

# U/Th Series Radionuclides as Coastal Groundwater Tracers

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## 1. Introduction

The study of coastal groundwater has recently surfaced as an active interdisciplinary area of research, driven foremost by its importance as a poorly quantified pathway for subsurface material transport into coastal ecosystems.<sup>1–10</sup> Key issues in coastal groundwater research include a complete geochemical characterization of the groundwater(s);<sup>11–13</sup> quantification of the kinetics of subsurface transport, including rock–water interactions;<sup>14–18</sup> determination of groundwater ages;<sup>19–20</sup> tracing of groundwater discharge into coastal waters using radiochemical fingerprints;<sup>21–24</sup> and an assessment of the potential ecological impact of such subsurface flow to a receiving water body.<sup>25–29</sup> For such applications, the isotopic systematics of select naturally occurring radionuclides in the U/Th series has proven to be particularly useful. These radionuclides (e.g., U, Th, Ra, and Rn) are ubiquitous in all groundwaters and are each represented by several isotopes with widely different half-lives and chemistries (Figure 1). As a result, varied biogeochemical processes occurring over a broad range of time scales can thus be studied.

In source rock, most U/Th series isotopes are in secular equilibrium; that is, the rate of decay of a daughter isotope is equal to that of its radiogenic parent, and so will have equal activities (in this context, the specific activity is simply a measure of the amount of radioactivity per unit amount).<sup>20,30,31</sup> In contrast, these nuclides exhibit strong fractionations within the surrounding groundwaters because of their respective physicochemical differences.<sup>32,33</sup> Disequilibria in U/Th series

radionuclides can thus be used to identify distinct water masses, quantify release rates from source rocks,<sup>34,35</sup> assess groundwater migration rates,<sup>36,37</sup> and assess groundwater discharge rates in coastal waters. Large isotopic variations also have the potential for providing precise fingerprints for groundwaters from specific aquifers<sup>38</sup> and have been explored as a means for calculating groundwater ages and estuarine water mass transit times.<sup>29,39–43</sup>

The highly fractionated nature of U/Th series nuclides in groundwater<sup>11,14,19,20,33,44–46</sup> is illustrated by the range in some measured activities (Figure 2). Highest activities are typically observed for  $^{222}\text{Rn}$ , reflecting the inert nature of this noble gas.<sup>47–49</sup> Groundwater  $^{222}\text{Rn}$  ( $t_{1/2} = 3.8$  days) activities are thus controlled only by rapid in situ decay (Table 1) and production within host rocks, without the added complications of reversible removal via adsorption or precipitation. Uranium, which is soluble as U(VI) in oxidizing waters, is present in intermediate activities in groundwaters that are moderated by redox-initiated removal onto aquifer rocks.<sup>50</sup> 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.<sup>51,52</sup> 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.



Peter W. Swarzenski received his education in chemical oceanography from the University of Colorado—Boulder as well as Louisiana State University and is currently a staff oceanographer at the U.S. Geological Survey office in St. Petersburg, FL. His specialty includes the use of U/Th series isotopes to examine a suite of coastal processes, including (1) submarine groundwater discharge, (2) river–ocean mixing and exchange processes across land–sea margins, and (3) coastal sediment dynamics. Currently he is involved in projects that address coastal groundwater fluxes into estuaries from Florida to California and abroad. Dr. Swarzenski is also involved in projects on the Louisiana shelf that address the delivery of sediment-hosted contaminants and historic hypoxia.

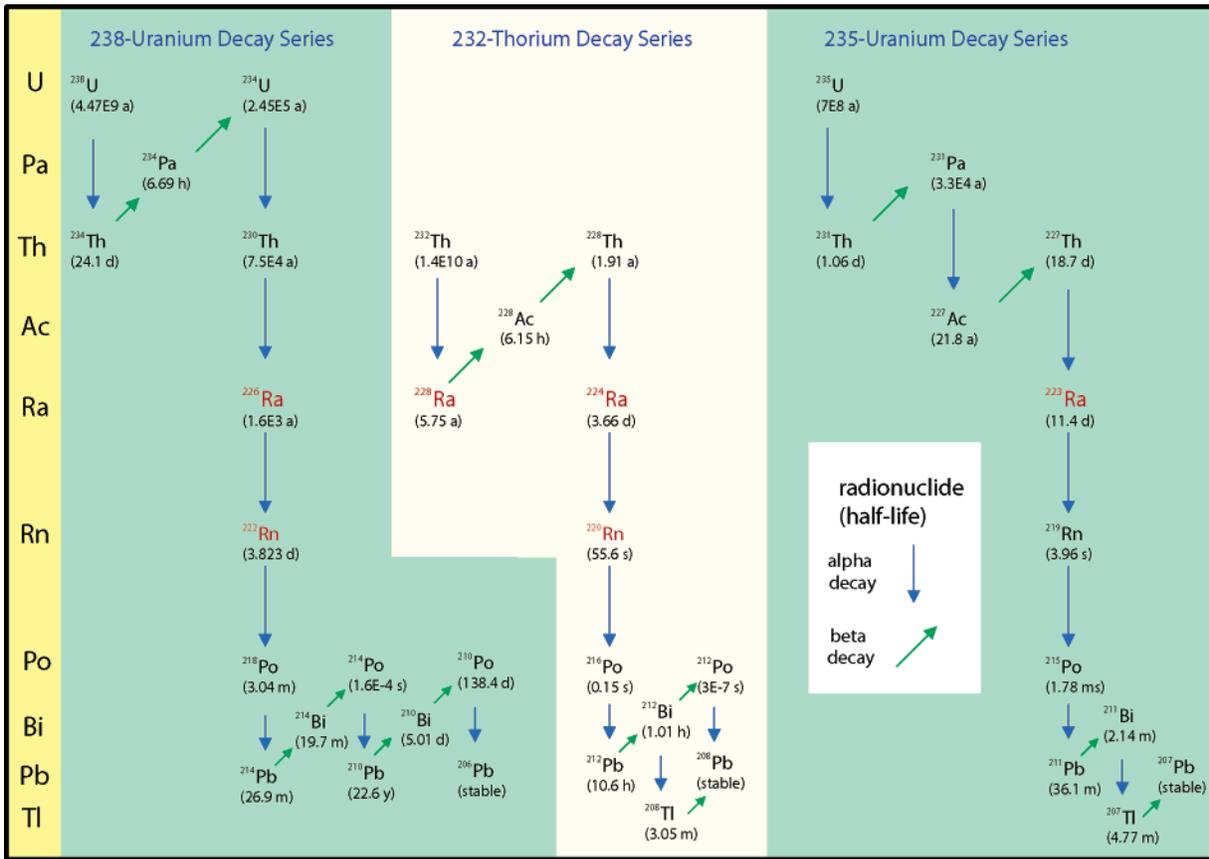


Figure 1. Schematic of the <sup>238</sup>U, <sup>232</sup>Th, and <sup>235</sup>U decay chains.

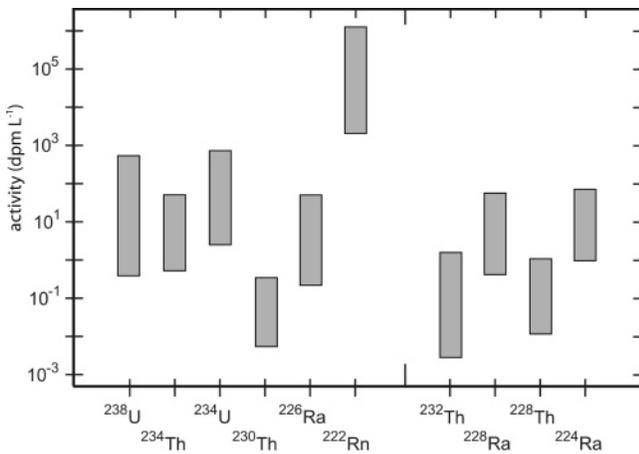


Figure 2. Comparison of select U/Th series radionuclide activities in select groundwater samples (after Porcelli and Swarzenski<sup>18</sup>). Data have been collated from Krishnaswami et al.,<sup>14</sup> Luo et al.,<sup>162</sup> and Tricca et al.<sup>12</sup>

Many studies have evaluated the behavior of select radionuclides in groundwater and surface water systems.<sup>19,20,31</sup> Recent advances in high-precision mass spectrometry<sup>53,54</sup> have opened new possibilities for more subtle interpretations in select long-lived U/Th series isotopes, such as U, Ra, Pa, and Th.<sup>55</sup> However, these techniques have yet to be fully developed, and as a consequence, such data remain largely scarce and underutilized. Although many different approaches have been developed to study radionuclide behavior in groundwater, all are based on principles of radioactive production and decay<sup>19</sup> and knowledge of source terms from weathering and recoil processes, as well as

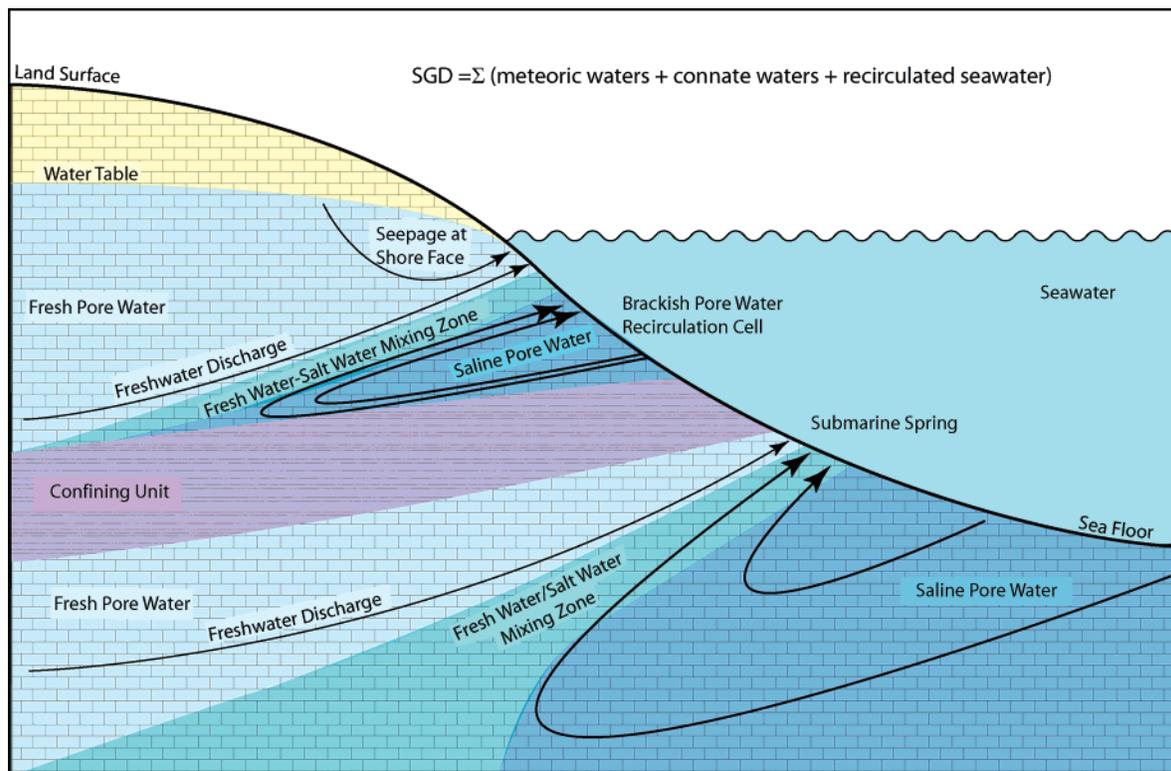
Table 1. Select U/Th Series Radionuclides Useful for Coastal Groundwater Studies (After Porcelli and Swarzenski)<sup>a</sup>

radio-nuclide	$t_{1/2}$	factors controlling groundwater activities
<sup>238</sup> U	$4.47 \times 10^9$ years	weathering, adsorption
<sup>234</sup> Th	24.1 days	recoil, strong adsorption, decay
<sup>234</sup> U	$2.45 \times 10^5$ years	weathering, adsorption
<sup>230</sup> Th	$7.57 \times 10^4$ years	recoil, weathering, strong adsorption
<sup>226</sup> Ra	$1.60 \times 10^3$ years	recoil, strong adsorption, decay, surface production
<sup>222</sup> Rn	3.823 days	recoil, decay, surface production
<sup>210</sup> Pb	22.6 years	recoil, strong adsorption, decay
<sup>232</sup> Th	$1.4 \times 10^{10}$ years	weathering, strong adsorption
<sup>228</sup> Ra	5.75 years	recoil, strong adsorption, decay, surface production
<sup>228</sup> Th	1.91 years	recoil, strong adsorption, decay, surface production
<sup>224</sup> Ra	3.66 days	strong adsorption, decay, surface production
<sup>220</sup> Rn	55.6 s	recoil, decay, surface production
<sup>235</sup> U	$7.13 \times 10^8$ years	weathering, adsorption
<sup>227</sup> Th	18.7 days	recoil, strong adsorption, decay, surface production
<sup>223</sup> Ra	11.7 days	recoil, strong adsorption, decay, surface production

<sup>a</sup> Adapted with permission from ref 18. Dpm is decays per minute (60 dpm = 1 Bq).

removal terms from the interaction with aquifer host rock surfaces by sorption and precipitation.<sup>18</sup>

This review is structured to present first a brief description of the background, driving forces, scales, and ecological significance of submarine groundwater discharge. Following this, a description of the geochemistry and behavior of select



**Figure 3.** Idealized hydrogeologic cross section at the land–sea margin, with respect to submarine groundwater discharge processes. (Copyright 2003 From *Coastal Aquifer Management—Monitoring, Modeling and Case Studies* by Cheng and Ouazar, Eds. Redrawn by permission of Routledge/Taylor & Francis Group, LLC.)

radionuclides in groundwater will be presented, and their application to tracing submarine groundwater discharge will be discussed.

## 2. Submarine Groundwater Discharge, SGD

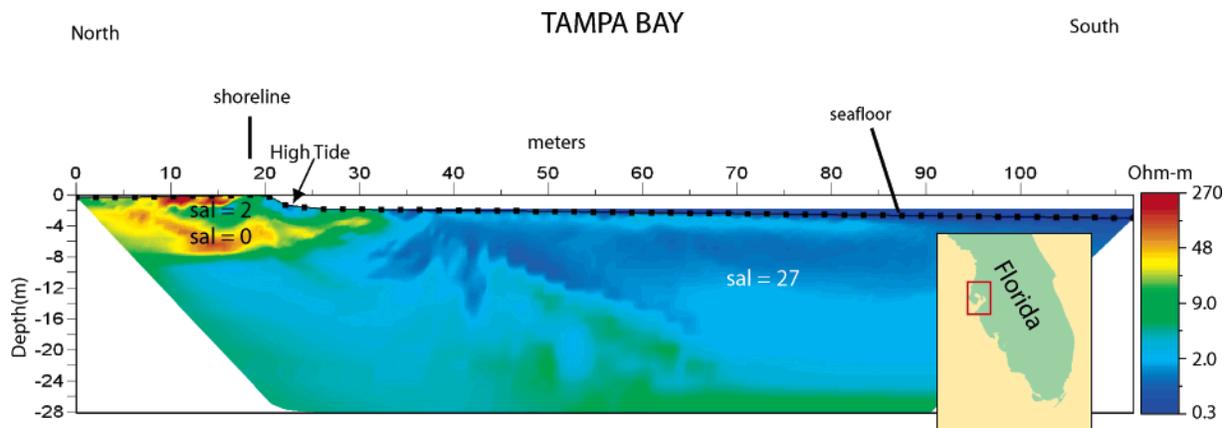
As a means to clarify potential confusion due to the cross-disciplinary nature of this subject matter,<sup>4,9</sup> in this text we will endorse Burnett and colleagues'<sup>2,56</sup> definition of submarine groundwater discharge (SGD) to include all bidirectional exchange of any water mass across the coastal seafloor without regard to its composition, its origin, or the driving processes (Figure 3). Pore fluids entrained within coastal sediments in this sense can be considered synonymous with the term groundwater. It is thus implied that the discharge of coastal groundwater can be either upward (i.e., discharge) or downward (i.e., recharge) and that the two need not balance one another. The net flow represents the difference between the two components.

Coastal groundwater almost always resides in a complex matrix of confined, semiconfined, and unconfined aquifer systems that are most always highly anisotropic in nature.<sup>57,58</sup> The saltwater–freshwater interface of a coastal aquifer may respond to many terrestrial and marine forcing factors, including the down-gradient flow of freshwater from coastal uplands.<sup>59–62</sup> As freshwater, driven by a positive inland hydraulic head, flows through a coastal aquifer, it can pull in saline groundwater that diffuses and disperses upward from a salty aquifer that underlies it.<sup>63,64</sup> For example, such a scenario exists in parts of Tampa Bay, where fresher or warmer waters may reside in quasi-equilibrium below more saline or colder groundwater (Figure 4). Superimposed upon this terrestrially driven circulation are a variety of marine-induced forces that result in flow into and out of the seabed,

even in the absence of a hydraulic head. Coastal aquifers, which have been described as so-called “subterranean estuaries”,<sup>5</sup> are thus reactors for a broad range of biogeochemical processes that can modulate the transfer of nutrients and other chemical constituents during their seaward transport.<sup>65–74</sup>

There are both marine and terrestrial processes responsible for the discharge of coastal groundwater.<sup>57,59,75,76</sup> For example, all of the following marine processes may affect rates of SGD: (1) tides, waves, storms, or density/current-driven gradients; (2) density-related convection cells, induced by the instability of freshened water masses residing below more saline water; (3) the dynamic alignment of the freshwater–saltwater interface in response to climatic and anthropogenic forcing; and (4) water level variations across permeable barriers (i.e., barrier islands).<sup>77–82</sup> On the terrestrial side, SGD processes are at least conceptually somewhat less complex.<sup>83</sup> Darcy’s law defining hydraulic gradient-driven flow is controlled by the underlying geologic framework and affected by both climatic and anthropogenic cycles.<sup>58,84</sup>

The discharge of coastal groundwater has historically been recognized as an important pathway for water and associated material transport to the sea.<sup>85,86</sup> Sailors, at least anecdotally, utilized submarine spring water at sites around the world to replenish their freshwater supplies, whereas coastal scientists have long recognized the importance of SGD in coastal biogeochemical cycles and water resource issues.<sup>87,88</sup> Whereas the material flux from rivers into the sea has been globally assessed with some confidence,<sup>89</sup> coastal groundwater inputs and their ecological impacts on coastal systems remain poorly known.<sup>1,90,91</sup> The discharge of groundwater into coastal waters may have important environmental consequences because groundwater often carries elevated concentrations of select nutrients, trace elements, radionuclides, and organics.<sup>28,92</sup>



**Figure 4.** Anisotropy of a coastal aquifer system: Tampa Bay, Florida, as evidenced from a high-resolution (2-m electrode spacing) time-series resistivity inversion of a sediment column underlying a shoreline in southern Tampa Bay. Red and orange hues reflect more resistive, that is, fresher, substrates.

Submarine groundwater discharge, expressed either as discrete spring discharge or diffuse seepage, may thus contribute directly to the environmental degradation of coastal waters.<sup>5,25,72</sup>

A subsurface route of nutrient transport to coastal waters has been shown to be involved in the onset of harmful algae blooms that often have widespread, deleterious impacts on the ecological health and economy of coastal waters.<sup>93–95</sup> Nitrogen transported in coastal groundwater has been shown to be an important component of the nutrient budget of New England<sup>65,96</sup> and South Carolina<sup>21</sup> saltmarshes. In Great South Bay, New York, Bokuniewicz<sup>76,97</sup> quantified SGD inputs, which were subsequently evaluated in terms of an important and substantial source of nitrate to the bay.<sup>98,99</sup> From a similar study of SGD-derived nutrient fluxes into Florida Keys surface waters, Lapointe et al.<sup>100</sup> observed elevated N and P fluxes that may also contribute to local phytoplankton blooms. In Tampa Bay, Swarzenski et al.<sup>43</sup> quantified SGD rates using Ra isotopes and then measured SGD-derived nutrient fluxes to the bay, which were at least on the same order of magnitude as riverine nutrient loading estimates. In the Loxahatchee River estuary of southeastern Florida, the role of SGD and SGD-derived nutrient fluxes was evaluated and compared to riverine estimates.<sup>29</sup> The direct discharge of submarine spring water into ambient seawater caused a measurable dilution of salinity in Discovery Bay, Jamaica,<sup>101</sup> and in the Atlantic Ocean off northeastern peninsular Florida.<sup>22</sup>

### 3. SGD Tracers

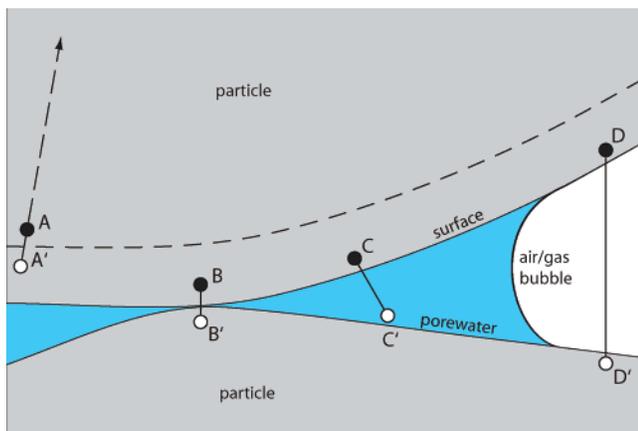
One of the simplest and most widely used devices built to measure direct fluid exchange rates across the sediment–water interface is the manual seepage meter.<sup>102</sup> The practicality of this device is offset only by the laborious nature of data collection and required redundancy or replication to ensure data quality.<sup>103–106</sup> Second-generation seepage meters that can function autonomously and can rapidly and precisely measure bidirectional fluid exchange rates have recently been developed<sup>107–114</sup> and can now provide much more subtle information on the response of fluid exchange rates to external forcing, such as tides and waves. A real limitation of any seepage meter is the small footprint of the instrument that can provide only site-specific information. Such is also the case in the deployment of piezometers or multiport samplers,<sup>115</sup> which can provide very detailed vertical information of water masses per site.

In contrast, select naturally occurring isotopes in the U/Th decay series measured in coastal surface waters and groundwater can provide local to regional scale submarine groundwater discharge information.<sup>18,116</sup> The application of select U/Th series radionuclides as unique tracers of SGD has developed along two contrasting themes: (1) the excess activity of a radionuclide in a coastal water body may be geochemically linked to groundwater discharge, and (2) vertical pore water and solid phase activities are assessed within the constraints of an advection/diffusion model.<sup>35,117–119</sup> The following section describes the groundwater behavior of select U/Th series radionuclides.

### 3.1. Uranium

In oxic waters, U exists as hexavalent U(VI), forming soluble complexes primarily with carbonate and phosphate under near-neutral pH conditions, whereas at lower pH values, U may also complex with sulfate and fluorides.<sup>120</sup> In saline groundwaters, U solubilities are generally higher, and chloride and sulfate complexes may become more important.<sup>18</sup> Activities of U in fresh groundwater are typically close to 1 ppb, and values over 1 ppm are generally found only in mineralized areas.<sup>20</sup> Under reducing conditions, U is present in the tetravalent and stable U(OH)<sub>4</sub>,<sup>121</sup> and the solubility limit of uraninite, UO<sub>2</sub>, sets the maximum U concentration to ~0.06 ppb.<sup>31</sup> Groundwaters that migrate into a redox front can thus precipitate U, which can then locally produce <sup>234</sup>U and <sup>234</sup>U/<sup>238</sup>U ratios in excess of 1.<sup>20,122</sup>

Both <sup>234</sup>U and <sup>238</sup>U are provided in secular equilibrium to the groundwater by simple weathering processes. In addition, “excess” <sup>234</sup>U is released by recoil processes within <sup>234</sup>Th-bearing minerals, followed by decay to <sup>234</sup>Pa (*t*<sub>1/2</sub> = 1 min) and then to <sup>234</sup>U.<sup>45</sup> α recoil is the process by which a radioactive daughter is mobilized from its initial position solely by the energy of an α decay.<sup>123</sup> Figure 5 illustrates various potential recoil effects in saturated particle lattices.<sup>124</sup> Additional release of <sup>234</sup>U may also occur during direct recoil processes.<sup>125–127</sup> Both recoil and weathering processes are proportional to the surface area of U-bearing phases, so variations in grain size or the mineral composition will not change the ratio of these supply rates.<sup>18</sup> In contrast, a change in the groundwater chemistry will affect the weathering rate but not the recoil rate, and so will produce a change in groundwater U isotopic composition.<sup>128,129</sup> Because the preferential loss of <sup>234</sup>U will result in a <sup>234</sup>U/<sup>238</sup>U activity ratio in the weathering mineral that is lower than 1, the

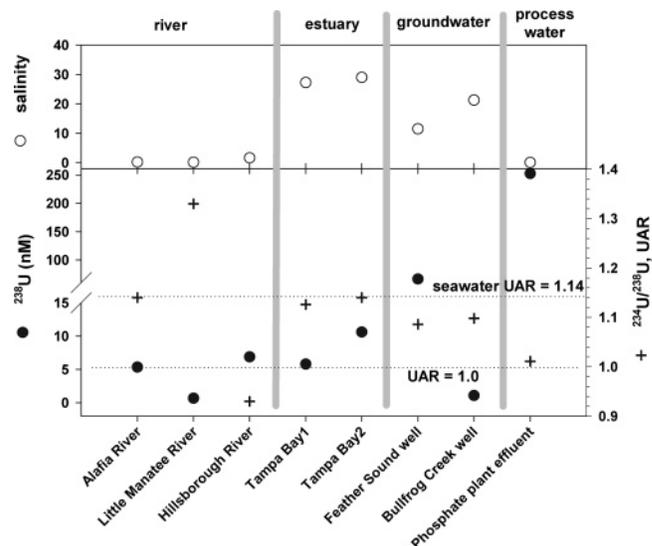


**Figure 5.** Schematic recoil effects in particle lattices, showing differences between particle, porewater, and air. A–A' show that recoiling Rn does not escape host mineral lattice; B–B' show recoil traveling directly into adjacent particle lattice; C–C' show recoil into porewater; and D–D' show recoil into the air/gas void, leaving Rn embedded in adjacent mineral lattice. (Redrawn from ref 124. Copyright 1996, with permission from Elsevier.)

release of this U by weathering processes will at least partially balance the recoiled  $^{234}\text{U}$ .<sup>130,131</sup>

In groundwaters,  $^{234}\text{U}/^{238}\text{U}$  ratios in excess of 1 can be produced if U is concentrated in secondary mineral phases and if weathering processes are generally less important.<sup>32</sup> For example, U can be precipitated when groundwaters become anoxic (i.e., roll front deposits) as reduced tetravalent U is much more insoluble than U(VI). Under these conditions, U concentrations can be expected to decrease dramatically, whereas  $^{234}\text{U}/^{238}\text{U}$  activity ratios will increase due to recoil processes from the precipitated phases.<sup>20</sup> Isotopic variations can also occur due to changes in groundwater chemistry or host rock characteristics.<sup>34,36,132–135</sup> 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. When consistent groundwater behavior is observed, U isotopes have been used to establish a groundwater chronology or pore water flow rates.<sup>19,34,136</sup>

Several recent studies have used U concentrations and isotope compositions to trace coastal groundwater flow patterns in the context of SGD.<sup>137,138</sup> For example, it has recently been suggested that some uranium may be effectively removed to anoxic sediments during recharge cycles of submarine groundwater. It is possible to use deficiencies in uranium activities in coastal waters, relative to expected concentrations based on the U/salinity ratio in seawater, to estimate SGD rates.<sup>139</sup> U isotope compositions potentially can provide an important tool for tracing groundwaters from different aquifer conditions.<sup>19,37,140,141</sup> However, clear interpretations of  $^{234}\text{U}/^{238}\text{U}$  activity ratios and quantification of the responsible processes remain difficult. For example, Figure 6 shows U concentrations and  $^{234}\text{U}/^{238}\text{U}$  isotope ratios in several riverine, coastal, and groundwater samples within Tampa Bay, Florida. Although the  $^{234}\text{U}/^{238}\text{U}$  isotope ratio shows considerable variability in the three inflowing river samples, in the bay proper, this ratio rapidly approaches the seawater value of 1.14.<sup>142</sup> Seawater and the coastal groundwater end-members may have specific isotopic signatures, and under ideal conditions, such end-member differences may yield useful information of the groundwater discharge



**Figure 6.** Salinity (A) and (B)  $^{238}\text{U}$  concentrations and  $^{234}\text{U}/^{238}\text{U}$  activity ratios (UARs) in river, coastal, and groundwater samples collected in Tampa Bay, Florida, and surrounding environs. Seawater UAR value<sup>142</sup> and secular equilibrium (1.0) value are shown for comparison. Data from Swarzenski et al.<sup>138</sup>

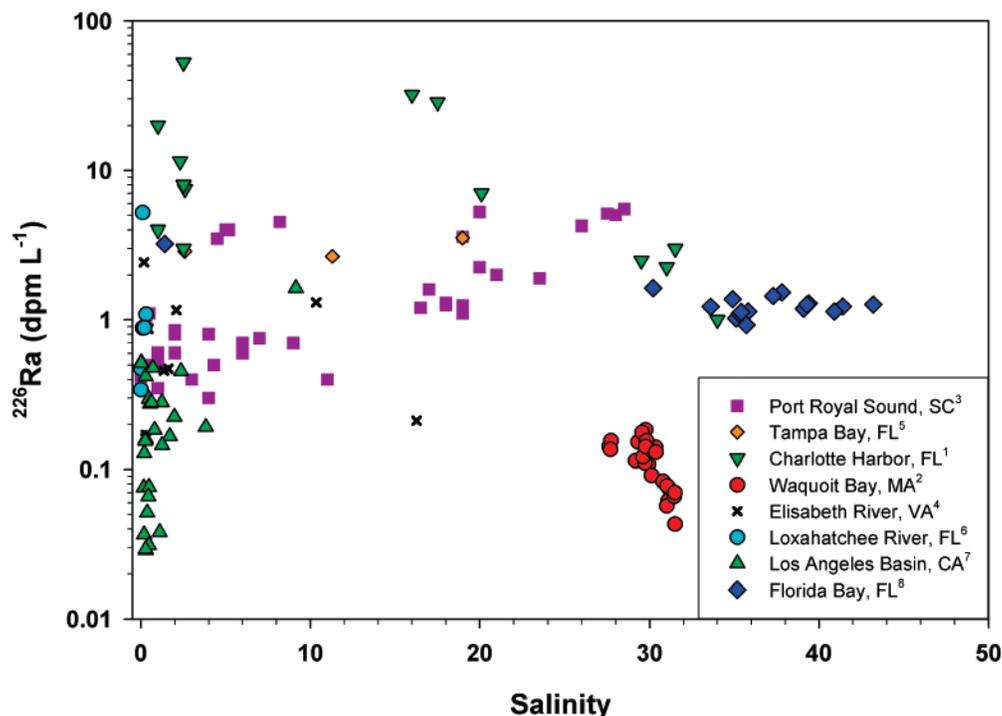
contribution into estuarine water. This may be especially useful when mixing is occurring between more than two end-members, including saline groundwater.<sup>19</sup>

### 3.2. Thorium

The six thorium isotopes ( $^{234}\text{Th}$ ,  $^{230}\text{Th}$ ,  $^{232}\text{Th}$ ,  $^{228}\text{Th}$ ,  $^{231}\text{Th}$ , and  $^{227}\text{Th}$ ) in the U/Th series (Figure 1) have half-lives that vary greatly from just over 1 day ( $^{231}\text{Th}$ ) to  $1.4 \times 10^{10}$  years ( $^{232}\text{Th}$ ). In low-pH groundwater, Th exists mostly as  $\text{Th}^{4+}$  or as sulfate and fluorine complexes,<sup>52,143,144</sup> whereas in higher pH groundwater,  $\text{Th}(\text{OH})_2^{2+}$  is thought to prevail. Due to the very high particle affinity of this element,<sup>18</sup> the longer-lived Th isotopes are particularly useful to assess the role of colloids and particles associated with weathering during groundwater transport.<sup>45,50,145,146</sup> Whereas it is certain that short-lived Th isotopes are strongly absorbed on aquifer solids,<sup>147</sup> results from delayed coincidence analysis<sup>148</sup> for  $^{223,224}\text{Ra}$  confirm the almost ubiquitous presence of  $^{228}\text{Th}$  in coastal groundwater. Thus, the behavior of Th isotopes in coastal groundwater requires further understanding regarding the irreversible retention of Th onto host colloids and particles.

### 3.3. Radium

There are four naturally occurring isotopes of Ra:  $^{226}\text{Ra}$  ( $t_{1/2} = 1600$  years) present in the  $^{238}\text{U}$  series,  $^{228}\text{Ra}$  (5.75 years) and  $^{224}\text{Ra}$  (3.66 days) in the  $^{232}\text{Th}$  series, and  $^{223}\text{Ra}$  (11.4 days) in the  $^{235}\text{U}$  series (Figure 1; Table 1). The differences in half-lives and unique parent–daughter relationships across different decay series have been utilized to study a variety of groundwater processes and water–rock interactions.<sup>149–152</sup> For the two short-lived Ra isotopes, the principal input term to groundwater is recoil, rather than weathering processes. Steady-state activities of  $^{223,224}\text{Ra}$  are thus often achieved in groundwater. Under low-salinity conditions, Ra occurs as  $\text{Ra}^{2+}$ , whereas sulfate, carbonate, and  $\text{Cl}^-$  complexes will occur in saline groundwater with high respective ligand concentrations.<sup>153</sup> Organic Ra complexes are generally not considered to be significant in fresh groundwater,<sup>51</sup> yet



**Figure 7.** Coastal groundwater  $^{226}\text{Ra}$  activities ( $\text{dpm L}^{-1}$ ) as a function of salinity from various sites in the United States. <sup>1</sup>Miller et al. (ref 159); <sup>2</sup>Charette et al. (ref 39); <sup>3</sup>Crotwell and Moore (ref 160); <sup>4</sup>Charette and Buesseler (ref 183); <sup>5</sup>Swarzenski et al. (ref 43); <sup>6</sup>Swarzenski et al. (ref 293); <sup>7</sup>Swarzenski (unpublished data); <sup>8</sup>Swarzenski (*Radium Isotopes as Tracers across the Sediment–Water Interface*; U.S. Geological Survey Open-File Report 00-482; Washington, DC, 2000).

colloid transport via clays and iron oxides may influence subsurface Ra transport. The solubility limit of Ra is generally not reached in fresh groundwater, but Ra can be precipitated in solid solution within Ca and Ba minerals.<sup>154,155</sup>

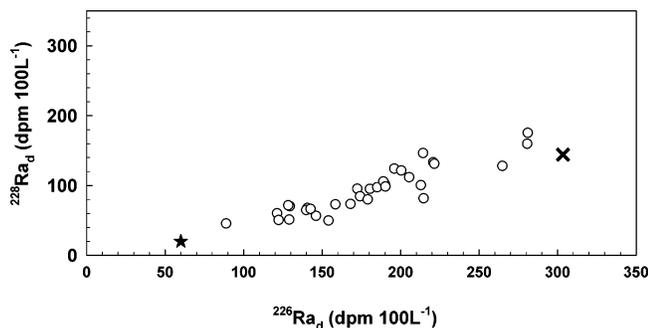
Adsorption onto aquifer solids exerts a strong control on the behavior of Ra in coastal groundwater, and adsorption rate constants are dependent on substrate type and the chemical composition of the groundwater.<sup>18</sup> Decreases in adsorption efficiency have been observed under conditions of increasing salinity,<sup>49,151</sup> due to such processes as cation competition and displacement, increases in mineral surface charge,<sup>35</sup> and increases in the stability of inorganic complexes.<sup>156</sup> In a coastal aquifer, fluctuating groundwater salinities at the freshwater–saltwater interface may cause Ra to adsorb onto aquifer surfaces, thereby becoming a localized source of  $^{222}\text{Rn}$ .<sup>157</sup>

### 3.3.1. Ra Isotope Systematics

$^{228}\text{Ra}$  and  $^{224}\text{Ra}$  are located within the  $^{232}\text{Th}$  decay series, and examining the behavior of these Ra isotopes in groundwater requires knowledge of their respective radiogenic parents,  $^{232}\text{Th}$  and  $^{228}\text{Th}$ .  $^{232}\text{Th}$  absorbed within aquifer minerals can produce  $^{228}\text{Ra}$  that is then ejected from the lattice structure by recoil.<sup>158</sup> In contrast, any  $^{232}\text{Th}$  that has been released by weathering will likely remain adsorbed at a surface site and will produce  $^{228}\text{Ra}$ , which will be recoiled back either into the mineral lattice or into groundwater (Figure 5). Any  $^{228}\text{Ra}$  present in groundwater is produced mostly by  $^{232}\text{Th}$  absorbed in aquifer minerals and on surfaces, and because it is strongly adsorbed, it can exchange with a much larger surface reservoir.<sup>18</sup> The decay  $^{228}\text{Ra}$  occurs via low energy  $\beta$  to the short-lived  $^{228}\text{Ac}$  ( $t_{1/2} = 6$  h), which subsequently decays rapidly to  $^{228}\text{Th}$ . It is likely that  $^{228}\text{Ac}$ , due to its short half-life, does not affect the subsequent supply of  $^{228}\text{Th}$ . Because the decays of both  $^{228}\text{Ra}$  and  $^{228}\text{Ac}$  are

low energy, there is no release of  $^{228}\text{Th}$  from the mineral by recoil. Consequently, the  $^{228}\text{Th}$  in the surface is supplied only by decay of the parent  $^{228}\text{Ra}$  reservoir already there, and the activity in groundwater is determined by interchange with the surface. This therefore directly connects the abundances of  $^{228}\text{Th}$  and  $^{228}\text{Ra}$ .<sup>151</sup> The groundwater activity of  $^{224}\text{Ra}$  is supplied mostly by recoil from  $^{228}\text{Th}$  absorbed in the host rock minerals, as well as  $^{228}\text{Th}$  adsorbed on mineral surfaces. The two remaining  $^{226,223}\text{Ra}$  isotopes in the  $^{238}\text{U}$  and  $^{235}\text{U}$  decay series, respectively, can be evaluated similarly.  $^{226}\text{Ra}$  and  $^{223}\text{Ra}$  are both products of the third  $\alpha$  decay, and so the effects of near-surface depletion or decay of recoiled precursors will be analogous to those of  $^{224,228}\text{Ra}$ .

Figure 7 shows the distribution of  $^{226}\text{Ra}$  activities as a function of salinity in varied coastal groundwaters from Florida, New England, and California.  $^{226}\text{Ra}$  activities are highest (up to  $50 \text{ dpm L}^{-1}$ ) in groundwaters of west-central Florida<sup>159</sup> and lowest (mean =  $0.2 \text{ dpm L}^{-1}$ ) in groundwaters from the Los Angeles basin in California. The pronounced lack of a relationship between  $^{226}\text{Ra}$  and salinity is strong evidence for the local geologic control on  $^{226}\text{Ra}$  production. For example, from a study of SGD in South Carolina, Crotwell and Moore<sup>160</sup> showed that groundwater  $^{226}\text{Ra}$  activities increased systematically almost 30-fold from  $0.2 \text{ dpm L}^{-1}$  at a salinity of 0.5 to  $\sim 5.5 \text{ dpm L}^{-1}$  at a salinity of 28. This observation is compatible with the much lower partitioning of Ra onto surfaces with an increase in salinity. Whereas the shorter-lived isotopes will generally adjust to changes in water chemistry,  $^{226}\text{Ra}$ , with a much longer half-life than the other Ra isotopes, requires a much longer distance along a groundwater flow line to achieve steady state. 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  $^{226}\text{Ra}$  both in the groundwater and on the surfaces.<sup>15,51,151</sup>



**Figure 8.**  $^{226}\text{Ra}$  versus  $^{228}\text{Ra}$  activities ( $\text{dpm } 100 \text{ L}^{-1}$ ) measured in coastal surface water ( $\circ$ ), coastal groundwater ( $\times$ ), and adjacent Gulf of Mexico seawater samples ( $*$ ) in Tampa Bay and surrounding environs (data from Swarzenski et al.<sup>43</sup>).

### 3.3.2. $^{226}\text{Ra}/^{228}\text{Ra}$ Activity Ratios

In groundwater, the  $^{226}\text{Ra}/^{228}\text{Ra}$  ratio is a function of the parent  $^{238}\text{U}/^{232}\text{Th}$  ratio in host material, and this ratio may thus yield information on the relative recoil rates of radionuclides within two separate decay series. Recoil may produce  $^{226}\text{Ra}/^{228}\text{Ra}$  ratios up to 1.75 times that of the host rock due to accumulation of preceding nuclides.<sup>161</sup> A  $^{238}\text{U}/^{232}\text{Th}$  activity ratio of  $\sim 0.8$  (equivalent to a Th/U weight ratio of 3.8) measured within the upper crust may be assumed to be representative of such a ratio in the host rock, although this can of course be substantially different in rocks such as limestone.<sup>18</sup> There is often a strong correlation between activities of  $^{226}\text{Ra}$  and total dissolved solids, as well as of Ca, Sr, and Ba, and some groundwaters may become saturated with either calcite and barite.<sup>144</sup> In a carbonate aquifer, observed groundwater  $^{226}\text{Ra}$  activities were up to 6 times that found in host rock, and it was suggested that this may be due to the production of  $^{226}\text{Ra}$  by either  $^{230}\text{Th}$  or  $^{238}\text{U}$  enrichments on particle surfaces.<sup>154</sup> A plot of  $^{226}\text{Ra}$  versus  $^{228}\text{Ra}$  activities ( $\text{dpm } 100\text{L}^{-1}$ ) in groundwater, coastal water, and adjacent Gulf of Mexico waters from Tampa Bay, Florida, is shown in Figure 8. From such a strong relationship between  $^{228}\text{Ra}$  and  $^{226}\text{Ra}$  in these varied waters, it is evident that the coastal water Ra activities exhibit a strong groundwater-borne signature.

### 3.3.3. $^{224}\text{Ra}/^{228}\text{Ra}$ Activity Ratios

These two Ra isotopes uniquely reside within the same  $^{232}\text{Th}$  decay series. They are directly related to one another via two  $\beta$  decay products ( $^{228}\text{Ac}$  and  $^{228}\text{Th}$ ) and one  $\alpha$  decay ( $^{224}\text{Ra}$ ), and differences in groundwater  $^{224}\text{Ra}/^{228}\text{Ra}$  activity ratios cannot be ascribed to differences in parent isotope distributions in host rock.<sup>151</sup> If secular equilibrium exists in host material, then the  $^{224}\text{Ra}/^{228}\text{Ra}$  activity ratios must equal 1. In fresh groundwater, the isotopic composition of  $^{224}\text{Ra}/^{228}\text{Ra}$  ranged from 0.5–2.1 within a sandy aquifer<sup>12</sup> to 1.0–4.2 for a basaltic aquifer,<sup>162</sup> and to 0.8–1.8 for arkose and glacial drift.<sup>14</sup> Much higher values have also been reported<sup>49,161</sup> and imply that other processes (e.g., remobilization of  $^{228}\text{Th}$ ) might be required to explain these higher ratios. Along a groundwater flowline,  $^{224}\text{Ra}$  will reach a steady-state concentration more rapidly than  $^{228}\text{Ra}$ , and so higher values of ( $^{224}\text{Ra}/^{228}\text{Ra}$ ) will be observed in recently recharged waters,<sup>12,161</sup> or immediately down-gradient of Ra precipitation.<sup>163</sup> Also,  $^{224}\text{Ra}$  may decay within the surface layer at a rate comparable to the desorption rate, resulting in a lower effective partitioning value for  $^{224}\text{Ra}$  over  $^{228}\text{Ra}$ .<sup>14</sup> In general, it appears that unusually high values are due to

circumstances where steady-state conditions have not been reached, whereas smaller variations are due either to the recoil loss and redistribution of  $^{228}\text{Th}$  or decay of  $^{224}\text{Ra}$  on surfaces where desorption rates are relatively long.

### 3.3.4. $^{223}\text{Ra}/^{226}\text{Ra}$ Activity Ratios

$^{223}\text{Ra}$  and  $^{226}\text{Ra}$  are both generated after three  $\alpha$  decays, and so groundwaters at steady state should have a  $^{223}\text{Ra}/^{226}\text{Ra}$  ratio similar to the rock  $^{235}\text{U}/^{238}\text{U}$  activity ratio of 0.046. Where  $^{226}\text{Ra}$  has not attained a steady-state activity, such as in a flowing groundwater after recharge or precipitation, higher  $^{223}\text{Ra}/^{226}\text{Ra}$  ratios may be observed.<sup>161,164</sup> For example, Martin and Akber<sup>164</sup> observed  $^{223}\text{Ra}/^{226}\text{Ra}$  ratios in excess of 0.046 in samples saturated in barite. These authors suggested that such elevated ratios are likely to be due to precipitation of both Ra isotopes, followed by more rapid return to steady state of the shorter-lived isotope. At this site, the presence of observed lower  $^{223}\text{Ra}/^{226}\text{Ra}$  and  $^{224}\text{Ra}/^{228}\text{Ra}$  activity ratios may be due to subsurface transport of the longer-lived Ra isotopes via colloids without rapid exchange with dissolved Ra.

### 3.3.5. $^{224}\text{Ra}/^{222}\text{Rn}$ Activity Ratios

The activities of  $^{224}\text{Ra}$  and  $^{222}\text{Rn}$  in groundwater are generally expected to be in steady state due to their short half-lives. Although typical bulk rock ( $^{238}\text{U}/^{232}\text{Th}$ ) activity ratios are close to unity, so that the recoil rates of  $^{224}\text{Ra}$  and  $^{222}\text{Rn}$  are similar, the ratio of the recoil supplies of  $^{222}\text{Rn}$  and  $^{224}\text{Ra}$  might be somewhat different due to different distributions between  $^{238}\text{U}$  and  $^{232}\text{Th}$ . Also,  $^{222}\text{Rn}$  is further down its decay series and is preceded by four  $\alpha$  decays, whereas  $^{224}\text{Ra}$  is preceded only by two, and so  $^{222}\text{Rn}$  production may be 50% higher due to precursors accumulated on surfaces. Measured  $^{224}\text{Ra}/^{222}\text{Rn}$  ratios in fresh groundwaters ranged from  $0.2 \times 10^{-4}$  to  $4.4 \times 10^{-4}$ .<sup>12,14,162</sup> Some variation in this activity ratio may be due to desorption rates that are comparable to the decay constant of  $^{224}\text{Ra}$ . Saline groundwaters typically exhibit higher  $^{224}\text{Ra}/^{222}\text{Rn}$  ratios,<sup>49</sup> consistent with expected reduced adsorption of Ra in such waters.

## 3.4. Radon ( $^{222}\text{Rn}$ ) and Thoron ( $^{220}\text{Rn}$ )

Two isotopes of radon are potentially of importance in coastal groundwater studies.  $^{222}\text{Rn}$  ( $t_{1/2} = 3.8$  days) is produced by the  $\alpha$  decay of  $^{226}\text{Ra}$  in the  $^{238}\text{U}$  decay series, whereas  $^{220}\text{Rn}$  ( $t_{1/2} = 55.6$  s) is formed by the  $\alpha$  decay of  $^{224}\text{Ra}$  (Figure 1). Radon, with an atomic number of 86, is the heaviest of the noble gases and, therefore, in groundwater is not easily ionized and so does not react with aquifer surfaces.<sup>165</sup> As a consequence,  $^{222}\text{Rn}$  is highly mobile with respect to transfer from the aquifer matrix to pore water and frequently has the highest observed groundwater activities (Figure 2). The production of Rn from the decay of Ra is accompanied by a recoil in the direction opposite to the emitted  $\alpha$  particle. The recoil range of an Rn atom is on the order of 40 nm in solids, 95 nm in water, and 64000 nm in air.<sup>124,166</sup> Krishnaswami et al.<sup>14</sup> suggested that  $^{222}\text{Rn}$  and all other U/Th series isotopes produced by  $\alpha$  decay are supplied at similar rates by such recoil. Therefore, the activities of  $^{222}\text{Rn}$  in groundwater may be used to calculate the recoil rate for all U/Th series nuclides produced by  $\alpha$  recoil. The only loss term for  $^{222}\text{Rn}$  is radioactive decay, and with a 3.8 day half-life, it will likely reach steady-state activities in most groundwater systems.

Observed groundwater  $^{222}\text{Rn}$  activities typically correspond to  $^{222}\text{Rn}$  release rates of up to  $\sim 10\%$  of the amount being produced in the aquifer rock.<sup>14</sup> This implies that  $\sim 20\%$  of the  $^{226}\text{Ra}$  in the host rock should exist within recoil distance of the surface.<sup>18</sup> Such high recoil rates cannot easily be supported by recoil from typical aquifer grain sizes with uniform parent Ra activities. Instead, various other causes for such high release rates have been invoked. For example, it is possible that  $^{226}\text{Ra}$  must be absorbed on very small grains or present on secondary phases, or  $^{226}\text{Ra}$  adsorbed on surfaces could preferentially produce  $^{222}\text{Rn}$  by weathering processes.<sup>157</sup> Another process that has been suggested for the elevated supply of  $^{222}\text{Rn}$  into the unsaturated zone is the leaching of radionuclides from adjacent minerals. Where fluctuations in the water table yield ephemerally saturated conditions, the decreased stopping power of air allows atoms ejected from minerals to be implanted across pore spaces. These atoms will then be available for subsequent leaching,<sup>123</sup> which would affect the supply of  $^{222}\text{Rn}$  from ephemerally flooded sediments.<sup>18,167</sup>

It is likely that U and Th may be heterogeneously enriched within aquifers in fine-grained clays or other aquicludes with low hydraulic conductivities that are not part of the main water-bearing deposits.<sup>138</sup> If these strata are interspersed within the aquifer rocks, then  $^{222}\text{Rn}$  could diffuse into the main groundwater flow, whereas other radionuclides would be retained by adsorption in the aquicludes.<sup>168</sup> Rama and Moore<sup>15</sup> suggested that  $^{222}\text{Rn}$  produced within a large volume of a mineral reaches the grain boundaries by diffusive transport in a hypothesized network of nanopores, whereas other nuclides would adhere to pore surfaces. Such a scenario would yield an elevated  $^{222}\text{Rn}$  release rate that would not apply to other nuclides. High release rates of thoron,  $^{220}\text{Rn}$  ( $t_{1/2} = 1$  min), have also been reported,<sup>15,169</sup> which would require even faster diffusive transport rates. Rama and Moore<sup>170</sup> showed that  $^{220}\text{Rn}$  diffusion through mineral slabs was uneven and suggested that this reflected nanopore geometry. Similarly, Andrews and Wood<sup>171</sup> suggested that  $^{222}\text{Rn}$  migrates along dislocation planes and grain boundaries in wall rocks. However, other experiments have not found clear evidence for the occurrence of such nanopores.<sup>11</sup> Additional studies of the role of nanopores on subsurface radionuclide transport are warranted.

#### 4. Tracing Coastal Groundwater Discharge with U/Th Series Isotopes

As discussed in the previous sections, complex water–rock interactions can impart unique radionuclide signatures to coastal groundwaters that are often distinctive from those in coastal surface waters. Within the past decade, numerous studies have utilized naturally occurring isotopes of Ra and Rn to quantify submarine groundwater discharge rates into coastal waters.<sup>4,21,22,24,39–43,48,80,118,160,172–184</sup> These studies build on the premise that Ra and Rn activities are usually significantly enriched in coastal groundwater relative to coastal surface water, are mostly conserved during coastal mixing, and can be measured precisely and quite easily. In the development of U/Th series SGD tracing techniques, delineating appropriate boundary conditions, defining water and constituent sources and sinks, establishing reasonable water residence time estimates, and measuring activities of the tracer in representative groundwaters, surface waters, and inflowing river waters are all required parameters. To construct a mass balance from which one can enumerate

SGD rates, source terms for the respective U/Th series radionuclides and associated water masses may include the open ocean, riverine inputs, coastal groundwater composition, in situ production, lateral water-column transport, sediment resuspension, sediment diffusion, and precipitation. Comparable loss terms may include in situ decay, lateral water-column transport, horizontal or vertical eddy diffusivity, and atmospheric evasion (including evaporation). Radium is often enriched in coastal groundwater relative to coastal surface waters, particularly where saline waters have recently come in contact with aquifer minerals. In the coastal waters of the South Atlantic Bight, Moore<sup>4</sup> utilized an observed excess in  $^{226}\text{Ra}$  relative to seawater values to derive SGD rates. In these waters,  $^{226}\text{Ra}$  activities were systematically highest in near-shore waters. From knowledge of the coastal water transit or residence time, which may be estimated using  $^{223,224}\text{Ra}$ , and assuming steady state, an offshore flux (e.g.,  $\text{dpm day}^{-1}$ ) of excess  $^{226}\text{Ra}$  can be derived as<sup>39</sup>

$$J_{^{226}\text{Ra}} = \left[ \frac{(^{226}\text{Ra}_{\text{av}} - ^{226}\text{Ra}_{\text{sea}}) \times V_{\text{bay}}}{T_r} \right] - [^{226}\text{Ra}_r Q_r] - [^{226}\text{Ra}_{\text{des}}] \quad (\text{dpm day}^{-1}) \quad (1)$$

where  $J_{^{226}\text{Ra}}$  represents the average measured activity in coastal waters,  $^{226}\text{Ra}_{\text{sea}}$  is the activity in the adjacent open ocean,  $T_r$  is an estimate of the estuarine transit time,  $Q_r$  is a river-discharge rate, and  $^{226}\text{Ra}_{\text{des}}$  is the calculated estuarine-wide regeneration rate of  $^{226}\text{Ra}$  from bottom sediments.

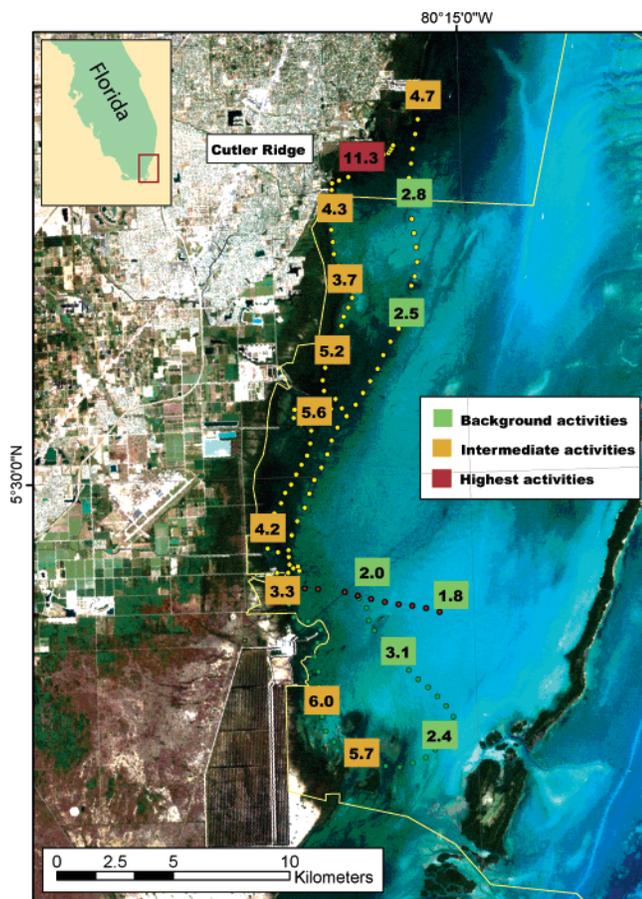
If this flux is supported solely by submarine groundwater discharge, then the rate of SGD can be estimated by dividing the radium flux simply by a representative average groundwater  $^{226}\text{Ra}$  activity.

$$\text{SGD} = \frac{J_{^{226}\text{Ra}}}{^{226}\text{Ra}_{\text{GW}}} \quad (\text{m}^3 \text{ day}^{-1}) \quad (2)$$

Burnett et al.,<sup>90,185</sup> Moore,<sup>4</sup> and colleagues have developed the following approach to quantify coastal groundwater exchange into coastal waters: (1) determine the range in representative radionuclide activities in a coastal aquifer; (2) determine the source and fate of these radionuclides in a surface water body; (3) assess the lateral exchange (e.g., transit/residence time) between the coastal ocean and the adjacent open ocean; and (4) develop a steady-state mass balance of radionuclide flux terms (see eq 1). In the case of  $^{222}\text{Rn}$ , an atmospheric evasion term must be included in the derivation of such a mass balance.

Resulting SGD rates, which can be expressed as  $\text{m}^3 \text{ day}^{-1}$ , per unit area (i.e.,  $\text{m}^3 \text{ m}^{-2} \text{ day}^{-1}$ ) or per m of shoreline ( $\text{m}^3 \text{ m}^{-1} \text{ day}^{-1}$ ), may be multiplied by average coastal groundwater nutrient or trace element concentrations to yield respective fluxes into coastal waters.

Burnett et al.<sup>90</sup> pioneered a nearly continuous radon monitor that can rapidly and accurately analyze  $^{222}\text{Rn}$  within either surface water or groundwater pumped directly into an air–water exchanger. In this exchanger that forces the inflowing water stream to disperse,  $^{222}\text{Rn}$  in the aqueous phase is allowed to equilibrate with radon in air. The activity of  $^{222}\text{Rn}$  in air is subsequently measured in a commercial radon-in-air monitor. More recently, a multidetector system has been developed that can be used in a continuous survey mode to map radon activities in the coastal zone.<sup>186</sup> By running as many as six detectors in parallel, one may obtain



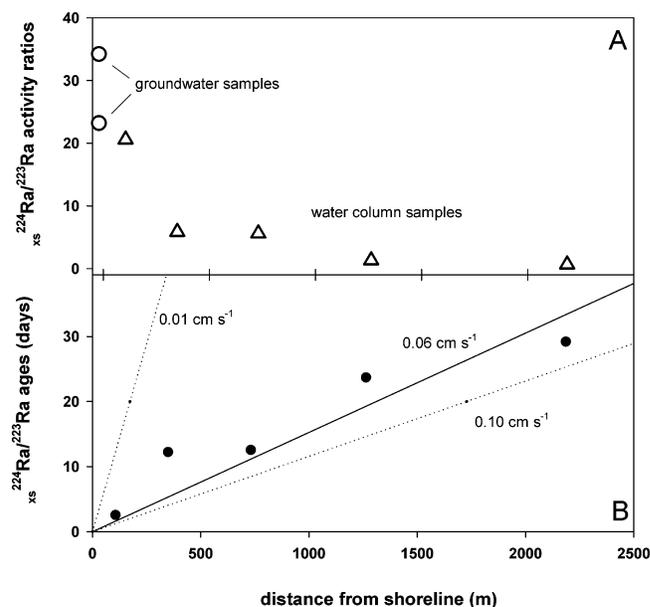
**Figure 9.** Near-continuous  $^{222}\text{Rn}$  activities ( $\text{dpm L}^{-1}$ ) measured using six Rn detectors plumbed in parallel in Biscayne Bay, Florida (from Swarzenski et al. *Novel Geophysical and Geochemical Techniques To Study Submarine Groundwater Discharge in Biscayne Bay, FL*; U.S. Geological Survey Fact Sheet 3117; Washington, DC, 2004).

as many as 12 readings per hour for typical coastal water Rn activities, with a precision of  $\sim 12\%$ . Figure 9, for example, shows results from such a nearly continuous  $^{222}\text{Rn}$  survey conducted using six detectors in Biscayne Bay, Florida. Highest radon activities ( $\sim 11 \text{ dpm L}^{-1}$ ) relative to background values of 2–3  $\text{dpm L}^{-1}$  were observed off Cutler Ridge, where Kohout<sup>187</sup> investigated subsurface freshwater/saltwater mixing dynamics and enhanced SGD.

Moore<sup>4,40,41,188</sup> developed an intriguing method to determine the apparent ages of freshened coastal water masses based on the activity ratio of the two short-lived Ra isotopes,  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$ . Assuming that the groundwater  $^{224}\text{Ra}/^{223}\text{Ra}_{\text{gw}}$  activity ratio remains constant and that the coastal water column activity ratio changes only by radioactive decay, then apparent coastal water mass ages can be calculated as

$$\left[ \frac{^{224}\text{Ra}}{^{223}\text{Ra}} \right]_{\text{estu}} = \left[ \frac{^{224}\text{Ra}}{^{223}\text{Ra}} \right]_{\text{gw}} \frac{e^{-\lambda_{224}t}}{e^{-\lambda_{223}t}} \quad (3)$$

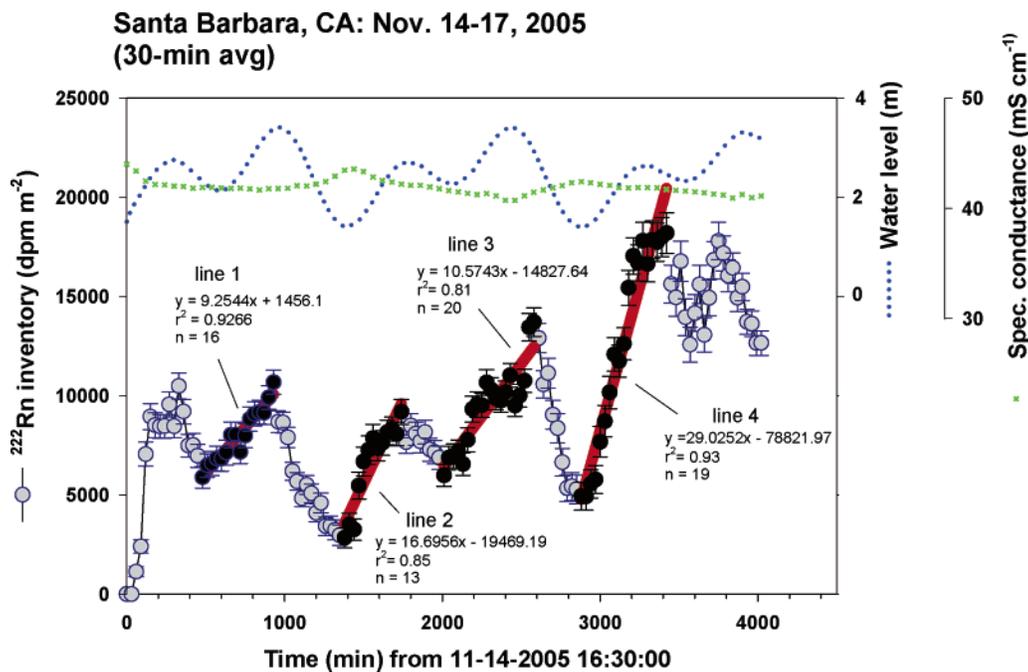
where  $[\text{xs } ^{224}\text{Ra}/^{223}\text{Ra}]_{\text{estu}}$  is the observed excess activity ratio in a coastal water,  $[\text{xs } ^{224}\text{Ra}/^{223}\text{Ra}]_{\text{gw}}$  is the average groundwater activity ratio,  $\lambda_{223}$  is the decay constant for  $^{223}\text{Ra}$  ( $0.0608 \text{ day}^{-1}$ ),  $\lambda_{224}$  is the decay constant for  $^{224}\text{Ra}$  ( $0.191 \text{ day}^{-1}$ ), and  $t$  is the calculated time elapsed between the groundwater activity ratio and the observed activity ratio. The  $^{224}\text{Ra}/^{223}\text{Ra}$  activity ratio must therefore decrease by the apparent half-



**Figure 10.** (A)  $^{224}\text{Ra}/^{223}\text{Ra}$  activity ratios as a function of distance (m) along a shore-perpendicular transect from the mean high-water line at Santa Barbara beach, California, offshore. (B) Apparent ages of coastal waters off Santa Barbara, CA, as derived using  $^{224}\text{Ra}/^{223}\text{Ra}$  activity ratios. From (B), water mass mixing velocities can be derived (i.e.,  $0.06 \text{ cm s}^{-1}$ ).

life of 5.4 days, so that older waters will have lower  $^{224}\text{Ra}/^{223}\text{Ra}$  activity ratios. Ages calculated with  $^{223,224}\text{Ra}$  are based on exponential decay laws rather than linear mixing and, thus, should be reported as apparent, not true, ages. Nonetheless, they do reflect a relative time history of dynamic coastal water masses that cannot be readily obtained using other techniques. These activity ratios may also be useful in identifying and quantifying groundwater-borne water from coastal water masses. Figure 10A shows  $\text{xs } ^{224}\text{Ra}/^{223}\text{Ra}$  activity ratios (AR) in two groundwater samples (average AR = 28.72) and five surface water column samples in the waters off Santa Barbara, CA. In these surface waters, this activity ratio decreased systematically with an increase in distance from shore. The  $\text{xs } ^{224}\text{Ra}/^{223}\text{Ra}$  activity ratio of the most inshore sample was closest to the average groundwater AR value, which suggests that the source of groundwater is most proximal to the shoreline. The most offshore sample had an  $\text{xs } ^{224}\text{Ra}/^{223}\text{Ra}$  AR of 0.64. Solely on the basis of these AR values, there appears to be little evidence coastal groundwater, with a unique isotopic composition, is being discharged beyond  $\sim 700 \text{ m}$ . As expected, the Ra-derived apparent ages of surface waters increased with increasing distance from the shoreline (Figure 10B). Given the sensitivity of this Ra technique, waters within the harbor proper are roughly 2 days old and approach an age of 30 days at the most distal site. A plot of distance from shoreline versus  $\text{xs } ^{224}\text{Ra}/^{223}\text{Ra}$  AR suggests that the coastal waters directly off Santa Barbara are being mixed at an average, apparent velocity of  $\sim 0.6 \text{ cm s}^{-1}$ .

Results from a 30-min averaged time-series experiment ( $^{222}\text{Rn}$  inventory,  $\text{dpm m}^{-2}$ , plotted as a function of time, min) in Santa Barbara harbor are shown in Figure 11. Where systematic increases in the  $^{222}\text{Rn}$  inventory were observed, a linear regression was used to calculate respective  $^{222}\text{Rn}$  fluxes ( $\text{dpm m}^{-2} \text{ min}^{-1}$ ). If one assumes that these observed fluxes are due solely to advection of Rn-rich coastal groundwater (the activity of  $^{222}\text{Rn}$  in two shallow, coastal well samples ranged from 600 to 1000  $\text{dpm L}^{-1}$ ), one can



**Figure 11.** Three-day time series of  $^{222}\text{Rn}$  inventories ( $\text{dpm m}^{-2}$ ) as a function of time (min) elapsed within surface waters of the Santa Barbara, CA, harbor. Also shown are harbor surface water level (m) and specific conductance ( $\text{mS cm}^{-1}$ ) values. Dark circles denote respective points used for the linear regressions that yield  $^{222}\text{Rn}$  fluxes ( $\text{dpm m}^{-2} \text{ min}^{-1}$ ). See text for further detail on the derivation of first-order submarine groundwater discharge rates from such  $^{222}\text{Rn}$  fluxes.

estimate a range of first-order SGD by dividing the fluxes by the measured groundwater activities. Such an approach yielded average SGD rates in Santa Barbara harbor that ranged from 2 to 6  $\text{cm day}^{-1}$ .

## 5. Future Studies

Recent studies of submarine groundwater discharge into coastal waters indicate that select long-lived and short-lived U/Th series isotopes show great promise as new tools to directly examine and quantify fluid exchange processes across the sediment–water interface. As new detection methods and further field validation strategies develop, for example, in situ  $^{222}\text{Rn}$  monitors<sup>90</sup> and delayed counting techniques, coastal scientists will be able to realistically identify and quantify SGD and associated fluxes into receiving coastal water bodies. Where previous studies have reported exchange rates based solely on information derived from single cores or benthic flux chambers under one small “footprint”, these new U/Th series methods can uniquely provide more synoptic, large-scale information. Often, it is these larger scale results that resource managers seek.

Ideally, a thorough SGD study should begin with a reconnaissance survey that includes geophysical streaming resistivity and nearly continuous  $^{222}\text{Rn}$  work to identify sites of enhanced fluid exchange across the sediment–water interface. Once such sites are established, direct measurements of this exchange via autonomous seepage meters and numerical modeling efforts to link coastal observations to a larger hydrogeologic framework should complement the use of U/Th series geochemical tracers. In concert, such an approach provides a powerful diagnostic suite of tools for regional scale SGD investigations.

Considerable advances continue to be made in the application of radionuclide tracers in coastal aquifer studies. Clearly, further studies are required to examine, for example, precise mechanisms of Rn and Ra release during subsurface

fresh water/seawater mixing and tidally driven water level fluctuations, to further constrain the controlling processes both on land and in the sea, and to refine the analytical methods (e.g., development of diffusion coils to concentrate Rn in water samples would eliminate the use of pumps and water/air exchangers). Although the use of Ra and Rn as quantitative coastal groundwater tracers has matured considerably during the past decade, placing these results and interpretations into a broader framework that covers a wide range of hydrogeologic settings may eventually yield a realistic typology of submarine groundwater discharge.

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