



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



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## ABSTRACT

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, <sup>223</sup>Ra, <sup>224</sup>Ra, <sup>228</sup>Ra and <sup>226</sup>Ra. 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 <sup>224</sup>Ra relative to <sup>228</sup>Ra 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<sup>6</sup> m<sup>3</sup> d<sup>-1</sup>) 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<sup>-2</sup> d<sup>-1</sup>) 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<sup>9</sup> mol DIC y<sup>-1</sup> and (51–94) × 10<sup>9</sup> mol TA y<sup>-1</sup>. 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 South-east 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 CO<sub>2</sub> to the atmosphere (Cai et al., 2011). As groundwater is highly enriched in CO<sub>2</sub> compared to surface waters, groundwater discharge can influence CO<sub>2</sub> 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 (<sup>226</sup>Ra, <sup>228</sup>Ra, <sup>223</sup>Ra and <sup>224</sup>Ra, with half-lives 1602 y, 5.75 y, 11.4 d and 3.66 d, respectively) have been shown to be powerful tools to assess 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 × 10<sup>5</sup> km<sup>2</sup>, with an annual discharge of 10<sup>5</sup> km<sup>3</sup> (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 flow from the dam due to which it acquires high salinity except during high discharge period. After the dam, the river is divided into two major distributaries – one flow toward the east forming the Gautami Godavari estuary and the other toward the south known as Vasishta Godavari estuary (Fig. 1). The Godavari estuarine system is located around 16°15'N and 82°5'E covering an area of 330 km<sup>2</sup>. The average annual rainfall is 1128 mm in this region in which nearly 90% of this rainfall is received during the six monsoon months from June to November (Fig. 2). The dam-controlled freshwater discharge into the Godavari estuary begins by June and continues until mid-December with its maxima in August. In general, there is virtually no controlled discharge from the dam between January and May. At its peak, the river discharge reaches up to ~10,000 m<sup>3</sup> s<sup>-1</sup> during Southwest monsoon period (June to August) (Acharyya et al., 2012). The estuarine mixing is predominantly driven by tidal 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<sup>-1</sup>. 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, dianoflagellates 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 near-shore biogeochemical solute budgets (Sanders et al., 2012; Stieglitz 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 km<sup>2</sup>) 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 (Y1, Y2, Y3, Y4, Y5, 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 (Fig. 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 Anthervedi, Dongi and Siddhantham were collected during November 2011 (Fig. 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 Coringa (Fig. 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 <sup>228</sup>Ra 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<sup>-1</sup>. Fiber samples were washed with distilled water, partially dried and measured for adsorbed short-lived <sup>223</sup>Ra

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