Submarine groundwater discharge and nutrient addition to the coastal zone of the Godavari estuary

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A B S T R A C T

Submarine groundwater discharge (SGD) represents a significant pathway of materials between land and sea, especially as it supplies nutrients, carbon and trace metals to coastal waters. To estimate SGD fluxes to the Godavari estuary, India, we used multiple tracers: salinity, Si, 223Ra, 224Ra, 228Ra and 226Ra. Tracer abundances were elevated in groundwater from the unconfined coastal aquifer and in surface water from the near shore zone; these enrichments decreased to low levels offshore, indicative of groundwater discharge. A model based on the decay of 228Ra relative to 226Ra was used to determine apparent water ages of various bays within the estuary. These ages ranged from 2.6 to 4.8 d during November 2011. Knowing the water age, the distribution of radium in the estuary, and the radium isotopic composition of groundwater enabled us to calculate SGD fluxes to the estuary. These fluxes (in units of 10^6 m^3 d^-1) were on the order of 5 in the Gautami Godavari estuary, 20–43 in the Vasishta Godavari estuary, and about 300 in Kakinada bay, where enhanced ion exchange processes and redox-controlled cycling in the mangrove ecosystem may contribute to higher fluxes. These estimates of water fluxes allowed us to determine the magnitude and seasonal variability in the nutrient fluxes to the estuary associated with SGD. These nutrient fluxes (in units of mmol m^-2 d^-1) ranged from 1–19 (N), 0.6–2.6 (P), and 5–40 (Si) in Gautami Godavari; 19–40 (N), 2.6–5.5 (P), and 200 (Si) in Vasishta Godavari; and 120–140 (N), 10 (P), and 220 (Si) in Kakinada bay. The high SGD fluxes to Kakinada bay contribute significant nutrients to this bay; considerably lower SGD fluxes to Vasishta Godavari still contribute significant nutrients to this estuary. Thus SGD represents a major source of new nutrients to these coastal ecosystems. For the entire Godavari estuarine system, SGD fluxes contribute (48–88) × 10^9 mol DIC y^-1 and (51–94) × 10^9 mol TA y^-1. These fluxes represent ~54 and ~62% of the riverine DIC and TA fluxes to the Godavari estuarine system. This study provides baseline data against which future changes in nutrient and carbon fluxes due to urbanization and economic growth over this region can be compared.

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1. Introduction

River-dominated coastal waters and the adjacent continental shelf are important marine regions where the continuous exchange of water and chemical constituents take place with open oceans and play a major role in terms of global biogeochemical cycles (Walsh, 1991). Interactions among carbon (C), nitrogen (N) and phosphorus (P) cycles along the atmospheric, freshwater, estuarine and marine continuum are integral to the partitioning of C within different biosphere sources. Over the past century, however, the development of new agricultural practices to satisfy a growing global demand for food has drastically disrupted the nitrogen cycle. This has led to extensive eutrophication of freshwaters and coastal zones as well as increased inventories of the potent greenhouse gas—nitrous oxide (Canfield et al., 2010). Though the oceans have long been known to play a key role in regulating C and providing climate feedbacks, the response from the coastal and estuarine ecosystems are attracting increasing attention as the aquatic and terrestrial environments have a large potential to slow or amplify global warming (Jarvie et al., 2012). Submarine groundwater discharge (SGD) from coastal aquifers has been recognized as an important component of the hydrological cycle (Burnett et al., 2006; Moore, 2010; Taniguchi et al., 2002). This discharge comprises both fresh groundwater and recirculated seawater transported to the adjacent sea by advection across the permeable sediment–water interface (Burnett et al., 2003). Several studies demonstrated the importance of SGD to marine budgets of nutrients, radionuclides, and trace elements (Carroll et al., 1993; Kelly and Moran, 2002; Lee and Kim, 2007; Statham, 2011; Street et al., 2008; Windom et al., 2006). Groundwater fluxes of N are linked to areas with high runoff and intensive anthropogenic activity on land, with Southeast Asia, parts of North and Central America, and Europe being hot spots (Beusen et al., 2013). Coastal systems play an important role in the global carbon cycle. Estuaries are an important component of the coastal zone in terms of environmental and socioeconomic impact.

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Most of the estuaries are heterotrophic (respiration exceeds gross primary production) and are a source of CO₂ to the atmosphere (Cai et al., 2011). As groundwater is highly enriched in CO₂ compared to surface waters, groundwater discharge can influence CO₂ evasion from surface waters (Atkins et al., 2013). The flow of excess nutrients into marine waters is a major concern (Vitousek et al., 1997) and can lead to a range of impacts on eutrophication (Knee and Paytan, 2011; Rabalais et al., 2002) and global nutrient cycling (Galloway et al., 2008; Slomp and Cappellen, 2004). While sources such as precipitation, river discharge, seawater exchange and nitrogen fixation are important to many coastal ecosystems, determining the contribution of nutrient delivered through SGD may also be essential (Seitzinger et al., 2010). In many temperate and tropical regions, seasonal patterns in the water cycle play an important role in controlling SGD (Cable et al., 1997; Michael et al., 2005).

In quantifying SGD to the coastal zone, U- and Th-series isotopes have been extensively used (Moore, 1996). Radium isotopes (²²⁶Ra, ²²²Ra, ²²⁴Ra and ²²³Ra, with half-lives 1602 y, 5.75 y, 11.4 d and 3.66 d, respectively) have been shown to be powerful tools to access the sources and quantify SGD fluxes to coastal waters. The direct parent of each radium isotope is a thorium isotope. Thorium is strongly adsorbed onto sediments and provides a source of radium isotopes which are produced on a range of timescales. Estuaries in India are influenced by monsoonal rainfall and have characteristic runoff periods (Sarma et al., 2011, 2012). In an attempt to study the SGD in a tropical monsoon estuary, we made systematic time-series measurement of Ra isotopes in the Godavari estuarine system in the east coast of India. Increasing population, industrial and agricultural development and urbanization is taking place over this region. As a baseline study, we have used Ra isotopes to evaluate water mass residence times and quantify the SGD fluxes to this large tropical estuary. This paper discusses the role of SGD in the Godavari estuarine system in controlling nutrient fluxes between land and sea during monsoon and non-monsoon periods to assess the ecological impact of these fluxes.

2. Methods and materials

2.1. Study area

This study is a part of our ongoing investigations on the behavior of nutrients and selected trace elements in Indian estuaries and quantification of SGD using Ra isotopes. Godavari is the largest monsoonal river in peninsular region of India. The Godavari river basin lies between 22°35′, 16°05′N and 73°25′, 83°08′E. The river originates near Nasik, at an elevation of 1065 m in the Deccan Plateau. The Godavari river catchment area is 3.1 x 10⁶ km², with an annual discharge of 10⁶ km³ (Rao, 1975). The catchment receives ~82% of the total annual rainfall during the southwest monsoon (June–October) and the remainder during the northeast monsoon (November–January).

Near the town Rajahmundry, the river flow is regulated by a century-old dam at Dowaleswaram. Consequently, the Godavari estuarine system has negligible flushing and is classified as a vertically mixed estuary. Tide is semidiurnal in nature with the amplitude of 1.5 m and average current speed of 1–2 m s⁻¹. The average water column depth of the estuary is ~7 m (Acharyya et al., 2012). On an annual scale, diatoms are the dominant group of phytoplankton found in the estuary, along with some nitrogen-fixing cyanobacteria, dinoflagellates and green algae (Acharyya et al., 2012).

Mangrove forests are the dominant intertidal vegetation of the tropics which are highly productive and contribute significantly to nearshore biogeochemical solute budgets (Sanders et al., 2012; Stiglitz et al., 2013). The Coringa river mangrove ecosystem is the second largest coastal ecosystem in the east coast of India, connected to Kakinada bay (area: ~150 km²) on its north and to the Gautami Godavari on its south (Fig. 1). The presence of river tributaries, viz. Gaderu (length: 11 km) and Coringa (length: 26 km), numerous canals along with dense mangrove vegetation makes it an important carbon and nutrient source to the adjacent Kakinada bay. The Kakinada bay opens into the sea on its northern side and is bordered along most of its eastern stretch by a narrow sand bar. Tidal amplitude in the bay varies between 2.3 and 4.5 m, though in the mangrove covered area, the tidal amplitude is comparatively low.

2.2. Sampling and measurements

Measurements in bay water were conducted from a motor boat. At each station, water temperature and salinity were obtained in situ using conductivity, temperature and depth (CTD) system (Sea Bird Electronics, USA, Model 19 plus). We collected samples from three connected systems in the Gautami Godavari estuary along the salinity gradient of the estuary proper, the mangrove creeks located in its delta, and the adjacent semi-enclosed Kakinada Bay as well as Vasishta Godavari estuary, capturing the steepest gradients in tracer and nutrient abundances at these well-mixed sites. Study sites were selected to cover a broad geographical area. The location map of the Godavari estuarine system along with the sampling sites is shown in Fig. 1. Surface water samples at the lower reaches of the Gautami Godavari estuary (V1, V2, V3, V4, V5, Y6, Y7 and Y8) were collected during low tide along the salinity gradient during October 2010, February 2011 and November 2011 (Tables S1 and S2). During post-monsoon period (October 2010), sampling was restricted up to Yanam in the Gautami Godavari only; whereas during November 2011, all the three estuaries were sampled from more locations (Tables S1 and S2). Kotipalli is about 15 km upstream of Yanam and mostly freshwater dominates throughout the year whereas salinity at Yanam varies from near freshwater to brackish water (salinity ~30) during no discharge period. River water as well as groundwater samples close to the estuary were collected from locations, viz. Yanam, Bhairavpalem, Kotipalli, Rajahmundry, Dangeru and Injiram most of which during November 2011 (Table 1; Tables S1 and S2). In addition to estuary, samples were collected upstream of the river (including samples from the major Dam). Several groundwater samples were also collected from open wells or hand pump operated regularly. The Vasishta Godavari opens into the Bay of Bengal at Antervedi (Fig. 1). Samples at the lower reaches of the Vasishta Godavari estuary (V0, V1, V2, V3, V4, V5 and V6) along with river water and groundwater samples at Antervedi, Dongi and Siddhantham were collected during November 2011 (Table 1; Tables S1 and S2). Three samples were collected from the Kakinada bay during November 2011; river water and groundwater samples were also collected at Kondapalli, Jagannathpuram and Koringa (Table 1; Tables S1 and S2).

Sampling and analysis of Ra isotopes were performed following the procedures of Moore (1976). Collection of large volume of seawater (80–100 L) is required to analyze the very low ²²³Ra activities characterizing waters from the Godavari estuarine system. Suspended sediments in the water samples were immediately removed by filtration cartridges (Pore size: 1 μm), with a pre-cartridge, if necessary (Du et al., 2013). 80 L of water was run through columns filled with ~20 g Mn-coated acrylic fibers at a flow rate ~0.5 L min⁻¹. Fiber samples were washed with distilled water, partially dried and measured for adsorbed short-lived ²²²Ra.
and $^{224}$Ra on a RaDeCC (Radium Delayed Coincidence Counter) system (Moore and Arnold, 1996), usually within 1–2 d of sampling. The delayed coincidence system utilizes the difference in decay constants of the short-lived Po daughters of $^{219}$Rn and $^{220}$Rn to identify alpha particles derived from $^{219}$Rn or $^{220}$Rn decay. The fibers were re-measured twice after 10 d and a month from the day of sampling. Results were corrected for $^{228}$Th supported $^{224}$Ra, when Th was significant (>2% of the $^{224}$Ra activity). The corrected $^{224}$Ra is defined as

$$^{224}\text{Ra}_{\text{corr}} = ^{224}\text{Ra} - ^{228}\text{Th}. \tag{1}$$

The uncertainties on the $^{223}$Ra and $^{224}$Ra measurements were estimated to be up to 7% using the equations of Garcia-Solsona et al. (2008) and the errors quoted for these isotopes are ±7% (Table S2).

After this counting, Ra isotopes, along with Mn from the fiber samples, were brought into solution by boiling with 2 M HCl and were co-precipitated with BaSO₄ after Ba carrier addition and homogenization. The BaSO₄ amounting to 500 mg was dried, weighed and sealed in a
plastic vial and was assayed for Ra isotopes after three weeks from sealing the vial to allow $^{222}$Rn and its daughters to grow into equilibrium with $^{226}$Ra (Rengarajan et al., 2002). Activities of $^{226}$Ra and $^{228}$Ra were measured by gamma spectrometry using a high-purity germanium (HPGe) well detector (Canberra, USA, Model GCW4023) coupled to a Digital Spectrum Analyzer (Canberra, USA, Model DSA 500). The detector is shielded with 15-cm thick lead to reduce the background activity. The detector had an active volume of 196 cm$^3$; with a well depth and diameter of 40 mm and 16 mm respectively. The resolution of the detector is 1.4 keV (FWHM) at 1.22 MeV. The $^{226}$Ra activity in samples was determined from the photon peaks of its daughters: $^{214}$Pb (295.22 and 351.99 keV) and $^{214}$Bi (609.32 keV) whereas the $^{228}$Ra activity was measured via the peaks of $^{228}$Ac at 338.63, 911.07 and 968.90 keV. The errors for the $^{226}$Ra and $^{228}$Ra measurements were 5–10%, including counting statistics and standard propagation of errors associated with the data reduction. Generally, it took 3–4 d counting time to achieve a statistical uncertainty of ~6% on the final Ra isotope concentrations. BaSO$_4$ blanks (500 mg recovered using the same procedure without passing seawater) were also counted periodically. Standards were made from BaSO$_4$ doped with U (4% and 2%) and monazite NBS standards as well as calibrated $^{226}$Ra standard. They were counted periodically to check the constancy of the efficiencies of the gamma detector during the counting period. Ra adsorption efficiencies onto Mn fibers were checked by connecting a second fiber column in series. Measured activities on the second column were close to zero for all the Ra isotopes in all samples, indicating that the adsorption in the first column was quantitative (Du et al., 2013).

Sub-samples (500 mL) for nutrient analyses were collected and the concentrations of nutrients were determined following standard procedures of Grasshoff et al. (1983) using a UV Vis spectrophotometer (Shimadzu, Japan, Model UV 1240). Samples were measured within 24–36 h after collection and were preserved using HgCl$_2$ and stored in a freezer prior to analysis. The analytical precision of NO$_3^−$, NO$_2^−$, NH$_4^+$, PO$_4^{3−}$ and Si(OH)$_4$ were ±0.01, ±0.02, ±0.02, ±0.02 and ±0.01 μmol L$^{-1}$, respectively. The concentration of dissolved inorganic nitrogen (DIN) is expressed as the sum of NO$_3^−$, NO$_2^−$ and NH$_4^+$ concentrations.

The total alkalinity (TA) was measured by potentiometric (Metrohm, Switzerland, Model 702 SM Titirino) Gran titration method following Standard Operating Procedures (SOP) suggested by Dickson and Goyet (1998). Dissolved inorganic carbon (DIC) was measured using a Coulometer (UIC Inc., USA, Model CM 5014) along with in-house automated sub-sampling system. The precision for pH, TA and DIC was 0.002, 2.0 and 1.8 μmol L$^{-1}$, respectively. The accuracy of the DIC measurement was tested using Certified Reference Material supplied by Dr. A.G. Dickson, Scripps Institute of Oceanography, USA and internal standards and found to be within 0.2%.

### 3. Results

Here we present all of the nutrient data from a total of 56 surface water samples (Table S1) along with Ra isotope data from 59 surface water samples (Table S2) from the Godavari estuarine region. Samples for Ra isotopes from bay water, river water and groundwater are 31, 12 and 16, respectively. Mean values with ranges of concentrations of nutrients and Ra isotopes along with total number of samples collected in the estuary/bay, river and groundwater during October 2010, February 2011 and November 2011 are presented in Table 1. Salinity at the mouth of the estuary was ~30.0 and it decreased gradually to near zero at Kotipalli. In general, during winter, the estuary is well mixed with respect to nutrients when samples were collected off Yanam. During November 2011, DIN, DSI, and DIP in the river water were in the range of 8.43–98.7 μM (Mean: 58.8 ± 23.2 μM) 238–569 μM (Mean: 62.8 ± 101.9 μM) and 0.24–28.7 μM (Mean: 5.15 ± 6.73 μM), respectively. Ammonium concentration varied from the lower to upper estuaries within 0.9 to 4.8 μM, 0.05 to 4.7 μM and 0.6 to 7.6 μM during October 2010, February 2011 and November 2011 respectively.

We sampled freshwater wells (salinity near zero) along the shoreline. There were large spatial variations in nutrient concentrations in the groundwater, ranging from 3.63 to 86.9 μM (Mean: 50.3 ± 23.3 μM) for NO$_3^−$, from 0 to 24.4 μM (Mean: 3.1 ± 6.0 μM) for NO$_2^−$ and from 0.05 to 7.62 μM (Mean: 2.41 ± 2.19 μM) for NH$_4^+$. Concentrations of DIN, DSI, and DIP in the groundwater were in the range of 4.6–95.5 μM (Mean: 54.1 ± 25.5 μM) 20.9–569 μM (Mean: 108.5 ± 129.5 μM) and 0.5–28.7 μM (Mean: 8.4 ± 8.3 μM), respectively. Similarly, groundwater samples have high concentrations of nutrients compared with surface seawater (Table 1). DSI displayed conservative mixing between a high groundwater end member and much lower values in seawater. In contrast, NH$_4^+$ and PO$_4^{3−}$ showed increases while NO$_3^−$ + NO$_2^−$ showed a decrease during the mixing of fresh groundwater with seawater in the estuary. The DIC concentrations in the groundwater ranged between 2.2 and 19.6 mM with a mean value of 7.9 mM. The total alkalinity (TA) varied from 2.3 and 22.1 mM with

### Table 1

<table>
<thead>
<tr>
<th>Sample type</th>
<th>No. of samples</th>
<th>DIN (μmol L$^{-1}$)</th>
<th>DIP (μmol L$^{-1}$)</th>
<th>DSi (μmol L$^{-1}$)</th>
<th>N/P ratio</th>
<th>$^{226}$Ra (Bq L$^{-1}$)</th>
<th>$^{228}$Ra (Bq L$^{-1}$)</th>
<th>$^{224}$Ra (Bq L$^{-1}$)</th>
<th>$^{223}$Ra (Bq L$^{-1}$)</th>
</tr>
</thead>
</table>
an average of 8.4 mM. Both DIC and TA showed large spatial and temporal variations.

Surface Ra activity showed considerable spatial and temporal variability in the study area (Table 1). Ra isotopes in the samples from Kakinada bay and Vasishta Godavari estuary, are relatively enriched compared to those from Gautami Godavari estuary. Riverine 228Ra, 226Ra, 224Ra, and 223Ra activities ranged between 9.66–150.7 dpm 100 L–1, 5.26–39.3 dpm 100 L–1, 1.11–113.4 dpm 100 L–1, and 0.01–2.69 dpm 100 L–1, respectively. Activities of 226Ra and 228Ra at estuarine samples at higher salinities observed in this study are comparable to those from other coastal studies over the Bay of Bengal (Moore, 1997; Rengarajan et al., 2002).

Groundwater 228Ra activities exhibit significant spatial variability, ranging from 9.8 to 45.6 dpm 100 L–1, averaging 123.3 ± 159.3 dpm 100 L–1 (n = 16). The corresponding 228Ra activities in the groundwater samples ranged from 6.25 to 69.5 dpm 100 L–1 with a mean value of 22.1 ± 20.8 dpm 100 L–1. The Ra activities in the wells near the mouth of the estuary were lower than those in the wells far from the mouth. Groundwater 224Ra and 228Ra activities ranged from 23.1 to 1060 dpm 100 L–1 and from 0.09 to 7.96 dpm 100 L–1, respectively.

4. Discussion

4.1. General patterns

Variations of (NO3− + NO2−), DSi, NH4+ and PO43− with salinity during winter (February 2011) and post-monsoon (October 2010 and November 2011) periods are shown in Figs. 3 and 4, respectively. Samples were collected off Yanam during October 2010 and February 2011, whereas all the three estuaries were sampled from more locations during November 2011. The concentrations of NH4+ and PO43− are not changed during February 2011 and show an increasing trend with salinity during October 2010. In November 2011, the trend observed during October 2010 is reversed in the case of nutrients: when NH4+ is increased, the concentration of (NO3− + NO2−) decreased. In general, NH4+ and (NO3− + NO2−) have two different sources to the estuary. By and large, NH4+ enters to the estuary or groundwater through anthropogenic route by way of fertilizer use (Seitzinger et al., 2002). Urea and di-ammonium phosphate are used widely in this zone as fertilizer and ~15% of the total fertilizer consumption over India is used up in this region (Department of Agriculture, Government of India, New Delhi, http://www.indiastat.com/agriculture/2/stats.aspx). If significant amount of nitrication occurs, it can be converted to NO3− but the rate of nitrication is quite low in the Godavari estuary (0.02–0.04 µM N L–1 d−1; Rao and Sarma, 2013). The variations of NH4+ and (NO3− + NO2−) depend perhaps on the balance between these two routes. Also NH4+ readily adsorbs onto mineral surfaces, hence the relative mobility of NH4+ ions are different between the soils of groundwater aquifer and water.

Though the Godavari estuary system receives significant amount of nutrients during monsoon period from the river discharge (Sarman et al., 2010), phytoplankton biomass is the lowest due to high turbidity. On the other hand, phytoplankton blooms occur during no discharge period, when no nutrients are received from the upstream river, due to closing of dam gates to conserve water for domestic and industrial needs. Sarman et al. (2010) hypothesized that the major source of nutrients to the Godavari estuary during no discharge period could be exchange at the sediment–water interface and groundwater to sustain high phytoplankton biomass. The gradient in nutrient concentrations between estuarine water and groundwater suggests that concentration of DIN, DIP and DSi were an order of magnitude higher in the groundwater than estuarine water (Table S1) and exchange between these two pools could be a potential source of nutrients to support phytoplankton biomass in the estuary during lean and no discharge periods. In order to evaluate the exchange between these two pools, distribution of Ra isotopes and nutrients were examined.

Ra isotope concentrations are generally higher in the Kakinada bay and Vasishta Godavari estuary, both having mangrove-covered area, than those values in the Gautami Godavari estuary. Tidally-driven circulation through burrows with multiple openings, created by macro-fauna in mangrove forests, enhances ion exchange processes and redox-controlled cycling between mangrove and coastal zone leading to enrichment of water with Ra isotopes (Gleeson et al., 2013; Stieglitz et al., 2013). Figs. 5 and 6 show scatter plots of 226Ra, 228Ra and 224Ra activities versus salinity in the surface water samples during winter (February 2011) and post-monsoon (October 2010 and November 2011) seasons, respectively. In general, Ra versus salinity plots reveal that all the four isotopes were distributed coherently in surface waters of the Godavari estuary, i.e. with low activities at zero salinity, followed by an increase with salinity until reaching the highest activities at salinities of 2.5–9.0 and Ra activities decreased toward the lowest values in high salinity seawater. Such a pattern has been observed in estuaries of other large rivers and may reflect release of Ra isotopes from particles into solution upon estuarine mixing (Krest et al., 1999; Moore and Krest, 2004). However, during the post-monsoon season (October 2010 and November 2011), 228Ra activity and salinity plot for the Gautami Godavari estuary samples shows an increase of 228Ra activity with increasing salinity (Fig. 5). This may be explained by increasing
river water discharge with higher concentrations of $^{228}$Ra and $^{226}$Ra from the Ganga (also known as Ganges) and the Brahmaputra to the Bay of Bengal during monsoon and efficient tidal mixing at the mouth of the estuary due to high discharge of the Godavari river as well as substantial increase from the release of $^{228}$Ra from suspended sediment load at mid-salinity range during huge dam water discharge prior to our sampling. The relationship between the dissolved $^{226}$Ra and salinity showed a pronounced enrichment of Ra (excess Ra) in the estuary relative to the theoretical conservative mixing between the river and ocean end-members. Early investigations concluded that the origin of this excess Ra was from desorption of Ra from the river-borne suspended particles and diffusion from the bottom sediments (Key et al., 1985; Moore, 1981). However, more recent studies have established that excess Ra from coastal groundwater is another important source in some estuaries (Moore, 1999; Yang et al., 2002).

4.2. Groundwater along the riverbank

Plots of Ra activities in river water samples collected in the Godavari estuarine system are shown in Fig. 7. Both $^{228}$Ra and $^{226}$Ra (except for two anomalous points) have a strong linear relationship with $^{226}$Ra. The ratio between $^{228}$Ra and $^{226}$Ra is primarily considered to indicate Ra sources rather than Ra-mobilizing mechanisms, and thus should be close to the $^{232}$Th/$^{238}$U activity ratio of the aquifer rocks (Dickson, 1990; Szabo et al., 2012). Our measured $^{228}$Ra/$^{226}$Ra activity ratio varies between 2 and 3.7, which compares favorably with those reported previously for the open ocean samples close to the estuary (Rengarajan et al., 2002). The high $^{228}$Ra/$^{226}$Ra activity ratio might indicate a higher Th/U ratio of the aquifer rocks but a more likely interpretation is that loss of $^{238}$U daughter products through alpha recoil results in excess $^{232}$Th over $^{230}$Th (the direct parents of $^{228}$Ra and $^{226}$Ra) thus producing a higher $^{228}$Ra/$^{226}$Ra activity ratio in groundwater (Vengosh et al., 2009). Higher $^{228}$Ra/$^{226}$Ra ratio has also been ascribed to rapid accumulation of $^{228}$Ra, with a relatively shorter half-life of 5.75 y, in shallow groundwater due to alpha-recoil mechanisms relative to slower build-up of long-lived $^{228}$Ra (Cherdyntsev, 1971).

Plots of Ra activities in groundwater collected in the Godavari estuary are shown in Fig. 8. In general, Ra is enriched in brackish groundwater relative to fresh groundwater (Krishnaswami et al., 1991; Mulligan and Charette, 2006) due to cation exchange processes. However, in some cases, high Ra activities in fresh groundwater have also been reported (Moore, 2003). Moore (1997) observed high flux of Ra from the Ganges–Brahmaputra river system during low river discharge period. During high discharge, coastal aquifers are recharged with freshwater, when the distribution coefficient ($K_d$) for Ra is high and can lead to its sorption to aquifer solids. Subsequently, during low river discharge, saline groundwater intrudes into the aquifer and desorbs the accumulated Ra, which is returned to sea via SGD. The observed lower Ra activities in wells near the mouth of the estuary compared to those values in wells far from it was probably due to
the different residence times of the well water. Near the mouth, the groundwater may rapidly discharge into the estuaries through tidal pumping. As most of the groundwater samples were collected from drinking water wells, the salinity of these samples was low. In freshwater, radium is strongly adsorbed onto particles. However, under increasing salinity, radium can be released into solution. These characteristics make radium an excellent tracer of brackish SGD (Charette et al., 2008). Due to our sampling from wells supplying potable water, we could not get any brine groundwater samples to know Ra concentrations in them. The depths of most wells ranged from 2 to 10 m, suggesting that they contained shallow groundwater from the surficial aquifer that was primarily recharged by rainfall in filtration. Compared to natural abundance ratios in Earth’s crust of 1.0 to 1.2, the groundwater mean $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio was $4.0 \pm 2.6$ (range: $1.45 - 10.7$; $n = 16$). Scatter plot of $^{228}\text{Ra}$ versus $^{226}\text{Ra}$ of all the groundwater samples with a significant positive correlation ($R = 0.957$) indicates a rather homogeneous source, consistent with shallow seepage from the surficial aquifer (Fig. 8). Surficial coastal aquifers that are continuously flushed with salt water have low activities of $^{226}\text{Ra}$. Deep aquifers that are flushed less efficiently have higher $^{226}\text{Ra}$.

4.3. Water mass residence time, $\tau$

Near-shore water residence times at our study sites are a complex function of wind, wave and tidally driven circulation and are likely to vary considerably in response to changing conditions. Water mass residence time, $\tau$, is defined as the time a water parcel has spent since entering the estuary through its boundaries (Charette et al., 2008). For this, the approach adopted by Moore et al. (2006) which considers continuous radium additions from sediments or SGD is used:

$$\tau = \left( F_{^{224}\text{Ra}}^{^{228}\text{Ra}} - I_{^{224}\text{Ra}}^{^{228}\text{Ra}} \right) / \lambda_{^{224}} \times C_{^{228}}$$

where $F_{^{224}\text{Ra}}^{^{228}\text{Ra}}$ is the $^{224}\text{Ra}/^{228}\text{Ra}$ activity ratio in the input water (representing pore-water ratio), $I_{^{224}\text{Ra}}^{^{228}\text{Ra}}$ is the $^{224}\text{Ra}/^{228}\text{Ra}$ activity ratio in the system. Here we used the $^{224}\text{Ra}/^{228}\text{Ra}$ activity ratio in the shallow groundwater upstream as the input water ratio for November 2011 (Kotipalli, Dongi and Jagannathapuram). It is assumed that most of the radium entering the system is from submarine groundwater discharge. During November 2010 and February 2011, sampling was up to Yanam in the Gautami Godavari estuary and the $^{224}\text{Ra}/^{228}\text{Ra}$ activity ratio of upstream river water sample at Yanam is used as the input water ratio. Charette et al. (2001) reported pore-water $^{224}\text{Ra}/^{228}\text{Ra}$ ratio of 5.6 for Waquoit Bay which is higher by a factor of –2 than the initial ratios we have used in this study. Water ages determined are on
average 4.8 ± 0.2, 2.6 ± 0.5 and 2.8 ± 0.4 d on the Gautami Godavari, Vasishta Godavari and the Kakinada bay, respectively, during November 2011 (post-monsoon). The corresponding water ages for the Gautami Godavari during November 2010 (post-monsoon) and February 2011 (winter) are 3.9 ± 1.5 and 2.9 ± 1.3 d respectively. The lower water age during winter corresponds to zero river water discharge from the Godavari during November 2010 (post-monsoon) and February 2011 (post-monsoon). The corresponding water ages for the Gautami Vasishta Godavari and the Kakinada bay, respectively, during November 2011. The high correlation ($R^2 = 0.916$) suggests a similar source for each isotope and no decay of $^{228}$Ra.

**4.4. The SGD estimation**

**4.4.1. SGD flux derived from a three end-member mixing model**

A three end-member mixing model that uses radium isotopes to estimate the fractions of (i) ocean water, (ii) shallow groundwater and (iii) upstream water from the Godavari river (Moore et al., 2006). Equations for water, $^{228}$Ra and Si balance are:

\[
f_{SNW} + f_R + f_{GW} = 1.0 \tag{3}
\]

\[
^{228}\text{Ra}f_S + ^{228}\text{Ra}_Rf_R + ^{228}\text{Ra}_{GW}f_{GW} = ^{228}\text{Ra}_M \tag{4}
\]

\[
Si_Sf_S = Si_Rf_R + Si_{GW}f_{GW} = Si_M \tag{5}
\]

where $S$, $R$ and $GW$ refer to the oceanic, riverine and groundwater end-members, respectively. The subscript $M$ represents the measured values for individual samples; the parameter $f$ is the fraction of water derived from the three end-members. $^{228}$Ra decay is negligible on the timescale of mixing processes in the study region. The equations may be solved for the fractions of each end-member.

\[
f_S = \frac{^{228}\text{Ra}_M - ^{228}\text{Ra}_R}{^{228}\text{Ra}_{GW} - ^{228}\text{Ra}_R} \left( Si_M - Si_R \right) \left( Si_{GW} - Si_R \right)^{-1} \tag{6}
\]

\[
f_{GW} = \frac{Si_M - Si_R}{Si_{GW} - Si_R} f_S \tag{7}
\]

\[
f_R = 1.00 - f_S - f_{GW} \tag{8}
\]

In this model, the biggest uncertainty rested with Ra for the groundwater end-member, because we lacked brackish groundwater Ra samples in our sampling. All the groundwater samples are from wells and hand pumps used for drawing potable water. We could not find saline groundwater in this region. Furthermore we measured the coastal ocean outside the estuary during October 2010, February 2011 and November 2011. However, the salinity of that sample ($S = 31.00$) was lower than that of open ocean and was clearly not free of the influence of estuarine water. Additional measurements are available from Rengarajan et al. (2002). Since there are seasonal differences in the coastal Ra activities, we have used the coastal ocean values from the same season of each sampling to determine the excess Ra activities in the estuary. The offshore values used for $^{228}$Ra and $^{226}$Ra are 19.4 ± 1.0 dpm 100 kg$^{-1}$ and 10.1 ± 0.3 dpm 100 kg$^{-1}$ for winter and 10.7 ± 0.7 dpm 100 kg$^{-1}$ and 6.1 ± 0.2 dpm 100 kg$^{-1}$ for post-monsoon, respectively (Rengarajan et al., 2002). The model results are shown in Fig. 9. The mixing model is sensitive to the assumed values for the average input of reactive silicate (DSi) and $^{228}$Ra and to measurement errors for individual samples. The estimated errors on these fractions obtained by propagating errors associated with Ra isotopes, are ~10%. In the case of the Gautami Godavari estuary, river water fraction is higher than that of groundwater during winter (February 2011) when river discharge from the dam is minimum. This could be due to the excess water coming out from drainage canals joining the river after irrigation of agricultural paddy fields in winter months. The volumetric discharge rate of SGD (m$^3$ d$^{-1}$) is calculated as:

\[
SGD = f_{GW} \times V/\tau \tag{9}
\]

where $V$ is the volume of the estuary (m$^3$) and $\tau$ is the radium-derived water age (d). The Ra based seasonal SGD fluxes for the Gautami Godavari estuary were calculated to be (6.8–12.7) × 10$^6$ m$^3$ d$^{-1}$.

**4.4.2. Radium mass balance approach for estimating SGD**

Second approach to quantify the SGD fluxes is based on Ra mass balance (Charette et al., 2008). In a defined system with an assumed steady state, the gain of Ra is equal to the loss (Moore et al., 2006). Enrichment of Ra isotopes in coastal waters has to be supported by (1) desorption of terrestrial sediment, and (4) river supply and SGD. Ra loss is due to (1) tidal mixing between bay water and open seawater and (2) decay of Ra isotope. The mass balance equation is:

\[
G_{des} + G_{diff} + G_{ero} + G_{riv} + G_{SGD} = L_{mix} + L_{dec} \tag{10}
\]

where $G_{des}$ is the desorption of Ra from the seabed sediment, $G_{diff}$ is the diffusion of Ra from the seabed sediment, $G_{ero}$ is the erosion of terrestrial sediments along the river bank, $G_{riv}$ is the Ra from the river, $G_{SGD}$ is the Ra from the SGD, $L_{mix}$ is the mixing loss of Ra due to tidal exchange
between the water of the estuary and open sea and the decay of radium, all computed in the unit of dpm d\(^{-1}\). The term \(Q_{\text{SGD}}\) can be calculated if all other terms are known. If Ra concentration in groundwater is known, the volumetric flow rate of SGD can be estimated as:

\[
Q_{\text{SGD}} = \frac{C_{\text{SGD}}}{C_{\text{gw}}}
\]

where \(Q_{\text{SGD}}\) is the SGD flux and \(C_{\text{gw}}\) is the Ra activity in groundwater. To estimate the diffusive Ra flux from bottom sediments, we took the globally available regeneration rate of 0.45 and 25 dpm m\(^{-2}\) d\(^{-1}\) for \(^{226}\)Ra and \(^{228}\)Ra respectively (Charette et al., 2001; Hancock et al., 2006; Krest et al., 1999; Liu et al., 2012) and the contribution of Ra fluxes from suspended, bank-eroded and bottom sediments (\(G_{\text{des}} + G_{\text{ero}} + G_{\text{diff}}\)) are calculated to be minimum (Moore, 1996) and neglected in further calculations. Under steady state, Ra inventory is sustained by supply of Ra from river and SGD. Thus, Excess Inventory of \(^{226}\)Ra (from SGD Flux) is given by:

\[
^{226}\text{Ra}_{\text{XS}} = \left(^{226}\text{Ra}_{\text{ES}} - ^{226}\text{Ra}_{\text{SW}}\right) \times V_{\text{ES}} \times \left(1/\tau\right) - \left(1/\tau\right) \left(^{226}\text{Ra}_{\text{R}} \times F_{\text{R}}\right)
\]

where \(^{226}\text{Ra}_{\text{ES}}, ^{226}\text{Ra}_{\text{R}}\) and \(^{226}\text{Ra}_{\text{SW}}\) are the concentrations of \(^{226}\text{Ra}\) in the estuary, river upstream and seawater, \(V_{\text{ES}}\) is the estuarine volume, \(\tau\) is the water mass residence time and \(F_{\text{R}}\) is the river water flux. To determine the radium enrichment in the estuary, we subtract the average coastal ocean values. The ocean end member was collected as far from the mouth of the Godavari estuary as possible in a small craft. However, the salinity of that sample (\(S = 31.00\)) was lower than expected for open ocean, so it was clearly not free of the influence of water from inside the estuary. Hence values reported earlier by Rengarajan et al. (2002) from Bay of Bengal for \(^{226}\text{Ra}\) and \(^{228}\text{Ra}\) closer to the estuary during the same seasons were used for seawater Ra values (refer to Section 4.4.1).

Table 2 summarizes all the sources that contribute to the total \(^{226}\text{Ra}\) and \(^{228}\text{Ra}\) in the Godavari estuary. While calculating the river water Ra fluxes for the Vasishta Godavari estuary and Kakinada bay, the river water flux used is one-third of that for the Gautami Godavari estuary (Kunte et al., 2013). Our estimated SGD fluxes for the Gautami Godavari estuary were (1.55–7.44) \(\times 10^6\) m\(^3\) d\(^{-1}\) and (1.34–5.60) \(\times 10^6\) m\(^3\) d\(^{-1}\) based on the mass balance of \(^{226}\text{Ra}\) and \(^{228}\text{Ra}\), respectively (Table 3). The offshore seawater and groundwater end member values used in

### Table 2

<table>
<thead>
<tr>
<th>Definition</th>
<th>(^{226}\text{Ra})</th>
<th>(^{228}\text{Ra})</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_{\text{ES}}) Ra end-member in the Godavari estuary (This study)</td>
<td>(1) 17.34 ± 0.22</td>
<td>(1) 46.38 ± 0.6</td>
<td>dpm 100 L(^{-1})</td>
</tr>
<tr>
<td></td>
<td>(2) 12.8 ± 0.23</td>
<td>(2) 36.48 ± 0.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3) 19.38 ± 0.38</td>
<td>(3) 46.0 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>(R_{\text{R}}) Ra concentration in river water (This study)</td>
<td>(1) 9.75 ± 0.42</td>
<td>(1) 22.26 ± 1.0</td>
<td>dpm 100 L(^{-1})</td>
</tr>
<tr>
<td></td>
<td>(2) 8.18 ± 0.36</td>
<td>(2) 23.94 ± 0.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3) 8.61 ± 0.42</td>
<td>(3) 19.78 ± 0.84</td>
<td></td>
</tr>
<tr>
<td>(R_{\text{GW}}) Activity of Ra in groundwater (This study)</td>
<td>(1) 96.5 ± 0.65</td>
<td>(1) 451.8 ± 4.25</td>
<td>dpm 100 L(^{-1})</td>
</tr>
<tr>
<td></td>
<td>(2) 31.04 ± 0.46</td>
<td>(2) 107.45 ± 1.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3) 69.5 ± 0.65</td>
<td>(3) 451.8 ± 4.25</td>
<td></td>
</tr>
<tr>
<td>(R_{\text{O}}) Ra activity in the offshore surface water Rengarajan et al. (2002)</td>
<td>10.1 (winter; salinity = 33.179); 6.1 (post-monsoon; salinity = 33.281)</td>
<td>19.4 (winter; salinity = 33.179); 10.7 (post-monsoon; salinity = 33.281)</td>
<td>dpm 100 L(^{-1})</td>
</tr>
<tr>
<td>(\tau) Water age</td>
<td>1.39</td>
<td></td>
<td>d</td>
</tr>
<tr>
<td></td>
<td>(2) 2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(V) Estuary volume</td>
<td>136 (\times 10^6) (winter); 190 (\times 10^6) (post-monsoon)</td>
<td></td>
<td>m(^3)</td>
</tr>
<tr>
<td>(F_{\text{R}}) Water discharge</td>
<td>(1) 539.9</td>
<td></td>
<td>m(^3) s(^{-1})</td>
</tr>
<tr>
<td></td>
<td>(2) 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3) 163.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A_{\text{S}}) Surface area of the estuary</td>
<td>16.5 (\times 10^6)</td>
<td>4.13 (\times 10^6)</td>
<td>m(^2)</td>
</tr>
<tr>
<td>(R_{\text{S}}) Diffusive flux of Ra Based on Krest et al. (1999), Hancock et al. (2006)</td>
<td>7.43 (\times 10^6)</td>
<td></td>
<td>dpm d(^{-1})</td>
</tr>
</tbody>
</table>

\(a\) Data from (1) October 2010, (2) February 2011, (3) November 2011.

\(b\) Measured at Rajamundry GW (November 2011).

\(c\) Measured at Bairavapalem GW (February 2011).
the calculation introduce some degree of uncertainties; to the extent that the estimated SGD flux can be considered to be of upper limit. A comparison of the available data on SGD over the Asian region is given in Table 4. The SGD fluxes over the Godavari estuarine system is significantly high when compared to river flux to the Bay of Bengal especially during the lean flow period.

Comparing the above two approaches, the SGD fluxes of (6.8–12.7) × 10^6 m^3 d^-1 via Ra–Si three end member mixing model and (1.34–7.44) × 10^6 m^3 d^-1 from Ra mass balance model, respectively, are obtained. A fair agreement between these two independent methods gives confidence that the estimated SGD fluxes are well grounded. These values are compared to the fluxes reported from the Southeast Asian shelf regions (Table 4).

4.4.3. SGD-derived nutrient and carbon fluxes

Since groundwater exchange is the major source of Ra isotopes to the river system, a significant positive correlation between Ra isotopes and dissolved nitrogen in river water generally provide further evidence for groundwater as a major source of nutrients to the estuarine system. In the Godavari estuarine system, a plot of river water NO_3 versus 226Ra gives a scatter. In some locations, groundwater NO_3 concentration was very similar to that of surface water (Table S1). Hence we suspect that nitrate in surface waters was partly derived by nitrification of groundwater-derived ammonium or by the breakdown of DON.

The nutrient fluxes contributed from SGD was computed from Ra-derived SGD fluxes and nutrient concentration difference between the groundwater and seawater (Table 1). We used values of macronutrients for the groundwater end-member during October 2010 and November 2011 from Rajamundry GW and for the Kakinada bay from Bairavpalem GW; whereas for the Gautami Godavari during February 2011, values for macronutrients are from Yanam GW. The estimated SGD-derived nutrient fluxes, to the Godavari estuarine system, ranged from 1.13–141.4, 0.59–11.1 and 5.19–232.1 mmol m^-2 d^-1 for DIN, DIP and DSi, respectively, using 226Ra and 228Ra (Table 3). The flux rates were higher by an order of magnitude in the Kakinada Bay followed by the Vasishta Godavari and the Gautami Godavari. On the other hand, the nutrient fluxes were higher during November compared to October and February in the Gautami Godavari estuary. Considering residence time of water during study period, the mean concentrations of nutrients in the estuary, the contribution of groundwater exchange to estuarine nutrients was evaluated. It was noticed that the groundwater in the study area represents a substantial contribution to the N and P loading to the Godavari estuarine system and were equivalent to 10–35% and 3–10% of the riverine inputs to the Godavari estuary for DIN and DIP, respectively, during the sampling period. The dry-deposition flux of nitrogen (N_{dip} + N_{dp}) to the Bay of Bengal ranged from 2 to 167 μmol m^-2 d^-1 (Srinivas et al., 2011), which is minor compared to the groundwater flux. This study further confirms that hypothesis of Sarma et al. (2010) that groundwater is a significant source of nutrients to the Godavari estuary during dry period (or no discharge period) to support phytoplankton biomass. The present study shows that 10–35% of the nutrients were contributed to the Godavari estuarine system through groundwater exchange to support ecosystem activities. This fraction seems to be almost equivalent to that found in the Pearl River (Liu et al., 2012) in the case of DIN; whereas significantly smaller in the case of DIP. In addition to the significant supply of DIN and DIP to the estuary from the groundwater, it modifies the N:P ratio that may have significant impact on the ecosystem structure and phytoplankton composition. The N:P ratio of the flux varied between 1.9 and 12.8 (Table 3) and showed significant spatial and temporal variability. These ratios are significantly lower than Redfield ratio of 16 suggesting that relatively higher phosphate is entering the system than what is expected equivalent to nitrogen. Sarma et al. (2009) observed variations in DIN:DIP ratios between 1.62 and 86 (Mean: 20.3 ± 14.3) in the Godavari estuary and higher values were noticed in the middle of January, end of March and at the beginning of August. In contrast, lower values were noticed in June, September, October, and November and they were associated with the low N:P fluxes from groundwater. Such low N:P ratios were associated with high micro- and nanoplanckton than picoplankton (Sarma et al., 2009). Bharati (2014) observed that bacillariophyceae group of

<table>
<thead>
<tr>
<th>Region</th>
<th>SGD(^4)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gautami Godavari estuary</td>
<td>(1.55–7.44) × 10^6 m^3 d^-1 (a)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>(1.34–5.60) × 10^6 m^3 d^-1 (b)</td>
<td></td>
</tr>
<tr>
<td>Vasishta Godavari estuary</td>
<td>20.20 × 10^6 m^3 d^-1 (a)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>40.02 × 10^6 m^3 d^-1 (b)</td>
<td></td>
</tr>
<tr>
<td>Kakinada bay</td>
<td>314.7 × 10^6 m^3 d^-1 (a)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>269.08 × 10^6 m^3 d^-1 (b)</td>
<td></td>
</tr>
<tr>
<td>Ganga–Brahmaputra Estuary</td>
<td>6.3–63 m^3 d^-1 (b)</td>
<td>Moore (1997)</td>
</tr>
<tr>
<td>Northern South China Sea shelf</td>
<td>2.2 × 10^6 m^3 d^-1 (a)</td>
<td>Liu et al. (2012)</td>
</tr>
<tr>
<td>Eastern Hainan Island (i) Ramen Bay</td>
<td>3.7 × 10^6 m^3 d^-1 (b)</td>
<td>Su et al. (2011)</td>
</tr>
<tr>
<td>(ii) Wanquan Estuary</td>
<td>7.36 × 10^6 m^3 d^-1 (b)</td>
<td></td>
</tr>
<tr>
<td>Changjiang effluent plume</td>
<td>2.1–10 × 10^6 m^3 d^-1 (b)</td>
<td>Gu et al. (2012)</td>
</tr>
<tr>
<td>Yellow Sea</td>
<td>(2.7–18.4) × 10^6 m^3 d^-1 (b)</td>
<td>Kim et al. (2005)</td>
</tr>
<tr>
<td>Coastal areas of Vizhinjam and Thiruvananthapuram</td>
<td>(1.6 ± 0.9) × 10^7 m^3 d^-1 (c)</td>
<td>Jacob et al. (2009)</td>
</tr>
<tr>
<td>Manila Bay, Philippines</td>
<td>2.36 × 10^6 m^3 d^-1 (c)</td>
<td>Taniuchi et al. (2008)</td>
</tr>
<tr>
<td>Narmada estuary</td>
<td>100–5500 m^3 d^-1 (d)</td>
<td>Rahman and Singh (2012)</td>
</tr>
</tbody>
</table>

\(^4\) SGD based on (a) 226Ra, (b) 228Ra, (c) 222Rn, and (d) 87Sr.
phytoplankton contributed significantly during no discharge period associated with low N:P ratio. This study suggests that modification of N:P ratios through groundwater discharge might have modified phytoplankton composition. However, further studies are required to confirm the same.

The total alkalinity (TA) and dissolved inorganic carbon (DIC) in the groundwater of the Ghatami Godavari estuary varied from 1716 to 15,788 and 1212 to 12,324 μM, respectively, and it is significantly higher than that of estuarine concentrations (1333–2241 and 953–3671 μM) suggesting that groundwater contained 3 to 4 times higher concentrations than estuary. Sarma et al. (2011) considered that the Godavari estuary is a perennial source of CO₂ to the atmosphere and the rate of flux is higher during high discharge period than no discharge period. It was noticed that in the estuary, relatively acidic nature was observed during high discharge period (<7.5) and pH increases to >8 during no discharge period. The increase in pH and dissolved inorganic carbon (DIC) may be contributed by fraction of seawater intruded into the estuary through tidal excursion. In such conditions, tight correlation is expected between salinity and TA or DIC. However, absence of such tight correlation suggests that significant contribution from groundwater exchange is possible to the estuary that lead to efflux of CO₂ to atmosphere. In order to examine this proposition, the contributions of DIC and TA from the SGD to the Godavari estuarine system were estimated using mean concentrations of TA and DIC that amounted to (47.8–88.4) × 10⁻³ mol m⁻³ and (50.9–94.0) × 10⁻³ mol m⁻³, respectively, which represent 54 and 62% of the riverine DIC and TA concentrations to the estuary. Our estimations are almost similar to those of the Pearl River (Liu et al., 2012) and the South Atlantic Bight (Moore et al., 2006).

Sarma et al. (2011) measured pCO₂ levels (221–34,026 μatm) in the Godavari estuary during peak discharge period which were far beyond the world’s polluted estuaries and was attributed to high bacterial respiration supported by terrestrial organic matter during later period. They further suggested that Godavari estuary cannot be classified as a polluted estuary based on the average N:P ratios of 20 ± 7 and it does not receive any significant domestic or industrial effluents. Besides other sources, such as large scale erosion and deforestation in the catchment area, leading to high amounts of organic carbon export that decomposes in the basin, groundwater exchange may also supply significant amount of inorganic carbon to the basin and therefore CO₂ flux to the atmosphere. However, delineating these two pools requires stable isotope studies to account for the contribution from groundwater to estuarine inorganic carbon system.

However, estimating SGD-derived nutrient, DIC and TA inputs by assuming that their concentrations measured in groundwater are representative of the fluid actually crossing the sediment–water interface may not be accurate. Nutrient enrichment due to organic matter remineralization in surface sediments may increase the flux (Jahneke et al., 2003), while removal through processes such as sorption and denitrification will decrease the flux (Capone and Slater, 1990). Therefore, caution is necessary. Spiteri et al. (2008) highlighted the need to account for redox-dependent transformation and removal processes for N and P as well as DOC in the aquifer when estimating rates of SGD of nutrients based on groundwater velocities and nutrient concentrations in field studies. Nevertheless, the contribution of nutrients and inorganic carbon from groundwater is significant to the estuary to support sustained biological production especially during dry periods, when no nutrients are supplied through river discharge, and thus turn out to be a perennial source of CO₂ to the atmosphere through air–water interface.

5. Conclusions

In the present study, estuarine, river and groundwater samples were collected from the Godavari estuary for Ra isotope measurements during three sampling campaigns, between October 2010 and November 2011. From the distribution patterns of the Ra isotopes in surface water and shallow groundwater, we draw the following conclusions.

Concentrations of Ra isotopes have distinct patterns with peak activity occurring at different seasons. Excess Ra inputs were found in the Kakinada Bay and to a lesser extent, the Vasishtha and Gautami Godavari estuaries. The radium sources from the river and the estuarine system cannot balance the radium budgets; thus another important source from groundwater discharge must be considered.

The conservative SGD water flux for the Gautami Godavari estuary based on excess ²²⁸Ra and ²²⁶Ra is (1.34–7.44) × 10⁸ m³ d⁻¹. A comparison of the nutrient fluxes through the subterranean groundwater discharge with the other nutrient mass balance components reveals that nutrient input to the coastal area via SGD is a potentially important source of nutrients and must be considered while assessing the nutrient budgets. In the Godavari estuary, the SGD-derived nutrient loading contributes up to 35% which is one of the major sources of nutrient to the estuary, especially during dry period when phytoplankton starve for nutrients due to drying of upstream river. In addition to this, submarine discharge of the nutrient-enriched groundwater with high N:P ratios may have an important impact on the coastal ecosystems by altering the N:P stoichiometric characteristics of the adjacent Bay of Bengal. In the future, a combination of continuing high inputs of nutrients through human activity and climate change may lead to enhanced eutrophication in coastal waters. SGD estimates are needed to effectively understand, predict and manage the impact of macronutrients on estuarine systems along with cycling of organic N and P, benthic exchanges and rates and magnitude of bacterially-driven processes.

The SGD is a significant source of inorganic carbon components (DIC and TA) and contributes up to 50% to the total fluxes to the Godavari estuary. The Godavari estuary is recently found to be a perennial source of CO₂ to the atmosphere. As an extension of this study, it would be interesting to examine what fraction of DIC from the SGD is exchanged with the atmosphere using stable isotopes of carbon in the future.

Acknowledgments

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Appendix A. Supplementary data

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References


waters enhanced by eutrophication. Nature Geosci. 4, 66–70. http://dx.doi.org/10.1038/ngeo1297.


