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Thank you for your assistance.
• Chemical cycling of Ba, Sr, Ca, U, Mn and Ra within a karst subterranean estuary is evaluated. • Terrestrial groundwater reflects aquifer rock trace element content for Sr, Ca, Ba, Mn and Ra. • Ra and Ba chemical cycling is decoupled; both demonstrate low salinity desorption. • Spring mixing zone Ba, Sr, Ca and Mn cycling is largely conservative between terrestrial groundwater and the ocean. • Karst subterranean estuaries are a significant source of Ra, Sr and U to the ocean.
Trace element geochemistry of groundwater in a karst subterranean estuary (Yucatan Peninsula, Mexico)

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Abstract

Trace element cycling within subterranean estuaries frequently alters the chemical signature of groundwater and may ultimately control the total chemical load to the coastal ocean associated with submarine groundwater discharge. Globally, karst landscapes occur over 12% of all coastlines. Subterranean estuaries in these regions are highly permeable, resulting in rapid infiltration of precipitation and transport of groundwater to the coast, and the predominant carbonate minerals are readily soluble. We studied the chemical cycling of barium (Ba), strontium (Sr), manganese (Mn), uranium (U), calcium (Ca) and radium (Ra) within the carbonate karst subterranean estuary of the Yucatan Peninsula, which is characterized by a terrestrial groundwater lens overlying marine groundwater intrusion with active submarine discharge through coastal springs. Terrestrial groundwater calcium (1–5 mmol kg\(^{-1}\)) and alkalinity (3–8 mmol kg\(^{-1}\)) are enriched over that predicted by equilibrium between recharging precipitation and calcite, which can be accounted for by groundwater organic matter respiration and subsequent dissolution of calcite, dolomite and gypsum. There is a close agreement between the observed terrestrial groundwater Sr/Ca, Mn/Ca, Ba/Ca and Ra/Ca and that predicted by equilibrium dissolution of calcite, thus the trace element content of terrestrial groundwater is largely determined by mineral dissolution. Subsequent mixing between terrestrial groundwater and the ocean in the actively discharging springs is characterized by conservative mixing of Sr, Mn, Ba and Ca, while U is variable and Ra displays a large enrichment (salinity: 1.9–34.9, Ba: 60–300 nmol kg\(^{-1}\), Sr: 15–110 μmol kg\(^{-1}\), U: 0.3–35 nmol kg\(^{-1}\), Mn: 0.3–200 nmol kg\(^{-1}\), Ca: 4.3–12.9 mmol kg\(^{-1}\), 226Ra: 18–2140 dpm 100 L\(^{-1}\)). The deep groundwater sampled through cenotes, local dissolution features, is typified by elevated Ba, Sr, Ca, Mn and Ra and the absence of U within marine groundwater, due to enhanced dissolution of the aquifer matrix following organic matter degradation and redox processes including sulfate reduction (salinity: 0.2–36.6, Ba: 7–1630 nmol kg\(^{-1}\), Sr: 1.3–210 μmol kg\(^{-1}\), U: 0.3–18 nmol kg\(^{-1}\), Mn: 0.6–2600 nmol kg\(^{-1}\), Ca: 2.1–15.2 mmol kg\(^{-1}\), 226Ra: 20–3120 dpm 100 L\(^{-1}\)). However, there is no evidence in the spring geochemistry that deep marine groundwater within this reaction zone exchanges with the coastal ocean via spring discharge. Total submarine groundwater discharge rates calculated from radium tracers are 40–95 m\(^3\) m\(^{-1}\) d\(^{-1}\), with terrestrial discharge contributing 75 ± 25% of the total. Global estimates of chemical loading from karst subterranean estuaries suggest Sr and U fluxes are potentially 15–28% and 7–33% of total ocean inputs (8.2–15.3 mol y\(^{-1}\) and 4.0–7.7 mol y\(^{-1}\)), respectively. Radium-226 inputs from karst subterranean estuaries are 34–50 times river inputs (6.7–9.9 × 10\(^{16}\) dpm y\(^{-1}\)).

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1. INTRODUCTION

Submarine groundwater discharge (SGD) is the transport of terrestrial sourced groundwater and groundwater of marine origin across the ocean-aquifer interface (Burnett et al., 2006). Many studies have shown that SGD is an important source of trace elements to the coastal ocean (Shaw et al., 1998; Basu et al., 2001; Moore et al., 2006; Beck et al., 2007; Bone et al., 2007; Moore, 2010; Santos et al., 2011; Beck et al., 2013; Gonneea et al., 2013). However, uncertainty remains concerning the total chemical flux via SGD, due in part to groundwater transit through the subterranean estuary (STE), the region of the coastal aquifer where sharp gradients in salinity, oxygen and redox state facilitate the biogeochemical cycling of trace elements (Moore, 1999; Charette and Sholkovitz, 2006; Kalens, 2006; Beck et al., 2007; Gonneea et al., 2008; Santos et al., 2011). To fully understand the impact SGD has on the coastal ocean and the role SGD plays in global ocean element budgets, we need to quantify how chemical cycling within the subterranean estuary impacts transport of dissolved species to the ocean.

Geochemical transformations within the salinity-mixing zone of the subterranean estuary have been observed at many sites characterized by permeable sand and dominated by aluminosilicate minerals (Charette and Sholkovitz, 2006; Beck et al., 2007; Gonneea et al., 2008; Santos et al., 2011). Karst subterranean estuaries, however, have three unique characteristics: (1) the water to rock ratio is much higher and more variable due to multiple scales of permeability; (2) carbonate minerals are readily soluble; and (3) groundwater mixing occurs during channelized conduit flow of both terrestrial and marine groundwater, with springs being the primary route of water exchange with the coastal ocean (Perry et al., 2002; Beddows et al., 2007; Fleury et al., 2007; Charette et al., 2008; Garcia-Solsona et al., 2010; Einsiedl, 2012). The key processes that may alter dissolved trace element distributions in the subterranean estuary include mineral dissolution/precipitation, adsorption/desorption reactions, redox cycling, and mixing between water sources. In the case of radioactive trace elements such as the isotopes of radium, radioactive production or decay must also be considered.

Globally, 12% of submarine groundwater discharge flows through karst subterranean estuaries (as reported in Beck et al. (2013)) calculated from aquifer lithologies presented in Gibbs and Kump (1994) and regional SGD estimates in Zekster et al. (2006). This study evaluates geochemical cycling of barium (Ba), uranium (U), strontium (Sr), manganese (Mn), calcium (Ca) and radium ($^{226}$Ra, $^{228}$Ra and $^{223}$Ra) within the Yucatan Peninsula karst subterranean estuary. These elements are of interest given their utility as tracers of environmental processes. For example, past oceanic productivity can be reconstructed from BaSO$_4$ burial rates (Paytan et al., 1996) while the oceanic Sr isotope record serves as a proxy for various inputs to the ocean, including continental weathering and hydrothermal circulation (Hess et al., 1986; Palmer and Edmond, 1989). Variability in oceanic Ca may be related to changes in ocean carbon cycling on long time scales (Griffith et al., 2008). Ra is used extensively as a tracer of groundwater discharge (Moore, 1996). Uranium serves as a proxy of ocean redox state (Tribovillard et al., 2006).

2. METHODS

2.1. Field site

The Yucatan Peninsula is a large karst platform (165,000 km$^2$) that is bordered by the Gulf of Mexico along the west and north coasts and by the Caribbean Sea on the east coast (Fig. 1). The peninsula is characterized by a humid tropical climate, with maximum daily temperatures ranging from 25 to 35 °C and average rainfall that varies spatially across the Peninsula from 555 to 1500 mm y$^{-1}$. Evapotranspiration rates are ~80% of total precipitation and invariant over the course of the year due to a low seasonal temperature difference and sustained vegetation growth (Bautista et al., 2009). The rainy season is from June through October with dry conditions prevailing from December through May, coinciding with cool temperatures (Giddings and Soto, 2003). From November through February temperatures are typically cool and north winds prevail. Tropical depressions, which frequently make landfall on the Yucatan Peninsula, result in large precipitation events (Boose, 2006). The Yucatan Peninsula consists of limestone, dolomite and evaporite deposits, which can reach up to 1,500 m thickness (Bauer-Gottwein et al., 2011). The permeability of the aquifer is so great that there are no streams or rivers. Preferential flow paths in the karst aquifer range in scale from large dissolution conduits (10–100’s of meters) to smaller scale fractures (1–10 cm), thus aquifer permeability is largely scale dependent. The hydraulic gradient is very low (1–10 cm km$^{-1}$) and flow is generally perpendicular to the coast (Hanshaw and Back, 1980; Beddows et al., 2007; Gonde, 2010). Marine groundwater lies beneath a freshwater lens across the entire northern Peninsula, with the depth to the saltwater interface increasing with hydraulic head elevation, as predicted by the Dupuit–Ghyben–Herzberg model. Close to the coast (<20 km), the halocline is at <40 m and it is possible to sample both terrestrial and marine groundwater through sinkholes, which are locally known as “cenotes” (Perry et al., 2009; Bauer-Gottwein et al., 2011). The freshwater portion of cenotes is typically oxic, with reducing conditions developing in the saline portions due to reduction of organic matter and presumably longer water residence times than terrestrial groundwater (Cervantes-Martinez et al., 2002; Perry et al., 2002; Schmitter-Soto et al., 2002; Torres-Talamante et al., 2011). A region of high permeability exists along the perimeter of the Cretaceous asteroid impact crater; known as the ‘Ring of Cenotes’, it bisects the coast at the Celestun and Bocas de Dzilam Lagoons (Perry et al., 1995).
The degree of karstification of the Yucatan Peninsula results in high permeability with minimal surface flow (Perry et al., 2009; Bauer-Gottwein et al., 2011). Since the major vector for terrestrial freshwater transport to the coast is via SGD, many studies have evaluated its impact on the coastal ocean, with a particular focus on nutrient loading and eutrophication (Smith et al., 1999; Herrera-Silveira et al., 2002; Aranda-Cirerol et al., 2006; Young et al., 2008; Morales-Ojeda et al., 2010; Price et al., 2010). Seminal studies by Perry et al. (2002, 2009) have utilized groundwater major ion (i.e. Cl\(^{-}\), Ca\(^{2+}\), Mg\(^{2+}\), K\(^{+}\), Na\(^{+}\), SO\(_4^{2-}\)) and strontium isotope chemistry to infer the subsurface geotragraphy of the Yucatan Peninsula and groundwater flow paths across the region.

### 2.2. Field methods

Samples were collected during four field campaigns (May 26–29, 2007; December 4–9, 2009; February 12–17, 2011; and October 22–25, 2011) from cenotes, springs, wells and coastal ocean waters (Fig. 1). Springs were actively discharging into the coastal ocean and were either submerged or within the tidal zone. Well samples were collected only from the east coast and were pumped from 15 cm diameter wells with slotted casings extending down to 5–18 m. Ocean samples were collected within 60 km of the coast. Cenotes were sampled with a Niskin bottle in 2007 and a Proactive Mega-Typhoon™ submersible pump in 2009 and 2011. Cenote radium samples in 2007 were combined from multiple Niskin bottles and ranged from 3.4 to 10 L, while sample volume in 2009 and 2011 was 22–30 L. Spring samples were collected by placing a submersible pump within the outflowing water, with 4–30 L collected for radium. Coastal trace metal samples were collected from a Niskin bottle deployed at 2 m and radium samples (44–84 L) were collected from the same depth using a pump. Trace metal samples were passed through a 0.2 μm filter into clean LDPE bottles and acidified to pH 1 with Optima nitric acid. Dissolved inorganic carbon (DIC) and total alkalinity samples were passed through a 0.2 μm filter into 125 mL glass bottles, poisoned with 50 μL saturated mercuric chloride upon sample collection and were kept free of air bubbles. Samples for radium were filtered through MnO\(_2\) impregnated acrylic fibers (hereafter referred to as Mn fibers) at a flow rate of 0.2–0.8 L min\(^{-1}\) to quantitatively sorb Ra onto the MnO\(_2\) (Moore and Reid, 1973).

Basic water chemistry data including salinity, dissolved oxygen, temperature, pH and oxidation–reduction potential (ORP, converted to Eh) were measured in the field with a YSI 600XLM or a YSI 6920V2 multi-parameter sonde in a flow-through cell (springs and cenotes) or directly in the coastal ocean. In addition, separate water samples were collected in 2009 and 2011 for salinity and were analyzed by a Guideline AutoSal instrument. Three samples of the surfical aquifer rock were collected in 2009 from the east coast.

### 2.3. Analytical methods

Uranium, barium, and strontium were measured via isotope dilution on a 20 times diluted sample. Briefly, 0.075 g of sample was spiked with \(^{135}\)Ba, \(^{236}\)U and \(^{84}\)Sr and diluted to 1.8 g with 5% Optima nitric acid. The resulting solution was analyzed on a Finnigan Element 2 high resolution inductively coupled plasma mass spectrometer (ICP-MS) at the Woods Hole Oceanographic Institution for masses \(^{84}\)Sr, \(^{88}\)Sr, \(^{135}\)Ba, \(^{136}\)Ba, \(^{236}\)U and \(^{238}\)U. The \(^{84}\)Sr peak was...
corrected for rubidium and krypton interferences. Manganese and calcium (for a subset of samples) were determined separately by diluting samples 20-fold with 5% Optima nitric acid and adding Indium (In) as an internal standard to account for instrument drift and matrix interferences of the solution. Count rates were normalized to In and concentrations were calculated from a standard curve. An additional subset of samples was run for Ca on a Dionex ion chromatograph. NASS-5, SLEW-3, SLRS-4 and IAPSO reference standards were run to determine accuracy, which was better than 1% for Ca, 5% for U, Sr and Ba, and 15% for Mn (Table S1). DIC and total alkalinity were measured within two weeks of collection. DIC was determined by acidification of 0.5 mL of a water sample and the subsequent quantification of CO2 with a non-dispersive IR detector (Li-Cor 6252). The analytical precision is ±3 μmol kg⁻¹. Total alkalinity was determined using Gran titration (Methrom 808 Titrand with 1 mL burette) with precision of ±4 μmol kg⁻¹. Both DIC and total alkalinity were calibrated by certified reference materials from A.G. Dickson of Scripps Institution of Oceanography. The aquifer rock samples were drilled to a fine powder, dissolved in 5% nitric acid and then trace elements were analyzed as described above.

The Mn fibers were rinsed with Ra-free water to remove salts, which interfere with counting (Sun and Torgersen, 1998), partially dried and placed within a delayed coincidence counter to measure 223Ra and 224Ra 1–6 days after collection (Moore and Arnold, 1996). For the oldest samples (6 days), only 30% of the initial 223Ra remained. Samples from 2007 were counted at four weeks and two months post sampling to correct 223Ra for 222Ac adsorbed to the Mn fibers. In 2009 and 2011, an additional count was done at 11 to 17 days post sampling to improve 222Ra measurements. Due primarily to low 223Ra activities and decay during transit from Mexico, the majority of groundwater 224Ra values were below detection and are not reported here.

Note that several water samples collected from deep cenotes for radium analysis were highly reducing, and despite aeration, the Ra could not effectively be removed from these samples due to loss of Mn oxide coating. Radium-223 activities and decay durations of the surficial rock samples were determined by dissolving 20–30 g of powdered carbonate in 20% HCl, which was then neutralized to pH 8 with NaOH. Mn fibers were added to each solution and shaken for 24 h to remove radium. The Mn fibers were then rinsed and counted as above.

Manganese fibers were ashed (820 °C, 16 h), homogenized and capped with epoxy, prior to being placed within a well-type gamma spectrometer to measure 223Ra (via 223Ac at 911 keV) and 228Ra (via 224Pb at 351.9 keV) (Charette et al., 2001). All detectors were standardized using a 226Ra NIST-certified Standard Reference Material (SRM#9467A) and a gravimetrically prepared ThNO3 powder, with Th daughters (228Ra) in equilibrium, which was dissolved and calibrated via isotope dilution MC-ICP-MS with the 228Ra NIST standard. These standard solutions were sorbed to Mn fibers and prepared in the same manner as the samples. Gamma counting detection limits (0.2 dpm) were calculated with the Currie Hypothesis test and were equivalent to 5 dpm 100 L⁻¹ for 4L cenote and spring samples and 0.2 dpm 100 L⁻¹ for 84 L offshore samples (De Greer, 2004). 223Ra and 228Ra activities were decay corrected to the time of collection. Aquifer rock samples were drilled to a fine powder, capped with epoxy as above and 223Ra and 228Ra were quantified on gamma detectors.

2.4. Geochemical modeling

We used model simulations to determine how organic matter respiration could alter the groundwater chemistry through enhanced mineral dissolution. All groundwater speciation and mineral solubility calculations were performed with PHREEQ (Parkhurst and Appelo, 2013). The modeling was done with the Pitzer aqueous-ion-interaction model using the PHREEQ reaction database. The actual composition of groundwater organic matter was not determined, so in our model we chose a simple organic substrate (CH2(OH)2) to react at a fixed pressure of 1.1 atm. Organic matter (0.1–16 mmol kg⁻¹) was first reacted in the groundwater and then the modeled solution was allowed to equilibrate with three different mineral assemblages: (1) 100% calcite (1 mol L⁻¹), (2) 95% calcite and 5% dolomite (MgCa(CO3)2) and (3) 95% calcite, 4.75% dolomite and 0.25% gypsum/anhydrite (CaSO4/ CaSO4·(H2O)). Typical contributions of dolomite to the aquifer matrix are 5%; however, in regions of the aquifer where dolomitization has occurred, such as near the impact crater, it may be as much as 50% (Schmitt et al., 2004; Tuchscherer et al., 2005; EscobarSanchez and Urrutia-Fucugauchi, 2010). Since all of our groundwater samples are from the top 50 m of the aquifer, an upper limit dolomite to calcite ratio of 5% is used in the modeling here.

1 The delayed coincidence counter employs a timed gate to differentiate between decay events associated with 224Ra (1/2(t1/2) = 3.6 d)221Ra (t1/2 = 55 s)220Po (t1/2 = 150 ms) and 222Ra (1/2(t1/2) = 22.3 d)218Po (t1/2 = 43 s)214Pb (t1/2 = 1.88 ms). 224Ra and 223Ra activities and decay durations of the surficial rock samples were determined by dissolving 20–30 g of powdered carbonate in 20% HCl, which was then neutralized to pH 8 with NaOH. Mn fibers were added to each solution and shaken for 24 h to remove radium. The Mn fibers were then rinsed and counted as above.
3. RESULTS

3.1. Barium

Barium concentrations in cenote waters are elevated over ocean end members, with the highest concentrations found in reducing cenote waters (Eh < 200, 400–600 nmol kg\(^{-1}\); Fig. 2a and Table S2); at depths >62 m in a cenote on the North coast (YT 175 and 176, Table S2), Ba values exceeded 1400 nmol kg\(^{-1}\). In contrast, low salinity spring, well and cenote samples had lower, but very similar Ba concentrations (~125 nmol kg\(^{-1}\)) with peak values observed at salinity ~2. This type of non-conservative enrichment has been previously observed for Ba in subterranean estuaries (Shaw et al., 1998; Charette and Sholkovitz, 2006; Santos et al., 2011). Spring samples
concentrations (Rushdi et al., 2000). The 223Ra spring samples do not display a distinct 228Ra = 1600 y) and 223Ra = 0.02–0.22 dpm g

3.3. Strontium

Calcium was only measured on a subset of the samples. Radium-226 (21/2 = 1600 y) and 223Ra (21/2 = 5.7 y) is comparatively less enriched (14 times) since its particle reactive parent (232Th) occurs in very low abundance in both seawater and carbonate minerals (Fig. 3). There are two conservative mixing relationships apparent in the strontium data (Fig. 2c and Table S2). Strontium concentrations range from 1 to 34 nmol kg

3.5. Calcium

Calcium was only measured on a subset of the samples. Calcium is conservative with respect to dpm 100 L

4. Discussion

4.1. Aquifer rock geochemistry

The Ba, Sr, U and Mn content of the Yucatan surficial aquifer rock collected 10 km inland is: Ba = 0.17 nmol g

3.4. Manganese

Manganese concentrations are generally less than 100 nmol kg

3.6. Radium isotopes

Radium-226 (21/2 = 1600 y) and 223Ra (21/2 = 11.4 d) are enriched 100 and 230 times, respectively in groundwater compared to coastal ocean activities. Radium-226 (21/2 = 5.7 y) is comparatively less enriched (14 times) since its particle reactive parent (232Th) occurs in very low abundance in both seawater and carbonate minerals (Fig. 3). There are two conservative mixing relationships apparent in the strontium data (Fig. 2c and Table S2). Strontium concentrations range from 1 to 34 nmol kg

3.2. Uranium

Low salinity cenote water samples range from 1.6 to 15.7 nmol kg

3.3. Strontium

There are two conservative mixing relationships apparent in the strontium data (Fig. 2c and Table S2). Strontium concentrations range from 1 to 34 mol kg

3.4. Manganese

Manganese concentrations are generally less than 100 nmol kg

3.5. Calcium

Calcium was only measured on a subset of the samples. Calcium is conservative with respect to...
430 ranged from 0.07–0.22 l mol g⁻¹/C₀, in close agreement with 431 samples from the east coast (0.17 l mol g⁻¹/C₀, Table 1) (Tuc- 432 hscherer et al., 2005). Sr content was slightly higher in the 433 sample reported here (3.3 versus 2.3–2.6 l mol g⁻¹/C₀), while 434 U and Mn are 30–40% lower in the sample analyzed here 435 than near the impact zone. These differences may be poten- 436 tially due to alteration associated with the bolide impact or 437 subsequent changes in hydrogeology and weathering (Sch- 438 mitt et al., 2004; Tuchscherer et al., 2005). There was a lar- 439 ger range in the sediment radium activities, particularly for 440 ²²³Ra and ²²⁶Ra (within the ²³⁵U and ²³⁸U decay series 441 respectively). The radium content of carbonate minerals is 442 largely determined by the U present at the time of forma- 443 tion, leading to a large range in radium activities (Langmuir 444 and Riese, 1985).

4.2. Geochemistry of the karst subterranean estuary 445 terrestrial end member

Numerous studies of this aquifer have shown that groundwater is in equilibrium with calcite, the primary aquifer mineral (Stoessell et al., 1989; Reeve and Perry, 1994; Perry et al., 2002, 2009). In addition, aragonite, celestite (SrSO₄) and evaporite layers (gypsum and anhydrite) occur in certain parts of the aquifer and dissolution of these minerals may further modify groundwater chemistry (Stoessell et al., 1989, 1993; Perry et al., 2002, 2009). Water in equilibrium with atmospheric CO₂ has a pH of 5.6; when this water reacts with calcite the resulting solution has a pH of 8.2, an alkalinity of 1100 μmol kg⁻¹ and a dissolved Ca concentration of 0.5 mmol kg⁻¹. In contrast, our samples of Yucatan terrestrial (salinity < 2) groundwater had an alkalinity of 6460 ± 1210 μeq kg⁻¹, DIC of 6630 ± 1230 μmol kg⁻¹, pH of 7.25 ± 0.56 and 3.8 ± 0.9 mmol kg⁻¹ dissolved Ca. To acquire this elevated alkali- nity, DIC and Ca content, further mineral dissolution must be induced under elevated groundwater pCO₂ concentra- tion and reduced pH. This modeling exercise is primarily meant to demonstrate the potential coupling between or- ganic matter respiration and mineral dissolution that is nec- essary to explain the elevated dissolved Ca (and by proxy trace elements associated with CaCO₃) in terrestrial groundwaters and is not exhaustive due to the paucity of carbonate chemistry available for this data set. We com- pared the total dissolved calcium, alkalinity and DIC of the modeled groundwater to a subset of samples (collected in 2009) for which carbonate chemistry (i.e. alkalinity, dis- solved inorganic carbon) was determined.

We reacted 0.1–16 mmol kg⁻¹ organic matter and then 477 allowed the resulting solution to reach equilibrium with cal- 478 lcite (1 mol L⁻¹), a mixture of calcite and dolomite (5%), 479 and a mixture of calcite, dolomite (4.75%) and gypsum 480 (0.25%) (Fig. 4). The dissolution of gypsum with at least 481 8 mmol kg⁻¹ of organic matter respiration is needed to ex- 482 plain the highest dissolved Ca values (>3 mmol kg⁻¹ 483 (Fig. 5)). We observed excess alkalinity in our samples 484 above model predicted values, while DIC values largely 485 agreed with modeled values (Supplemental Fig. 1). This is 486 potentially due to organic matter contributions to total 487 alkalinity that may be difficult to quantify without further 488 sampling and analyses (Kim et al., 2006; Kim and Lee, 489 2009). Perry et al. (2002) suggest that shallow root systems 490 in the coastal aquifer may contribute organic matter to the 491 groundwater.

We posit that the dissolved Ca load of terrestrial 492 groundwater is a function of the amount of organic matter 493 respiration that has occurred during transit of the ground- 494 water through the aquifer and the aquifer mineral matrix, 495 resulting in a range of potential pH, alkalinity, DIC and 496 Ca concentrations for the terrestrial end member. With 497 the available data it is not possible to determine the exact 498 combination of organic matter respiration and calcite,
500 dolomite and gypsum dissolution that has occurred within each terrestrial groundwater sample, rather we use the model results and data to place bounds on the potential for enhanced dissolution and to explain the relatively high groundwater trace element concentrations we report here.

If chemical equilibrium with aquifer minerals, as discussed above, controls the terrestrial groundwater elemental concentrations (i.e. outside of the salinity mixing zone), the relative proportion of the element/calcium ratio (E/Ca) in the aquifer matrix (E/Ca solid) to groundwater (E/Ca groundwater) can be predicted from the partition coefficient (Kd):

$$K_d = \frac{E/Ca_{\text{solid}}}{E/Ca_{\text{groundwater}}}$$  

Calcite partition coefficients are readily available to calculate the equilibrium groundwater E/Ca for Ba, Sr, U, Mn and Ra (Table 2). The partition coefficient varies with temperature and environmental conditions (Kitano and Yucatan aquifer and global average limestone Ba, Sr, U, Mn and Ra isotope concentrations.

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Table 1

Yucatan aquifer and global average limestone Ba, Sr, U, Mn and Ra isotope concentrations.

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<td>This study</td>
</tr>
<tr>
<td>Global limestone</td>
<td></td>
</tr>
<tr>
<td>Yucatan</td>
<td>This study</td>
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<tr>
<td>Global limestone</td>
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<tr>
<td>Yucatan</td>
<td>This study</td>
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<td>Global limestone</td>
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<td>Global limestone</td>
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<tr>
<td>Yucatan</td>
<td>This study</td>
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<tr>
<td>Global limestone</td>
<td></td>
</tr>
<tr>
<td>Yucatan</td>
<td>This study</td>
</tr>
<tr>
<td>Global limestone</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. Ca plotted against DIC for terrestrial (salinity < 2) groundwater samples collected in Dec. 2009 (diamonds). Also shown is the predicted Ca:DIC relationship following organic matter degradation as modeled using PHREEQ (Parkhurst and Appelo, 2013) for equilibrium with 1 mol L⁻¹ calcite (dashed line); 95% calcite, 5% dolomite (dotted line) and 95% calcite, 4.75% dolomite and 0.25% gypsum (solid line). Vertical hatch marks and numbers in bold indicate the amount of organic matter respired at each point.

Fig. 5. Predicted terrestrial groundwater dissolved Ca versus salinity following 1 mmol kg⁻¹ (dotted lines) and 8 mmol kg⁻¹ (dashed lines) organic matter respiration in equilibrium with 1 mol L⁻¹ calcite; 95% calcite (C), 5% dolomite (D); and 95% calcite 4.75% dolomite and 0.25% gypsum (G). Addition of dissolved Ca through conservative mixing with ocean waters is shown in the solid line; this contribution has also been added to the mineral equilibrium lines. See Fig. 4 for dissolved Ca in terrestrial groundwater at additional organic matter respiration amounts. All terrestrial (salinity < 2) groundwater samples with measured Ca are shown.

The values used here are based on empirical studies of modern calcite, and may vary for the specific conditions present in the Yucatan aquifer, yet are sufficient to evaluate if the trace element content of terrestrial groundwater results from equilibrium dissolution of aquifer rocks. In addition, the extent to which E/Ca of groundwater due to dissolution can be constrained also depends on potential variability in E/Ca solid. The available data for the Yucatan (Table 1) suggests the range of E/Ca in the unaltered aquifer matrix is small. Dolomite is a minor mineral in the portion of the aquifer studied here, but may have a different trace element content than calcite (Dawson and Hinton, 2003). The Sr/Ca ratio of the terrestrial end member (2.4 ± 2.6 mmol mol⁻¹) is near that predicted by equilibrium with calcite (3.3 mmol mol⁻¹, Fig. 6 and Table 2). Some well samples have much larger Sr/Ca ratios, coincident with the high Ba/Ca ratios, potentially due to groundwater interactions with aragonite and/or celestite, which have a higher Sr content than calcite. Predicted equilibrium dissolved Ba/Ca is slightly greater than the value observed in the terrestrial groundwater samples (Fig. 6, Table 2). Some well samples (from the east coast) have much higher Ba and ²²⁸Ra than expected, potentially due to interaction with aragonite, which has a higher Ba content than calcite. Terrestrial groundwater U/Ca ratios (2.1 ± 1.4 µmol mol⁻¹, Fig. 6) also agree with those predicted by equilibrium with calcite (1.6 µmol mol⁻¹, Table 2). Terrestrial groundwater Mn/Ca ratios (16 ± 70 µmol mol⁻¹, Fig. 6) also agree with those predicted by equilibrium with calcite (26 µmol mol⁻¹, Table 2). Terrestrial groundwater ²²⁶Ra/Ca, ²²⁸Ra/Ca and ²²³Ra/Ca fall within the predicted ranges (Fig. 7). Terrestrial groundwater trace element and radium concentrations thus appear to largely be explained by dissolution of calcite, the main aquifer mineral, although U is elevated potentially due to complexation with carbonate (see Section 4.3.3).

Table 2
Element radius, calcite partition coefficient and predicted dissolved E/Ca.

<table>
<thead>
<tr>
<th>Element</th>
<th>Radius*</th>
<th>Kd calcite</th>
<th>Predicted dissolved E/Ca (µmol mol⁻¹ or dpm mmol⁻¹)</th>
<th>Kd Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>1.38</td>
<td>0.8</td>
<td>21.25</td>
<td>–</td>
</tr>
<tr>
<td>Sr</td>
<td>1.21</td>
<td>0.1</td>
<td>3300</td>
<td>–</td>
</tr>
<tr>
<td>U</td>
<td>1.00</td>
<td>0.2</td>
<td>1.6</td>
<td>–</td>
</tr>
<tr>
<td>Mn</td>
<td>0.83</td>
<td>50</td>
<td>26.24</td>
<td>–</td>
</tr>
<tr>
<td>²²⁸Ra</td>
<td>1.48</td>
<td>0.5</td>
<td>0.36–1.2</td>
<td>–</td>
</tr>
<tr>
<td>²²³Ra</td>
<td>1.48</td>
<td>0.5</td>
<td>0.034–0.056</td>
<td>–</td>
</tr>
<tr>
<td>Ca</td>
<td>1.06</td>
<td></td>
<td>0.004–0.044</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 2.

* Ionic radii from Shannon (1976).
  a Rihs et al. (2000).
  b Kitano and Oomori (1971).

Fig. 6. Ba/Ca, Sr/Ca, Mn/Ca and U/Ca ratios for terrestrial cenote and well (salinity < 2) samples. Also shown is the predicted ratio from the statistically significant spring mixing relationships (i.e. Ba intercept/Ca intercept, Table S3). The groundwater E/Ca ratio in equilibrium with aquifer calcite according to Eq. (1) is also shown. Note separate axis for U/Ca on right.
4.3. Geochemistry of the karst subterranean estuary mixing zone and marine groundwater

The processes that may modify groundwater geochemistry within the mixing zone include: (1) chemical equilibrium between groundwater and the aquifer matrix as discussed in Section 4.2, (2) conservative mixing between terrestrial and ocean end members, (3) desorption/sorption exchanges with mineral surfaces and (4) in situ production and decay for radium isotopes. Mixing between seawater and terrestrial groundwater is predicted to enhance dissolution of the aquifer minerals (Hanshaw and Back, 1980; Stoessell et al., 1989). To determine if mixing induced dissolution was important for the subterranean estuary under study here, we modeled mixing between terrestrial groundwater and the ocean. The calcite saturation index (SI) is calculated according to:

$$\text{SI} = \log \left( \frac{a\text{Ca}^{2+} a\text{HCO}_3^-}{a\text{H}^+ K_{\text{calcite}}} \right)$$

where $a\text{Ca}^{2+}$ refers to the dissolved Ca activity, $a\text{HCO}_3^-$ is the carbonate activity and $a\text{H}^+$ is pH. $K$ is the equilibrium constant for the formation of calcite (CaCO$_3$) calculated using the temperature-salinity dependence as founding PHREEQ. Even with the limited set of samples from 2009 where carbonate chemistry was determined, we observed a range of possible terrestrial end members. The two groundwater end members with a pH of 7.44 and 8.44, alkalinity of 6890 and 7410 mmol kg$^{-1}$ and 2.8 mmol kg$^{-1}$ Ca did not result in corrosive mixing with seawater, however, a groundwater end member with a pH of 6.95, alkalinity of 6321 mmol kg$^{-1}$ and 3.4 mmol kg$^{-1}$ Ca was corrosive upon mixing (Fig. 8). As discussed previously, such a terrestrial groundwater end member results only after respiration of 16 mmol kg$^{-1}$ of organic matter and equilibration with calcite. There is no evidence for non-conservative addition of Sr, Mn, Ba and U, as might be expected upon mixing induced dissolution, in the spring samples ranging in salinity from 2 to 35. We thus conclude that dissolution may occur during some groundwater mixing, but this phenomenon is not ubiquitous across the Yucatan Peninsula.

4.3.1. Barium and radium

Ba serves as a chemical analogue for Ra since they are both group II alkaline earth metals and have comparable ionic radii (Table 3). Similar distributions of barium and long-lived radium isotopes have been observed in subterranean estuaries where conservative mixing dominates (Kiro et al., 2012), where ionic strength dependent desorption occurs (Gonneea et al., 2013) and in carbonate groundwater systems where precipitation/adsorption reactions dominate (Rihs et al., 2000).

Long-lived Ra isotopes are expected to be in secular equilibrium with parent nuclides in marine carbonate deposits of this age (surface outcrops are largely Pliocene, with older rocks deeper in the aquifer (Perry et al., 2009)). The parent nuclide activity is a function of seawater $^{232}\text{Th}$ and $^{238}\text{U}$ at the time of deposition, the calcite partition coefficient for the parent nuclide (Eq. (1)) and any subsequent weathering or alteration that may impact U or Th content. Considering the limited number and large range of Ra/Ca in rock samples measured here, the potential range in aquifer rock Ra/Ca may be even greater. However, the $^{228}\text{Ra},^{228}\text{Ra}$ groundwater activity ratio largely falls within the bounds of the measured rock ratios (Fig. 7).

Spring Ba concentrations fall on a conservative mixing line with a zero salinity intercept of 200 mmol kg$^{-1}$ (dashed line in Fig. 3a), greater than the observed terrestrial end member (122 ± 75 mmol kg$^{-1}$). Ba peaks at salinity ~2, the lowest salinity spring sample (Fig. 9). Conversely, there is no evidence of conservative mixing in spring $^{226}\text{Ra},^{228}\text{Ra}$ or $^{223}\text{Ra}$ activities, nor is there a clear trend of salinity dependent desorption influencing all spring samples. The observed decoupling between long-lived Ra isotopes and Ba is unusual within the subterranean estuary (Fig. 10).
One potential explanation is that adsorption of alkaline earth elements increases with ionic radius, thus Ra, with a larger ionic radius than Ba, would be less mobile than Ba (Stumm and Morgan, 1996). Sorption of divalent cations onto calcite has been shown to inhibit movement of dissolved species within aquifers. Under the pH and carbonate ion concentrations present in the Yucatan STE (Stoessell et al., 1989), empirical adsorption coefficients for Ra and Ba predict little change in adsorption across the mixing zone (Zhu, 2002). In addition, there is much greater variability in terrestrial end member Ra2+ than in Ba concentrations due a greater range in aquifer rock Ra.

Deep cenotes were reducing and anoxic as evidenced by the presence of H2S in these samples (indicated by strong H2S smell upon sampling). Perry et al. (2002) suggests that these conditions are due to reduction of terrestrial organic matter that has accumulated in the bottom of cenotes. This organic matter is reduced first using oxygen, then NO3-, MnO2 and finally SO42- (Stumm and Morgan, 1996). Ba concentrations in reducing cenotes in excess of that predicted by barite (BaSO4) solubility (modeled saturation in

Table 3
Radium-tracer based submarine groundwater discharge estimates.

<table>
<thead>
<tr>
<th>Location</th>
<th>Date</th>
<th>SGD (m-3 m-1 d-1)</th>
<th>T_w (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>West coast</td>
<td>Oct-01</td>
<td>50</td>
<td>13</td>
</tr>
<tr>
<td>West coast</td>
<td>Jul-02</td>
<td>73 (40)</td>
<td>7</td>
</tr>
<tr>
<td>North coast</td>
<td>May-07</td>
<td>95</td>
<td>12</td>
</tr>
<tr>
<td>West coast</td>
<td>May-07</td>
<td>36</td>
<td>14</td>
</tr>
<tr>
<td>North coast</td>
<td>Dec-09</td>
<td>84</td>
<td>13</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>67 (61)</td>
<td></td>
</tr>
</tbody>
</table>

T_w of July 2002 transect is much lower than the other time periods. Value in parentheses indicates SGD if average T_w from all time periods is used rather than 7 days.

Fig. 8. Predicted calcite saturation index (Eq. (2)) based on mixing between three different terrestrial end members and ocean waters. Mixing between the pH 8.44 and 7.44 (resulting from 0.1 and 4 mmol kg-1 organic matter respiration in equilibrium with calcite respectively) and ocean waters does not result in undersaturation (saturation index < 0). However, the pH 6.95 terrestrial end member does produce corrosive waters upon mixing with the ocean. Also shown (solid line) is the mixing relationship predicted by Stoessell et al. (1989) for Yucatan groundwaters. Mixing induced dissolution is therefore a function of the amount of organic matter respired in the terrestrial end member.

Fig. 9. a) 228Ra:226Ra activity ratios and b) 223Ra:226Ra activity ratios. Solid lines denote the measured aquifer rock activity ratios.

Fig. 10. 226Ra plotted against Ba. The relationship between these elements is somewhat decoupled, particularly in the terrestrial cenote and well samples, potentially due to reduced mobility of the large Ra2+ ion compared to Ba2+. There is a linear relationship between a subset of spring (gray squares) and reducing cenote (triangles) samples where conservative mixing of these elements dominates.
Fig. 2a assumes seawater SO₄²⁻ concentrations are presumably due to the depletion of SO₄²⁻ in the reducing zone. 226Ra and 223Ra activities are quite high in reducing cenote waters, with a large range in 226Ra/Ca and 226Ra/223Ra ratios (0.01–13 and 0.003–0.703 dpm mmol⁻¹, respectively) suggesting that in addition to enhanced aquifer matrix dissolution, Mn-oxide cycling in these reducing environments may maintain elevated Ra activities.

4.3.2. Manganese and uranium

U readily complexes with carbonate, increasing the mobility of uranium in groundwater (Langmuir, 1978). Indeed, terrestrial groundwater U/Ca ratios (2.1 ± 1.4 μmol mol⁻¹, Fig. 6) are higher than predicted by chemical equilibrium with calcite (1.6 μmol mol⁻¹, Table 2). At the high alkalinity (>3 mmol kg⁻¹) and neutral pH values of terrestrial groundwater, dissolved U is largely present as uranyl carbonate complexes, which impede sorption and thus maintain the high U concentrations in terrestrial groundwater and across the spring mixing zone. Under the reducing pH and Eh conditions of the deep cenotes, reduction of uranyl (VI) species to U(IV) results in precipitation of highly insoluble uranium minerals or sorption onto calcite, accounting for the observed removal of U from groundwater (Fig. 2b) (Langmuir, 1978). Likewise, Mn is elevated (100–2600 nmol kg⁻¹) in reducing cenote waters likely due to Mn(IV) reduction.

4.4. Chemical fluxes associated submarine groundwater discharge

Both the water flux and concentration of discharging water must be known to calculate chemical fluxes associated with SGD. We first calculate the radium-tracer based total SGD and compare these values with terrestrial groundwater fluxes derived from recharge-based estimates. We then assign end member concentrations to discharging water and calculate potential trace element fluxes from the Yucatan Peninsula to the coastal ocean. Finally, we explore the potential magnitude of fluxes from karst subterranean estuaries globally and place these estimates in the context of ocean element cycles.

4.4.1. Ra-tracer based SGD estimates

Despite the large variability in Ra activities, these isotopes remain excellent tracers of SGD due to the high concentration gradient between groundwater and seawater. Radium based estimates of SGD were calculated along the west and north coasts of the Yucatan Peninsula in May 2007 and December 2009 (Table 3). In addition, data from offshore radium transects completed in October 2001 and July 2002 were used to extend the temporal and seasonal range of SGD estimates (Young et al., 2008). SGD fluxes are based on coastal ocean radium surveys (Fig. 11). These surveys extend from the coast 3.5–60 km, however the near-shore 222Ra gradient was very steep. In addition, production of 222Ra from shelf sediments (max water depth of 10 m out to 60 km) appears to be large relative to the SGD-derived 222Ra flux over the full transect distance (see Section 4). Thus, we used 222Ra data within 2 km of shore (shaded area in Fig. 11) to calculate the inventory of the long-lived 222Ra according to:

\[ \text{R}_{\text{SGD}} = \frac{(222\text{Ra}_{\text{transient}} - 222\text{Ra}_{\text{exchange}}) \times T_w}{V_{\text{transect}}} - 226\text{Ra}_{\text{sediment}} \]  

where 222Ra_{transient} is the average activity of the coastal ocean, 222Ra_{exchange} is the activity of the water exchanging with this volume, (shelf waters > 2 km: 20 dpm 100 L⁻¹); V_{transect} is the volume of the coastal ocean box; T_w is the average residence time of the water in the box; and 226Ra_{sediment} is the sediment flux (Moore, 1996; Charette et al., 2001). Sediment production of 226Ra was calculated assuming 230Th activities in offshore sediments were in secular equilibrium with the sediment 226Ra activity measured in onshore carbonate sands with a partition coefficient of 1 (Beck and Cochran, 2013). 222Ra_{sediment} fluxes were calculated according to:

\[ \text{R}_{\text{sediment}} = \text{R}_{\text{rock}} \times \rho \times \text{depth} \times \text{f}_{\text{desorb}} \times \text{area} \times \frac{\text{R}_{\text{SGD}}}{226\text{Ra}} \]  

where 226Ra_{rock} is the activity of the rock (Table 1), ρ is the density of carbonate sands (2.7 g cm⁻³), the sediment depth which is flushed with overlying water is 10 cm, the area is shoreline normalized out to 2 km and λ_{226} is the decay constant of 226Ra. Sediment regenerated fluxes are minimal at 30 dpm m⁻² d⁻¹ along a 2 km transect, compared to a 226-Ra_{SGD} of 10⁵–10⁶ dpm m⁻¹ d⁻¹ of shoreline calculated according to Eq. (3). Thus we conclude that SGD is the main source of 226Ra to coastal waters.

We used the short-lived 222Ra to calculate T_w, water residence time, according to:

\[ T_w = \frac{\ln \left( \frac{223/222\text{Ra}_{\text{transient}}}{\text{R}_{\text{SGD}}/\text{R}_{\text{SGD}}} \right)}{\lambda_{223}} \]  

where 223/222Ra_{transient} is the activity ratio of the coastal ocean, 223/222Ras_{transient} is the activity ratio of discharging groundwater (spring average of 0.12) and λ_{223} is the decay constant for 223Ra (Moore, 2000). This model assumes a discrete input at the coast, with mixing and decay controlling the 223/222R sensory. An alternative method for calculating residence time is the continuous input model whereby a radium source with a known 223:222 activity ratio is added along the entire transect (Moore et al., 2006). Sediment generated 222Ra inputs likely occur along the shallow Yucatan coast, however, it is unlikely that the 223:222 activity ratio via sediment production will be the same as groundwater discharge, since dissolution and desorption control long-lived concentrations in groundwater, while radioactive decay would be the primary source from coastal sediments. The sediment generated 222Ra flux (calculated according equation 4) is 10⁴ dpm m⁻² d⁻¹, 16–40% of SGD-derived 222Ra flux. This production of 222Ra along the transect is apparent in 223:222 activity ratios that increase with distance from shore (Fig. 11b). Thus, the ages calculated for the Yucatan coast may be an underestimated.
Here we use the average spring activity for $^{226}\text{Ra}_{GW}$ (1180 ± 490 dpm 100 L$^{-1}$). Uncertainty is introduced into these estimates primarily from uncertainty in the $^{226}\text{Ra}$ inventory (10%), water ages (30–60%) and in the groundwater end member (40%). Error propagation results in 80–100% uncertainty in total SGD estimates.

Total SGD ranged from 40–95 m$^3$ m$^{-1}$ d$^{-1}$. In May 2007 we had measurements along both coasts, and discharge was greater along the North coast (95 m$^3$ m$^{-1}$ d$^{-1}$) than the West coast (40 m$^3$ m$^{-1}$ d$^{-1}$, Table 3). Here we assume that the sampled springs are representative of submarine groundwater discharge in this region, which may additionally include diffuse discharge away from springs. The salinity of the spring samples used to calculate the Ra end member ranged from 2 to 35, with an average of 9 ± 9, suggesting approximately 75 ± 25% of the discharge was terrestrial, with the remainder due to mixing with marine groundwater. This is in contrast to many other shelf-scale SGD studies where the majority of the SGD is marine in origin (e.g. Moore, 1996; Burnett et al., 2007; Prieto and Destouni, 2011).

The hydrology of the Yucatan Peninsula has been explored in depth through both field studies and modeling approaches (Hanshaw and Buck, 1980; Beddows et al., 2007; Gondwe et al., 2010; Bauer-Gottwein et al., 2011). Such studies have assumed that terrestrial discharge was bal-

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anced by net groundwater recharge, which was reported to be 26 m³ m⁻³ d⁻¹ averaged annually over the 1100 km coastline of the Yucatan Peninsula aquifer (essentially the coastline north of 19°N, Hanshaw and Back, 1980; Gondwe et al., 2010). In all instances the Ra-tracer based discharge shown here is greater than the previously reported terrestrial discharge (Table 3). Patterns of temporal variability in either the marine or terrestrial component of discharge cannot be constrained by the limited number of SGD estimates presented here. Assuming 75% of total discharge is of terrestrial origin, as indicated by spring salinity, we estimate this flux for our study to be 45 ± 20 m³ m⁻¹ d⁻¹.

4.4.2. Yucatan Peninsula trace element fluxes

We extrapolated the spring element concentrations and terrestrial and total SGD estimates across the entire Yucatan coast (1100 km) to calculate trace element fluxes to the ocean. Such an extrapolation is possible for several reasons. First, the conservative mixing behavior observed in actively discharging springs (over a relatively wide spatial scale) for Sr, Ba and Mn and relatively invariant U concentrations simplifies estimates of SGD-derived fluxes since end-member concentrations are well constrained. Spring Sr and Mn concentrations lie along a mixing line between terrestrial concentrations with karst aquifers. In contrast, shoreline normalized fluxes reported for a site in the northeast Gulf of Mexico (Santos et al., 2011) and Waquoit Bay, MA (Gonneea et al., 2013). Sr fluxes calculated for the Yucatan are 2.1–4.0 x 10⁶ mol y⁻¹ (Table 4), 1–3% of the total global SGD Sr flux (Beck et al., 2013). Yucatan SGD-associated fluxes are 1.0–2.0 x 10⁶ mol y⁻¹ (Table 3). U removal

Table 4
Trace element end member and flux from the Yucatan Peninsula.

<table>
<thead>
<tr>
<th>Element</th>
<th>River EM (mmol kg⁻¹ or Ra dpm 100 L⁻¹)</th>
<th>Karst EM (mmol kg⁻¹ or Ra dpm 100 L⁻¹)</th>
<th>Ratio Karst/River EM</th>
<th>Yucatan karst flux (mol or Ra dpm yr⁻¹)</th>
<th>River Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba-salinity 2⁺</td>
<td>168</td>
<td>190</td>
<td>1.2</td>
<td>2.3–3.7 x 10⁶</td>
<td>-</td>
</tr>
<tr>
<td>Sr</td>
<td>685</td>
<td>20,100</td>
<td>29</td>
<td>2.1–4.0 x 10⁵</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1208</td>
<td>20,100</td>
<td>17</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>U</td>
<td>1.56</td>
<td>10</td>
<td>6.4</td>
<td>1.0–2.0 x 10⁵</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>2.14</td>
<td>103</td>
<td>4.7</td>
<td>1.1–2.0 x 10⁶</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>620</td>
<td>103</td>
<td>0.17</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>127</td>
<td>0.81</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>²²⁶Ra-salinity 5⁺</td>
<td>5.3</td>
<td>1000</td>
<td>190</td>
<td>1.7–2.6 x 10¹⁵</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td>1000</td>
<td>96</td>
<td>1.3–2.6 x 10¹⁵</td>
<td>-</td>
</tr>
</tbody>
</table>

* Ba and Ra concentrations peak at salinities greater than the pure terrestrial groundwater end member. Thus the SGD flux at salinity 2 (for Ba) and 5 (for Ra) is calculated according to: SGD = SGD territorial + SGD marine x (salinity of SGD II - salinity of SGD I), where x refers to the salinity of interest. SGD territorial is 26–46 m³ m⁻³ d⁻¹ (Hanshaw and Back, 1980; Gondwe et al., 2010) and salinity of SGD II is 9.9.

† Karst Ba and ²²⁶Ra end members were modified to exclude the component from recirculated marine groundwater. Thus 200 nmol kg⁻¹ Ba was reduced to 190 nmol kg⁻¹ to account for seawater Ba in the SGD flux at salinity 2, while ²²⁶Ra was reduced from 1000 to 996 dpm 100 L⁻¹ at SGD flux at salinity 5.

‡ Yucatan Peninsula fluxes are calculated for the entire 1,100 km coastline north of 19°N.

⁎ Gaillardet et al. (2003).

⁴ Peucker-Ehrenbrink et al., 2010.

⁵ Chabaux et al., 2003.

⁶ Bender et al. (1977).

occurs within the deep groundwater reaction zone, however, the residence time of this region with regard to coastal recharge rates, it is likely that discharge along karstic coastlines is greater than the global average due to the high permeability of these aquifers and typically high precipitation rates. A wide range of terrestrial groundwater discharge rates in karst regions have been reported, from \(2 \text{ m}^3 \text{ m}^{-1} \text{ d}^{-1}\) at one site in Ireland (Einsiedl, 2012) to \(120 \text{ m}^3 \text{ m}^{-1} \text{ d}^{-1}\) along the Spanish coast (Garcia-Solsona et al., 2010). Taken together, these global fluxes represent a reasonable estimate of chemical export from karst subterranean estuaries. We have not attempted to propagate errors on these estimates, due to limited data on global karst STE and member concentrations and water fluxes.

Submarine groundwater discharge from karst subterranean estuaries is an important source of U, Sr and Ra to the global ocean (Table 5). We found that the Yucatan U end member was 6.4 times greater than the global riverine end member (Table 4, Gaillardet et al. (2003)) making carbonate karst subterranean estuaries potentially an important global source of U (4.0–7.7 × 10^6 mol y^{-1}), 7–33% of river flux, Table 5). Dunk et al. (2002) calculated global SGD-derived U inputs of 9.3 ± 8.7 × 10^6 mol y^{-1}. The global flux we report here is 43–83% of this value, but is derived only from the 12% of the global coastline that is karstic.

The average Sr concentration in Yucatan terrestrial groundwater samples (20.1 μmol kg^{-1}) was 17 times greater than the global riverine end member (1.21 μmol kg^{-1}, Table 4, Peucker-Ehrenbrink et al., 2010) resulting in a Sr flux from karstic subterranean estuaries of \(8.2–15.3 \times 10^9\) mol y^{-1}, ~25% of total river-derived Sr flux (Table 5). This value is within the global meteoric SGD derived Sr flux to the ocean reported by Beck et al. (2013) (7–28 × 10^9 mol y^{-1}). In addition, the global karst SGD Sr flux is about an order of magnitude larger than the SGD derived Sr flux from groundwater discharge in the Ganges–Brahmaputra River system (9 × 10^9 mol y^{-1}) (Basu et al., 2001).

The dominance of groundwater as a source of radium to the ocean has long been recognized (e.g. Moore, 1996; Moore et al., 2008). Here we focus on export of the

### Table 5

<table>
<thead>
<tr>
<th>Source</th>
<th>Ba (10^9 mol y^{-1})</th>
<th>Sr (10^9 mol y^{-1})</th>
<th>U (10^9 mol y^{-1})</th>
<th>Mn (10^9 mol y^{-1})</th>
<th>^226Ra (10^{15} dpm y^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>River</td>
<td>6.3</td>
<td>29.47</td>
<td>23.59</td>
<td>4.6–23</td>
<td>0.8–2.0</td>
<td>a–j</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>4.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Aeolian</td>
<td></td>
<td>4.3</td>
<td></td>
<td>13.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weathering/diagenesis</td>
<td>1.8</td>
<td></td>
<td></td>
<td>4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Karst groundwater discharge</td>
<td>0.089–0.145</td>
<td>8.2–15.3</td>
<td>4.0–7.7</td>
<td>4.2–7.9</td>
<td>67–99</td>
<td>This study</td>
</tr>
</tbody>
</table>

*Guillaudet et al. (2003).*

1Peucker-Ehrenbrink et al. (2010).

2Dunk et al. (2002).


4Bender et al. (1977).

5Martin and Knauer (1980).


7Statham et al. (1998).


9Moore et al. (2008).

10Palmer and Edmond (1989).
longest-lived isotope, $^{226}$Ra, since it makes up the majority
of the ocean radium inventory. Sparse measurements of riv-
erine dissolved $^{226}$Ra activities suggest a median end mem-
ber of 10 dpm 100 L$^{-1}$ (Chabaux et al., 2003), although
Gaillardet et al. (2003) reports a lower value of 4.5. Conclusions

Water discharge estimates for the Yucatan coast range from 36 to 95 m$^{-1}$ due to organic
matter degradation results in enhanced dissolution of aque-
erifer minerals and elevated dissolved trace element concentra-
tions. Thus, in this setting, the aquifer mineral geochemistry
strongly influences groundwater trace element loading.
Clearly complimentary analysis of aquifer sediments will
enhance studies of subterranean estuary geochemistry in
carbonate karst settings. In addition, desorption at low
salinity within the mixing zone elevates Ba, $^{226}$Ra and
$^{238}$Ra, while carbonate complexation maintains high U
concentrations. Ba, Sr, Ca, and Mn all display conservative
mixing in the shallow subterranean estuary typified by
coastal springs. Thus there is no evidence of mixing induced
dissolution in this portion of the Yucatan STE. Within the
deep reducing groundwater, redox processes result in U re-
moval and high Mn concentrations, while Ba, Ca, Sr, $^{226}$Ra
and $^{228}$Ra are elevated due to enhanced dissolution. Sub-
marine groundwater discharge associated transport of U,
Mn and Sr may be calculated with a relatively straightforward
approach since there is minimal chemical alteration
upon mixing within the Yucatan karst STE. Even for Ba,
which exhibits a peak at low salinities (2), the terrestrial
component of discharge dominates the chemical flux.

Since we do not observe a large enrichment in Ba, Ca, Sr,
Ra or depletion of U in spring samples, we conclude that
the deep reducing marine groundwater is not actively dis-
charging. Rather, we suggest that the deep anoxic cenote is
a groundwater reaction zone that does not take part in shal-
low subterranean estuary mixing. Additionally, there is no
evidence of elevated Sr or depleted U in near shore samples
(Charette et al., 2008). Thus, chemical cycling within the re-
gegional terrestrial-marine groundwater mixing zone (such as
U removal) is not expected to affect large scale SGD associ-
ated chemical transport to the coastal ocean. However, it is
possible that the deep aquifer dominated by reducing marine
groundwater exchanges with the coastal ocean outside the
bounds of our study domain (60 km from shore).

Submarine groundwater discharge estimates for the
Yucatan Peninsula range from 36 to 95 m$^{3}$ m$^{-1}$ d$^{-1}$, and
contained as much as 75 ± 25% terrestrial groundwater, in contrast to many other shelf-scale studies where the recir-
culated marine component dominates. First order estimates
of global fluxes of Sr, U and Ra from karst subterranean estuaries, which only make up 12% of all coastal aquifers,
indicate that submarine groundwater discharge fluxes from
dkarst subterranean estuaries are significant contributors to
the global ocean budgets of these elements. Recently Beck
et al. (2013), presented evidence that SGD is an important
source of Sr to the ocean and that isotopic exchange within
the subterranean estuary results in groundwater discharge
of a more radiogenic end member. Uranium cycling within
the subterranean estuary and subsequent discharge via
SGD has been postulated as both a potential source (Dunk
et al., 2002) and sink (Charette and Sholkovitz, 2006;
Moore and Shaw, 2008; Santos et al., 2011). There is a need
to expand the study of chemical cycling within subterra-
nean estuaries to include a greater diversity of aquifer
lithologies and morphologies, as well as mixing regimes, to
more fully constrain the potential role SGD plays in global
ocean element budgets. For example, relatively little is
known about either discharge or chemical cycling within
fractured bedrock (Oberdorfer et al., 2008) or volcanic is-
land systems (Peterson et al., 2009; Knee et al., 2010; Povi-
cec et al., 2012), although a substantial amount of
groundwater discharge and/or enriched fluid concentra-
tions may result in enhanced chemical fluxes from these
types of subterranean estuaries.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found,
in the online version, at http://dx.doi.org/10.1016/j.gca.2014.01.037.

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