Water Research 102 (2016) 11–31

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Submarine groundwater discharge and nutrient loadings in Tolo Harbor, Hong Kong using multiple geotracer-based models, and their implications of red tide outbreaks

Xin Luo [a, b], Jiu Jimmy Jiao [a, b, *]

[a] Department of Earth Sciences, The University of Hong Kong, PR China
[b] The University of Hong Kong, Shenzhen Research Institute (SRI), Shenzhen, PR China

ARTICLE INFO

Article history:
Received 17 December 2015
Received in revised form
31 May 2016
Accepted 6 June 2016
Available online 8 June 2016

Keywords:
Geotracer models
SGD
Groundwater borne nutrients
Climatological parameters
Red tide outbreaks
Phosphate limited embayment

ABSTRACT

Multiple tracers, including radium quartet, ^{222}Rn and silica are used to quantify submarine groundwater discharge (SGD) into Tolo Harbor, Hong Kong in 2005 and 2011. Five geotracer models based on the end member model of ^{228}Ra and salinity and mass balance models of ^{226}Ra, ^{228}Ra, ^{222}Rn, and silica were established and all the models lead to an estimate of the SGD rate of the same order of magnitude. In 2005 and 2011, respectively, the averaged SGD based on these models is estimated to be $\approx$ 5.42 cm d^{-1} and $\approx$2.66 cm d^{-1}, the SGD derived DIN loadings to be 3.5 $\times$ 10^5 mol d^{-1} and 1.5 $\times$ 10^5 mol d^{-1}, and DIP loadings to be 6.2 $\times$ 10^3 mol d^{-1} and 1.1 $\times$ 10^3 mol d^{-1}. Groundwater borne nutrients are 1–2 orders of magnitude larger than other nutrient sources and the interannual variation of nutrient concentration in the embayment is more influenced by the SGD derived loadings. Annual DIP concentrations in the harbor water is positively correlated with the precipitation and annual mean tidal range, and negatively correlated with evapotranspiration from 2000 to 2013. Climatologically driven SGD variability alters the SGD derived DIP loadings in this phosphate limited environment and may be the causative factor of interannual variability of red tide outbreaks from 2000 to 2013. Finally, a conceptual model is proposed to characterize the response of red tide outbreaks to climatological factors linked by SGD. The findings from this study shed light on the prediction of red tide outbreaks and coastal management of Tolo Harbor and similar coastal embayments elsewhere.

1. Introduction

During the past decades, submarine groundwater discharge (SGD) has gained considerable concerns from marine chemists and hydrogeologists since the SGD has proved to be a significant component of global water budget and plays a vital role in water transport and chemical fluxes at the coastal zones (Moore, 1996, 1999; Charette et al., 2001; Burnett et al., 2003; Slomp and Van Cappellen, 2004a, Moore, 2010). The SGD is comprehensively defined as any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force (Burnett et al., 2003). Numerous studies have proved that SGD can induce the loadings of nutrients (Hwang et al., 2005a; Lee et al., 2012; Luo et al., 2014), heavy metals and rare earth elements (Kim and Kim, 2011; Ganguli et al., 2012), dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) (Kim et al., 2011; Liu et al., 2011; Cyronak et al., 2013), heat (Santos et al., 2011) etc. Large SGD derived chemicals loadings, especially loadings of nutrients, significantly affect coastal ecosystems such as corals, mangroves and are attributable to the red tide occurrence (Gobler and Sanudo-Wilhelmy, 2001; Hu et al., 2006; Lee and Kim, 2007; Lee et al., 2010; Blanco et al., 2011; Su et al., 2013b).

Radium quartet, naturally occurring from uranium - thorium series, are highly concentrated in coastal groundwater due to high desorption rate and mobility in saline environment (Krishnaswami et al., 1982; Luo et al., 2000), which makes them ideal tracers to examine groundwater discharge in various environments such as the subterranean estuaries, continental shelves and lakes (Moore, 2003; Charette, 2007; Swarzenski et al., 2007a; Raanan et al., 2009). Moreover, radium quartet are used to quantify the water

* Corresponding author. Department of Earth Sciences, The University of Hong Kong, Room 302, James Lee Science Building, Pokfulam Road, Hong Kong.
E-mail address: jjiao@hku.hk (J.J. Jiao).

http://dx.doi.org/10.1016/j.watres.2016.06.017
0043-1354/

mixing within embayments, continental shelves as well as open sea (Moore, 2000; Hancock et al., 2006; Moore et al., 2006). Short-lived radium isotopes, ^{223}Ra ($t_{1/2}$ = 11 d) and ^{224}Ra ($t_{1/2}$ = 3.65 d), are proved to be effective in estimating mixing rate and diffusivity near shore and in embayments (Hancock et al., 2006; Liu et al., 2011; Luo et al., 2014; Wang et al., 2015b). Long-lived radium isotopes, ^{226}Ra ($t_{1/2}$ = 1605 yrs) and ^{228}Ra ($t_{1/2}$ = 5.7 yrs), are more frequently used in quantifying the SGD and the water mixing rates in the large scale systems such as continental shelves and open seas (Kim et al., 2005; Kawakami and Kusakabe, 2008; Moore et al., 2008; Su et al., 2013a; Wang et al., 2015a). Besides radium quartet, ^{222}Rn, as a soluble and mobile gas, is also prevailingly used to quantify the SGD (Cable et al., 1996; Burnett and Dulaiova, 2006; Tse and Jiao, 2008) because ^{222}Rn is highly concentrated in groundwater due to continuous alpha recoil supply from its parent ^{226}Ra in the bedrock and aquifer matrix and its conservative behavior (Ku et al., 1992; Luo et al., 2000).

The catchment of Tolo Harbor, with an area of 160 km^2, is bounded by series of mountain blocks. The annual precipitation is 2030 mm. There are six main rivers and streams, namely Lan Tsuen (LT) River, Shan Liu (SL) Stream, Shing Mum (SM) River, Tai Po (TP) River, Tai Po Kau (TPK) Stream and Tung Tze (TT) Stream (Fig. 1a) around the harbor. The total annual runoff is 4.5×10^7 m^3 (Luo et al., 2014). The bedrock within the catchment is mainly formed by middle Jurassic – lower Craterous volcanic rocks. The main faults are trended from southwest to northeast (Fig. 1a). Ruxton (1957) indicates that the superficial materials, including the mantle of the weathering rock, colluviums and alluviums and beach sand, form a shallow unconfined aquifer with a depth around 20 m. Jiao et al. (2006) suggest that there would be a relatively deep confined aquifer beneath the seabed which consists of mud and sandy mud with a clay content of 10–30% (Shaw, 1992).

Tolo harbor, a semi-closed embayment, is located at the northeast of New Territories, Hong Kong. It extends 20 km from southwest to northeast and is connected to Mirs Bay via Tolo Channel with an entrance width less than 1.5 km (Choi and Lee, 2004). It has an area of 52 km^2, a coastal line of 82 km and an average depth of 12 m (Lee et al., 2012; Luo et al., 2014). In the past 30 years, the population along the harbor has increased from 70,000 to 1 million after 2000. A large amount of nutrients are loaded into the harbor from the sources including anthropogenic sewages, atmospheric deposit, sediment release and groundwater discharge (Lee and Arega, 1999; Hu et al., 2001; Wai et al., 2005, 2010; Lee et al., 2012). Semi-closed topography and long water residence time prevent the nutrients to be effectively removed (Choi and Lee, 2004; Luo et al., 2014). Preliminary SGD studies within this district have been conducted since 2005, which reveals that the SGD can derive a large amount of nutrients into the embayment and enhance the primary productivities (Tse and Jiao, 2008; Lee et al., 2012; Luo et al., 2014). High frequency of red tides has been reported since 1980s within the harbor (Hodgkiss and Ho, 1997; Xu et al., 2004b). The increase of N: P ratio in the harbor water is assumed to be the main controlling factor that leads to red tide outbreaks (Hodgkiss and Ho, 1997).

On the basis of data of radium quartet, ^{222}Rn and nutrients in the two sampling years of 2005 and 2011, attempts are made to quantify the SGD with five geotracer-based models: three-end-member model, ^{226}Ra mass balance models, ^{228}Ra mass balance models, ^{222}Rn mass balance models and silica budget model in this study. The SGD derived nutrients are then estimated. With a wide range of climatological, geochemical data and red tide record from 2000 to 2013 within the catchment, attempts are also made to explore the relation of the red tide occurrences to climatologically driven SGD variability.

2. Materials and methods

2.1. Field works and analysis

Field works were mostly conducted in 2005 and 2011. For radium was extracted from 25 to 50 L of seawater, 10 L of river water and 2–5 L of well water within MnO_2 fibers (Moore, 1976). Radium particulate desorption experiments were also done for river samples as described by Moore and Scott (1986). ^{222}Rn samples in seawater were measured by RAD7 Big Bottle System as described by Lee and Kim (2006), and in groundwater was measured with RAD H_2O (Durridge Co.). Nutrient samples were taken with 50 ml bottles (Nalgene, Co.) and stored in a freezer under −4 °C till the measurements. Salinity and temperature were measured in situ with a TLC meter (Solinst, Co.)

^{223}Ra and ^{224}Ra were measured with Radium Delayed Coincidence Counting (RaDeCC) as described by Moore and Arnold (1996). The detecting uncertainty is 7–15% for ^{224}Ra and 12–20% for ^{223}Ra (Moore and Arnold, 1996; Garcia-Solsona et al., 2008; Moore, 2008; Luo et al., 2014). ^{226}Ra were measured with RAD7 after the nuclide in secular equilibrium with ^{222}Rn (Kim et al., 2001; Lee et al., 2012). ^{228}Ra was measured with RaDeCC via measuring ^{228}Th ingrown from ^{228}Ra and calculating the initial ^{228}Ra (Moore, 2008; Kiro et al., 2013; Charette et al., 2015). The detection uncertainty for ^{226}Ra and ^{228}Ra is 10–20% and 7–15%, respectively. Dissolved inorganic nitrogen (DIN, the sum of NO_3^-, NO_2^- and NH_4^+), dissolved inorganic phosphorous (DIP), and dissolved inorganic silicate as $Si(OH)_4$ were detected with flow injection analysis (FIA) equipped with auto-sampler (QuickChem® 3000) in the School of Biological Sciences of the University of Hong Kong (Kim et al., 2011; Luo et al., 2014).

2.2. Time series data

Various marine chemical, climatological and red tide outbreak record datasets from 2000 to 2013 are collected from several departments of the Hong Kong Government. The nutrient data were collected from 9 marine stations including TM2 to TM7 in the harbor and MM6 and MM17 in the open sea and 6 river stations from 2000 to 2013 established by Environmental Protection Department (EPD), Hong Kong. Surface runoff dataset were also collected from riverine monitoring stations by EPD. Climatological data including rainfall, evapotranspiration (ET), tidal range, mean sea level (MSL) were collected from Hong Kong Observatory (HKO). Generally, daily rainfall data are collected from 6 auto-recorded weather stations installed within the Tolo Harbor control zone catchment as shown in Fig. 1a. Daily ET data were collected from the station installed at King's Park (22°18′43″, 114°10′22″), which is about 10 km from Tolo Harbor. Daily tidal range data and mean sea level (MSL) were collected from the tidal gauge station installed at Tai Po Kau (22°26′33″, 114°11′2″) by HKO as shown in Fig. 1a. All the daily data are yearly bin-averaged for the convenience of discussion. Red tide outbreak data were collected from Agriculture, Fisheries and Conservation Department (AFCD), Hong Kong. Red tide occurrences and types were yearly binned for discussion convenience.

3. Results

3.1. Radium quartet results

The results of radium quartet, in different water end members are listed in Tables S1-S3. The activities of radium quartet in the seawater of Tolo Harbor are within the range of radium activities in