



# Submarine groundwater discharge as an important nutrient source influencing nutrient structure in coastal water of Daya Bay, China

Xuejing Wang<sup>a,b</sup>, Hailong Li<sup>a,c,\*</sup>, Chunmiao Zheng<sup>a</sup>, Jinzhong Yang<sup>b</sup>, Yan Zhang<sup>d</sup>, Meng Zhang<sup>d</sup>, Zhanhui Qi<sup>e</sup>, Kai Xiao<sup>d</sup>, Xiaolang Zhang<sup>a</sup>

<sup>a</sup> School of Environmental Science and Engineering and The Key Laboratory of Soil & Groundwater Pollution Control of Shenzhen City, Southern University of Science and Technology, Shenzhen 518055, China

<sup>b</sup> School of Water Resources and Hydropower Engineering, Wuhan University, Wuhan 430072, China

<sup>c</sup> State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing 100083, China

<sup>d</sup> MOE Key Laboratory of Groundwater Circulation & Environment Evolution and School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing 100083, China

<sup>e</sup> South China Sea Fisheries Research Institute, Chinese Academy of Fishery Sciences, Guangzhou 510300, China

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## Abstract

As an important nutrient source for coastal waters, submarine groundwater discharge (SGD) has long been largely ignored in Daya Bay, China. In this study, we estimate the fluxes of SGD and associated nutrients into this region using a  $^{224}\text{Ra}$  mass balance model and assess the contribution/importance of nutrients by SGD, benthic sediments, local rivers, and atmospheric deposition. The results of  $^{224}\text{Ra}$  mass balance show that the estimated SGD ranges from  $(2.76 \pm 1.43) \times 10^6 \text{ m}^3/\text{d}$  to  $(1.03 \pm 0.53) \times 10^7 \text{ m}^3/\text{d}$  with an average of  $(6.32 \pm 2.42) \times 10^6 \text{ m}^3/\text{d}$ , about 16 times the total discharge rate of local rivers. The nutrient loading from SGD is estimated to be  $(1.05\text{--}1.99) \times 10^5 \text{ mol/d}$  for  $\text{NO}_3\text{-N}$ ,  $(4.04\text{--}12.16) \times 10^3 \text{ mol/d}$  for DIP, and  $(3.54\text{--}11.35) \times 10^5 \text{ mol/d}$  for Si. Among these considered nutrient sources, we find that SGD is the primary source for Si and  $\text{NO}_3\text{-N}$ , contributing 68% and 42% of all considered sources, respectively. The atmospheric  $\text{NO}_3\text{-N}$  flux is comparable to that from SGD. The local rivers are the most important source for DIP, contributing 75% of all considered sources. SGD with high N:P ratio ( $\text{NO}_3\text{-N/DIP}$ ) of 37.0 delivers not only a large quantity of nutrients, but also changes nutrient structure in coastal water. Based on a DIP budget, primary productivity is evaluated to be 54–73 mg C/m<sup>2</sup> d, in which SGD accounts for approximately 30% of total production. This study indicates that SGD is a key source of nutrients to coastal waters and may cause an obvious change of primary production and nutrient structure in Daya Bay.

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**Keywords:** Submarine groundwater discharge; Nutrient loadings; Radium isotopes; Primary production; Daya Bay

## 1. INTRODUCTION

Nutrient level has been one of the key indicators evaluating the “health status” of ecological environment in an aquatic system. Submarine groundwater discharge (SGD), an important process of interaction between groundwater and seawater, has been widely recognized as a significant

\* Corresponding author at: School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China.

E-mail address: [lihailong@sustc.edu.cn](mailto:lihailong@sustc.edu.cn) (H. Li).

transport pathway of material (i.e., nutrients, metals, carbon, and rare earth elements) into coastal waters (Moore, 1996; Taniguchi et al., 2002; Burnett et al., 2006; Moore, 2010; Rodellas et al., 2015; Johannesson et al., 2017). Most importantly, nutrient loadings from SGD have been shown to rival those from local rivers, benthic sediment diffusion, and atmospheric inputs in some coastal areas owing to significant amount of SGD and enrichment of nutrients in SGD (Kim et al., 2005; Swarzenski et al., 2007; Hwang et al., 2010; Rodellas et al., 2015). Many studies have suggested that various environmental problems such as harmful algal blooms and red tides in coastal zones are closely related to this process (Hu et al., 2006; Lee and Kim, 2007; Blanco et al., 2011; Luo and Jiao, 2016). In order to evaluate the ecological importance of nutrient inputs on coastal ecosystems, it is essential to determine the contributions of main nutrient sources such as SGD, local rivers, atmospheric deposition, benthic sediments, and aquaculture.

As a semi-enclosed bay in the northwestern part of the South China Sea with both tropical and subtropical characteristics, Daya Bay is an important coastal environment. With rapid population growth and economic development, nutrient inputs from aquaculture, urbanization and anthropogenic sources have increased in the past decades and led to ecological and environmental changes in the aquatic system (Wang et al., 2008). Consequently, Daya Bay is facing many ecological problems, such as serious eutrophication with the frequent occurrence of harmful algal blooms (Song et al., 2004; Song et al., 2009; Wang et al., 2011). Although routine environmental investigations (hydrographic, chemical and biological parameters monitoring) have been conducted in this region 30 years ago (Zhou et al., 1998), there are few studies related to SGD (Wang et al., 2017), and the importance of SGD has long been largely ignored. In addition, nutrient fluxes attributed to SGD, benthic sediments, local rivers, atmospheric deposition, and aquaculture are seldom simultaneously investigated and reported.

This study aims to estimate the fluxes of SGD and the associated nutrient inputs into Daya Bay using the geochemical tracer radium isotopes and to evaluate the respective contributions of nutrients by SGD, benthic sediments, local rivers, and atmospheric deposition. Focusing on these purposes, we conducted a cruise to survey the short-lived  $^{224}\text{Ra}$  activities and nutrient concentration in waters of Daya Bay during December 2015 (winter). The vertical mixing rate used to calculate the benthic  $^{224}\text{Ra}$  fluxes was estimated based on a one-dimensional (1-D) vertical diffusion model and the vertical distribution of  $^{224}\text{Ra}$ . SGD flux was estimated based on a  $^{224}\text{Ra}$  mass balance model. Nutrient fluxes contributed by SGD, local rivers, benthic sediments, and atmospheric deposition and their influences on nutrient structure were compared, analyzed and discussed.

## 2. MATERIALS AND METHODS

### 2.1. Study area

Daya Bay (22.45–22.83°N, 114.50–114.89°E) is located in the eastern coast of Guangdong Province, China, and

is a semi-enclosed subtropical bay of northern South China Sea (Fig. 1). It has a north-south length of ~30 km and a width of ~20 km, with a water area of ~560 km<sup>2</sup>. The average water depth is 10 m and approximately 60% of the area is less than 10 m in depth (Fig. 1). The main types of bottom sediments are silty clay and clayey silt in the north and south of the bay, respectively (Li et al., 2002). According to Gao et al. (2010), the distribution of these two types of bottom sediments is approximately divided by the bathymetric line of 10 m. The percentages of fine fraction (clay + silt) are >90%. Sediments close to the mouth of the bay, however, have relatively less clay but more silt than those of the other areas. The grain sizes are well-distributed in the upper 1.0 m sediments (Liu et al., 2009; Wang et al., 2011). The tidal current is dominated by an irregular semi-diurnal component with a mean tidal range of ~1.01 m.

The region has a subtropical monsoonal climate with an annual average temperature of 22 °C and an average precipitation of 1700 mm. Rainfall is abundant and occurs mostly (80%) from April to September. The surface sediments in coastal plain are mainly characterized by the medium fine sand with a thin thickness, in which the amount of water is small. The occurrence and distribution of groundwater in this region are mainly controlled by meteorological hydrology, topography, stratigraphic lithology, and geological structure. The rainfall infiltration is changing with the seasons; in the rainy season, the groundwater recharge is large and the groundwater level rises, while the fluxes of the spring water and rivers increase. The main discharge ways of groundwater is flowing into the local rivers and coastal ocean. There is no large river discharging into the bay but several small seasonal rivers such as the DanAo (R1), Suzhou (R2), Zhuyuan (R3), and Baiyun (R4) Rivers (Han, 1995). The DanAo River is the largest one running into the northwestern part of the bay with a mean flux of  $3.14 \times 10^5 \text{ m}^3/\text{d}$ . The southwest monsoon prevails from May to September, while the northeast monsoon predominates from October to April of next year. With a rapid economic development, Daya Bay has become a diverse area rife with agricultural, aquacultural, seaport transportation, and tourist activities (Sun et al., 2016).

### 2.2. Sampling

The cruise for water sampling in the bay was carried out from 16 to 19 December 2015. The distribution of the sampling stations is shown in Fig. 1. We collected 63 seawater samples at 27 stations, 19 shallow coastal groundwater samples at 10 stations and 4 river water samples for radium extraction. The technique for radium extraction was introduced by Moore (1976) and widely used in many studies (Moore, 1996; Kim et al., 2005; Wang et al., 2015; Luo and Jiao, 2016). In brief, water samples of known volume (30 L for seawater and river water, 2–10 L for coastal groundwater) were pumped from different depth and filtered through a 0.45- $\mu\text{m}$  filter, and passed slowly (flow rate less than 1 L/min) through a column filled with ~25 g of manganese-coated acrylic fiber (Mn-fiber) for extracting radium isotopes (Moore, 1976). The coastal groundwater

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