aquifer will have its own fresh water/saltwater interface, and deeper aquifers will discharge further offshore (Freeze and Cherry 1979). Submarine groundwater discharges can be spatially as well as temporally variable since there are a variety of both natural and anthropogenic influences (i.e., sea-level, tides, precipitation, dredging, groundwater withdrawals) that can have strong effects (Zektzer and Loaiciga 1993).

Theoretically, submarine groundwater discharge can occur wherever a coastal aquifer is hydrogeologically connected to the sea (Moore and Shaw 1998; Moore 1999). Artesian or pressurized aquifers can extend for considerable distances from shore, and where the confining units are breached or eroded away, groundwater can flow directly into the sea (Manheim and Paull 1981; Moore 1998). While the magnitude of this submarine groundwater discharge is often less than direct riverine runoff, recent studies have shown that coastal aquifers may contribute significant quantities of fresh water to coastal bottom waters (Zektzer et al. 1973; Moore 1996; Burnett et al. 2001b, 2002). Although it is unlikely that submarine groundwater discharge plays a significant role in the global water budget (Zektzer and Loaiciga 1993), there is strong evidence that suggests that the geochemical signature of many redox sensitive constituents is directly affected by the exchange of subsurface fluids across the sediment-water interface (Corbett et al. 2000a,b,c; Lapointe et al. 1990). This fluid exchange includes direct upward groundwater discharge as well as the reversible exchange at the sediment-water interface (i.e., seawater recirculation) as a result of tidal pumping (Li et al. 1999; Hancock et al. 2000).

Standard seepage meters have traditionally provided physical, time dependent measurements of submarine groundwater discharge, while first order diffusion models have produced elemental flux estimates based on dissolved pore water profiles (Cable et al. 1996b; Corbett et al. 2002b). Both techniques yield evidence for substantial localized submarine groundwater discharge, but these methods fail to provide insight into larger scale, more synoptic estimates for exchange across the sediment/water interface. Due to the patchiness and generally unpredictable nature of submarine groundwater discharges, a tracer capable of integrating the spatial heterogeneities of most coastal bottom sediments is needed. To address this issue, W.S. Moore and W. Burnett and their colleagues have utilized the four naturally occurring isotopes of radium and ^{222}Rn to study both local and regional scaled submarine groundwater discharge.

3.2. Tracing groundwater using ^{222}Rn and the Ra quartet

An ideal submarine groundwater discharge tracer should be highly enriched in groundwater relative to seawater, behave conservatively (i.e., non-reactive) or at least predictably and also be easy to measure. The four isotopes of Ra and ^{222}Rn follow these constraints reasonably well and have recently been utilized to identify and quantify submarine groundwater discharge to various coastal oceans (Krest et al. 2000; Bollinger and Moore 1993; Webster et al. 1995). One strong advantage of these radiotracers over seepage meters is that the coastal water column effectively integrates the submarine groundwater discharge signal over a broad area and time period.

Ra is continually produced in sediments by the decay of insoluble Th parents (see Fig. 7). While in fresh water Ra is bound tightly to particle surfaces, in seawater Ra readily undergoes cation exchange with other dissolved constituents. This provides an additional source of Ra to the water column, which controls the frequently observed non-

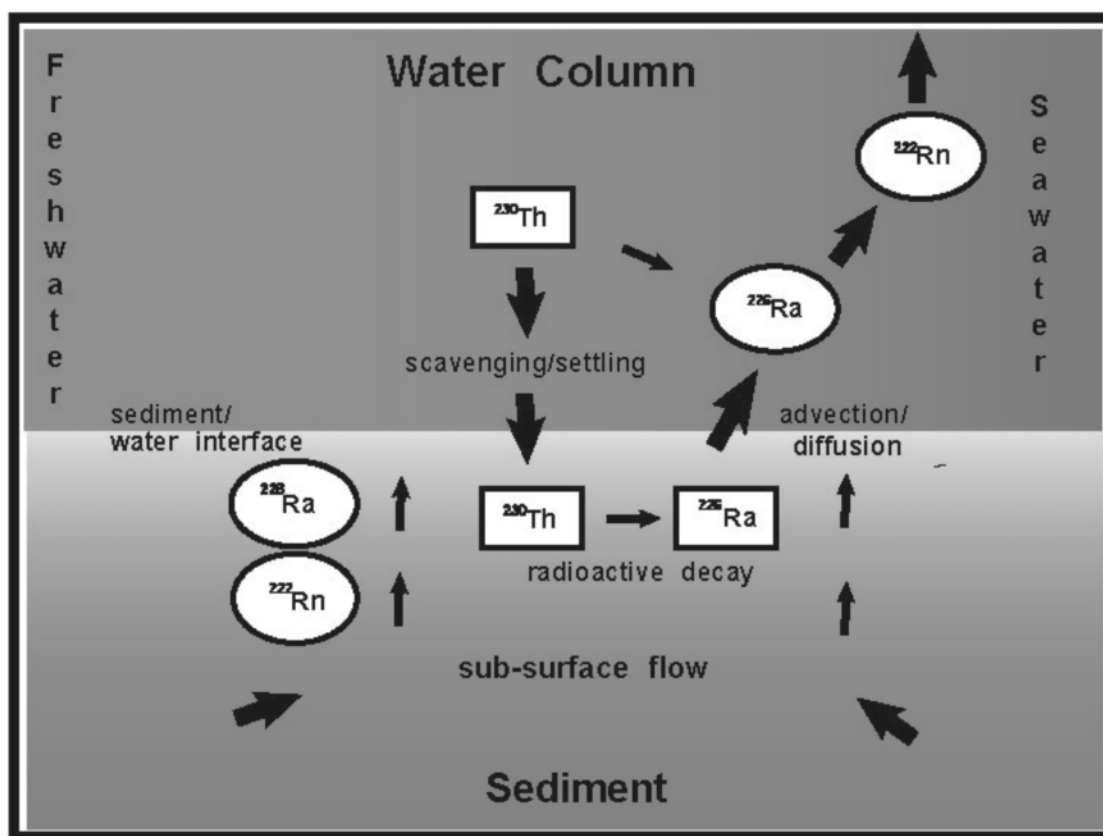


Figure 7. Sediment contains ^{230}Th derived both scavenged from the water column during particle settling and contained in solid material. ^{226}Ra produced in the sediments is highly soluble in pore waters and diffuses into the overlying water or is advected across the sediment-water interface by discharging groundwater. ^{222}Rn is produced within the water column from dissolved ^{226}Ra and within the underlying sediments.

conservative distribution in estuaries (Torgersen et al. 1996). The specific source terms for this additional Ra include: 1) Ra produced from bottom sediments (Bollinger and Moore 1993; Rama and Moore 1996; Hancock et al. 2000), 2) Ra desorbed from suspended particulates (Yang et al. 2002) and 3) Ra advected upward either by the discharge of submarine groundwater (Moore and Shaw 1998) or by reversible exchange across the sediment-water interface; i.e., the flow of recirculated seawater (Hancock and Murray 1996; Moore 1997; Hancock et al. 2000).

The utility of radium as an effective tracer of submarine groundwater discharge is a function of 1) its sedimentary source in fresh waters that typically produces a signal that is highly enriched relative to coastal water, 2) its mobility in brackish waters and in seawater, and 3) the wide range in half-lives of the four Ra isotopes (3.8 days to 1600 years) that corresponds to that of a range in relevant submarine groundwater discharge processes. By developing a simple estuarine mass balance model for Ra, the flux of submarine groundwater and any associated constituents can then easily be derived. Moore (1996) suggested that the discharge and exchange of freshened groundwater across the sediment-water interface had to be the primary source of ^{226}Ra enrichment in a large coastal region of the S. Atlantic Bight. Estimates of submarine groundwater discharge derived only from ^{226}Ra activities need further calibration as the reversible water mass exchange across the sediment-water interface may serve as a “Ra-pump.” Corbett et al. (1999) evaluated groundwater discharge into Florida Bay by comparing

^{222}Rn activities with CH_4 concentrations and a positive relation between methane and ^{222}Rn was observed. Similar results were found by Cable et al. (1996a) and Kim and Hwang (2002). The location of high groundwater fluxes inferred from Ra and Rn concentrations has been corroborated by direct seepage measurements (Cable et al., 1996a; Corbett et al. 2000b). However, seepage meters provide a measurement of the local water flux across the sediment-water interface, while the chemical tracers provide a more integrated flux estimate to the overlying water. Burnett et al. (2002) brought together a suite of geochemical tracers and physical data in an effort to quantify the links between tracer concentrations and groundwater fluxes. However, further data is required to obtain sufficient coverage across an individual estuary and separate all the possible sources of Ra and Rn isotopes in order to derive a first-order estimate of groundwater fluxes to the entire estuary. While these studies establish that U- and Th-series can be used to identify groundwater discharges in coastal and estuarine systems, further work is required to quantify the associated integrated groundwater fluxes of broad areas.

Recent studies of submarine groundwater discharge into estuaries indicate that select long-lived and short-lived U/Th series isotopes show great promise as new tools to directly examine exchange processes and rates across the sediment-water interface. As new detection techniques and field validation methods develop, e.g., *in situ* ^{222}Rn monitors (Burnett et al. 2001a), coastal scientists will for the first time be able to realistically identify and quantify submarine groundwater discharge. Ideally, a thorough submarine groundwater discharge study should include direct measurements (e.g., seepage meters) and numerical modeling efforts to calibrate the geochemical tracers for quantifying groundwater discharges at the particular estuary. In concert, such an approach provides a powerful diagnostic tool for regional scale submarine groundwater discharge investigations.

4. OPEN ISSUES

Considerable advances continue to be made in the understanding of radionuclide migration in the natural environment. Overall, these models have provided an important framework for understanding the behavior of these nuclides. Clearly, further studies are required to examine different aquifer environments, to further constrain the controlling processes, to refine the analytical tools for calculating retardation rates, and to determine how the data gathered from naturally occurring radionuclides can be extrapolated to the higher concentrations of anthropogenic isotopes. In addition to exploring radionuclide behavior under specific conditions, there are some important broad issues that still require further close attention.

4.1. The effects of well construction and sampling

The question of how well groundwater samples represent the aquifer is generally not discussed in research studies of radionuclides. Contamination studies frequently utilize monitor wells that have been specifically designed and constructed for sample collection. Issues that are considered include the use of non-corroding well materials such as PVC, drilling methods that minimize (but cannot completely avoid) disruption of the surrounding aquifer, extraction of drilling muds by well development, and well screens that target restricted sampling depths. There have been various studies that have examined the impact of sampling procedures on sample integrity. However, other studies that do not have the luxury of installing dedicated wells often utilize other types of wells, such as those for water supply. While there is rarely the opportunity to investigate the potential impact on the sample parameters of interest, it is worth considering some of the factors that may cause deviations in the data. During drilling, a large region around the wells is disrupted, changing stratification, packing, and porosity. A pack of clean sand is

generally placed around the well screen; this has very different characteristics from the aquifer, and the time that water spends in this region is dictated by the flow rate in the aquifer, a factor that may be important for the shortest-lived radionuclides. Cement seals used to isolate the screened region from the overlying borehole can contaminate wells if not emplaced properly (Barcelona and Helfrich 1986). Well casing material can also affect water chemistry (e.g., Barcelona and Helfrich 1986). Steel casing, often used for water wells, can release Fe and Fe colloids due to corrosion (Degueldre et al. 1999). Well development generally follows construction, and in removing drilling fluids and muds, fine material in the aquifer may also be redistributed. The rates of purging to remove stagnant water within a well have been found to affect trace element and contaminant concentrations, and more stable concentrations tend to be found when low turbidities are achieved by using low pumping rates in a variety of aquifer conditions (e.g., Puls and Powell 1992; McCarthy and Shevenell 1998; Gibs et al. 2000). Low purge rates have been used to collect U samples using dedicated bladder pumps (Shanklin et al. 1995), although such equipment is generally only practical at continually monitored sites. Waters from different levels or used for drilling may also be drawn into a well, and result in substantial chemical changes (Grenthe et al. 1992).

Overall, it is not possible to evaluate whether any of these factors have compromised the data included in published studies. More research is required to determine how U- and Th-series nuclides are affected by various well construction methods and sampling procedures, how reliable are data from wells not designed for trace element monitoring, and if there are any factors that have affected the data collected from past studies. Most importantly, radionuclide studies must incorporate greater awareness of the potential problems, summarize whatever details are available regarding the wells used, and consider potential problems where the relevant information is not available.

4.2. Quantification of model parameters

There are various parameters and assumptions defining radionuclide behavior that are frequently part of model descriptions that require constraints. While these must generally be determined for each particular site, laboratory experiments must also be conducted to further define the range of possibilities and the operation of particular mechanisms. These include the reversibility of adsorption, the relative rates of radionuclide leaching, the rates of irreversible incorporation of sorbed nuclides, and the rates of precipitation when concentrations are above Th or U mineral solubility limits. A key issue is whether the recoil rates of radionuclides can be clearly related to the release rates of ^{222}Rn ; the models are most useful for providing precise values for parameters such as retardation factors, and many values rely on a reliable value for the recoil fluxes, and this is always obtained from ^{222}Rn groundwater activities. These values are only as well constrained as this assumption, which therefore must be bolstered by clearer evidence.

4.3. Interpreting model-derived information

Evaluations of the behavior of naturally occurring nuclides can provide data on the distributions of radionuclides in groundwater, host minerals, and on sorption sites. However, identifying the causes of variations requires further chemical data and laboratory experiments. Variations due to differences in adsorption that are related to changes in chemistry must be investigated by establishing correlations with water chemistry parameters and confirmation from adsorption experiments that the variations can be explained quantitatively. The effects of colloids on radionuclide transport must also be investigated. Further studies are needed to determine whether radionuclide behavior can be successfully evaluated using approaches integrating field and laboratory investigations.

4.4. Inputs at the water table

Modeling of the transport of the long-lived nuclides, especially U, require knowledge of the input at the water table as a boundary condition for aquifer profiles. There are few studies of the characteristics of radionuclides in vadose zone waters or at the water table. Significant inputs are likely to occur to the aquifer due to elevated rates of weathering in soils, and this is likely to be dependent upon climatic parameters and has varied with time. Soils may also be a source of colloids and so provide an important control on colloidal transport near recharge regions.

4.5. Applications to pollutant radionuclide migration studies

A large number of studies have examined the migration of naturally occurring actinides at potential waste repositories or natural analogue sites. The role of these studies in radionuclide containment performance assessments has been discussed by Ivanovich et al. (1992a) and Smellie et al. (1997). Reservations have been put forward about the applicability of the information obtained from natural radionuclide modeling studies to anthropogenic nuclides that may be released at higher concentrations and in waters that have distinctive characteristics (McKinley and Alexander 1996). It is indeed clear that such studies cannot fully examine all the important characteristics at sites to support concrete predictions about pollutant migration. The magnitudes and patterns of adsorption rates under low concentrations and at present conditions can be defined, and these can provide broad survey information for more targeted exploration and benchmarks for assessing the relevance of laboratory results. Further information is of course required to extrapolate these results to quantify behaviors under different conditions. For example, the extent to which there are changes in sorption or precipitation due to greater radionuclide concentrations (e.g., due to nonlinear adsorption isotherms), or due to accompanying changes in water chemistry or colloid concentrations, must be quantified. Therefore, while predictions cannot be always directly made from the models described here to other conditions, the information provided must undoubtedly constitute an important component in any site study. Overall, the challenge remains to clearly characterize the present behavior of naturally occurring radionuclides and confidently extrapolate this to conditions created by pollutant releases.

4.6. Tracing groundwater discharges

The use of Ra and Rn as quantitative coastal groundwater tracers is still in its infancy. A clearer understanding of comprehensive Ra input and removal processes across the sediment-water interface needs further development in a wide range of hydrogeologic settings and within the context of integrated estuarine studies. Studies are obviously required which combine comprehensive sampling of an estuary along with the associated river and surrounding groundwaters, and consider the gathered data in the context of a well-characterized hydrological framework.

Overall, there are many issues that remain to be studied in greater detail. However, with further understanding of how U, Th, Ra, Rn, and Pb behave in diverse aquifer environments, studies utilizing U- and Th- decay series systematics will become increasingly useful for characterizing groundwater transport of trace elements and tracing groundwater flow.

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