

The HKU Scholars Hub

The University of Hong Kong



Title	Estimation of submarine groundwater discharge in Plover Cove, Tolo Harbour, Hong Kong by 222Rn
Author(s)	Tse, KC; Jiao, JJ
Citation	Marine Chemistry, 2008, v. 111 n. 3-4, p. 160-170
Issued Date	2008
URL	http://hdl.handle.net/10722/58646
Rights	Marine Chemistry. Copyright © Elsevier BV.

1	Estimation of submarine groundwater discharge in Plover
2	Cove, Tolo Harbour, Hong Kong by ²²² Rn
3	
4	Kiu Chung Tse, Jiu Jimmy Jiao*
5	Department of Earth Sciences, the University of Hong Kong,
6	Hong Kong Special Administrative Region, China
7	
8	*Corresponding author
9	
10	

11 Abstract

12 Algal blooms in Tolo Harbour, Hong Kong have received much attention and submarine groundwater discharge is speculated to be a significant pathway carrying 13 nutrients into the constricted estuary. Plover Cove, a small cove in the Harbour, was 14 selected for SGD analysis using ²²²Rn budget. The volumetric SGD rates are estimated to 15 be about 8,000 m³/day for neap tide and about 17,000 m³/day for spring tide. Result of 16 17 nutrient analysis of the porewater indicates that the nutrient loading through this pathway 18 is speculated to be crucial for eutrophication in Tolo Harbour. Current practice for the 19 management of algal blooms in Hong Kong, in which nutrient loading through SGD was 20 ignored, has to be reviewed and the control measures of groundwater contamination are 21 obviously required.

22

Index terms: Geochemical tracers; Groundwater hydrology; Groundwater transport;
Hydrological cycles and budgets; Pollution: urban, regional and global.

26 Introduction

25

27 Tolo Harbour is located in the northeastern part of Hong Kong's New Territories 28 (Figure 1). It is susceptible to pollution because of the bottlenecked coastline 29 configuration as well as the prevailing northeasterly wind direction (Yin, 2003). Current 30 is low for the harbour and the estimated water residence times in the inner harbour range 31 from 16-42 days (Hodgkiss and Yim, 1995). All these factors result in preventing the 32 pollutants to be removed effectively. While the harbour is already under stress due to 33 natural factors, urban development since 1970s has further deteriorated the water quality. Dramatic expansion of human population, from 70 000 in 1973 to 1 000 000 in 1990, has 34 35 degraded the environment.

As a consequence, algal bloom incidents increased from 1 per year in 1978 to over 40 in 1988 (Holmes, 1988; Environmental Protection Department (EPD), 2004). Holmes (1988) has attributed the environmental degradation to reduction of the mangrove coastline through the process of land reclamation. The mangrove coastline serves as an effective sink for nutrients, so the loss of this natural resource shifts the primary biological productivity to planktonic algae.

In order to alleviate the pollutant loading on Tolo Harbour, the government has 42 43 enforced the Tolo Harbour Action Plan in 1988 which included livestock waste control, 44 sewage treatment modification, effluent export scheme, legistration enforcement and 45 landfill restoration. An ecosystem model, which was developed for the Hong Kong 46 government, claimed that the concentrations of ammonia and nitrate could drop to zero 47 after the Action Plan was implemented (Holmes, 1988). After the action plan has been 48 implemented, the number of algal bloom incidents has been decreased to ~10 incidents 49 per year. The total phytoplankton densities, however, were still 2-6 times higher at

2

50 stations in Tolo Harbour and Channel than those in other water control zones over Hong 51 Kong (EPD, 2004). Xu et al. (2004) showed that the loadings of total phosphorus and 52 total nitrogen in Tolo Harbour even reached another peaks in 1996 and 1998 respectively. 53 It is speculated that the phytoplankton may be sustained by nutrients from other sources.

54 Hodgkiss and Ho (1997) suggested that implementation of the Tolo Harbour Action 55 Plan resulted in a lower N:P ratio which led to a shift in algal species compostion from 56 diatoms to dinoflagellates and the dominance of dinoflagellates was the major cause of 57 the dramatic increase in red tide occurrence. This replacement of algal species was neither 58 found by Yung et al. (1997) nor supported by the long-term monitoring by EPD. Hu et al. 59 (2001) conducted a sediment diffusion experiment by placing undisturbed sediment core 60 into a settling column in laboratory and adding water sample collected from 61 corresponding site. They demonstrated that sediments can release 0.5 mmol of 62 orthophosphate phosphorus and 2.2 mmol of nitrate-nitrite nitrogen per square metre per 63 day.

Recently research in other coastal areas indicates that the direct discharge of groundwater into the coastal zone may be a potentially significant pathway of dissolved nutrients into the coastal environment (Laroche et al., 1997; Griggs et al., 2003; Miller and Ullman, 2004). Terrestrial groundwater can discharge into the sea directly in response to the hydraulic gradient, with groundwater head higher than sea level (Johannes, 1980). Li and Jiao (2002) proposed a tide-induced seawater-groundwater circulation that SGD happens even in the absence of net inland recharge of groundwater.

71 It is speculated that eutrophication in Tolo Harbour may be attributed to the nutrient 72 fluxes through the pathway of submarine groundwater discharge (SGD). Tolo Harbour is 73 enclosed by such a large catchment that the amount of SGD is believed to be comparable 74 to the river water flux. This study focused on Plover Cove that has no major river system. Plover Cove is adjacent to a mountain range including Wong Leng (639 m) and Pat Sin Leng (500-600 m), with a surface area of around 4 km² (Figure 1). Radium study was conducted for Tolo Harbour (Tse, 2006) and based on this radium study, Plover Cove is identified as a key area in Tolo Harbour receiving potentially significant amount of SGD and details of the radium study can be found in Tse (2006). The current paper focuses on radon study and the SGD flux was estimated by ²²²Rn following the approach described by Burnett and Dulaiova (2003).

82 Background of the Site

The overall surface area for Tolo Harbour is 52 km^2 including the part of Tolo Channel. In the inner harbour the water depth is less than 10m, while along the channel the average depth is about 12 m. The mean sea level is 1.15 m above Principal Datum (mPD), with average diurnal tidal range of 0.97 m (EPD, 1994). There are several rivers entering Tolo Harbour and according to the monitoring data between 1998 and 2004 from EPD, the total annual discharge rate is $3.61 \times 10^{10} \text{ m}^3/\text{yr}$. The mean annual rainfall is 2214 mm.

Tolo Harbour is enclosed by a large catchment with an area of 50 km². The catchment is formed by three main mountainous blocks divided by the new towns Tai Po and Sha Tin. The geology was described in detail by Tam (1980), Addison (1986) and Lai et al. (1996). The district is formed mainly of Mesozoic stratified pyroclastic rocks sandwiched between the Mesozoic sedimentary rocks, with sandstone, siltstone and conglomerate above and marine mudstone and siltstone below.

The volcanic rocks are intruded by a complex granitic pluton at the age of Late Jurassic to Early Cretaceous, which crops out at the low-lying areas. A series of faults trending northeast and northwest was generated and one of the biggest faults is the Lai 99 Chi Kok – Tolo Channel Fault which belongs to a fault zone extending across Sha Tin
100 Valley to Tolo Channel.

101 The superficial soils, including the mantle of weathered rock, colluvium, alluvium and 102 beach sand are considered as shallow unconfined aquifer, which can be over 20 m thick 103 (Ruxton and Berry, 1957). The sandy deposit is subsequently replaced by silt or marine 104 mud in the estuary which serves as an extensive layer of aquitard. There are successive 105 layers of marine and alluvial deposits underlain the Holocene marine mud, which 106 indicates that channelized sand bodies can be found offshore as confined aquifers. These 107 channels are potentially fresh if they are hydraulically connected with the recharge area 108 onshore.

109 The bedrock, according to the degree of decomposition, varies from fresh rock to 110 residual soil. Fracture zones exist along the rockhead below the decomposed rock which 111 form a relatively deep confined aquifer (Jiao et al., 2005; Jiao et al., 2006).

112 Grant (1989) investigated the permeability in Lam Tsuen and Tolo Harbour Areas and 113 in his study, the permeabilities of alluvial plain and terrace lands are 1.17×10^{-4} m/s and 114 2.17 x 10⁻⁴ m/s respectively.

115

116 Methodology

The SGD flux was estimated by ²²²Rn following the approach described by Burnett and Dulaiova (2003). In general, ²²²Rn concentration in the system is influenced by various sources and sinks, such as ingrowth from ²²⁶Ra dissolved in the water, tidal effect, atmospheric loss, diffusion from sediments, mixing loss to the open sea and SGD (Figure 2). An increase or decrease of ²²²Rn concentration over a time interval is referred to the net balance between these sources and sinks during that period. ²²²Rn concentrations in coastal waters are measured continuously to determine the difference between two successive measurements. This is then corrected for all other sources and sinks to obtain the ²²²Rn flux attributed to SGD. With this flux divided by ²²²Rn concentration in fresh groundwater or porewater, the SGD flux is computed.

127
$$F_{SGD} = F_t - F_{sed} - F_o + F_{atm} + F_i + F_m$$
(1)

128 where F_{SGD} is the ²²²Rn flux attributed to SGD

129 F_t is the difference in concentrations of excess ²²²Rn between two successive 130 hours

- 131 F_{sed} is the flux diffused from sediments
- 132 F_o is the flux leaving with the outgoing tide
- 133 F_{atm} is the flux into the atmosphere
- 134 F_i is the flux entering with the incoming tide
- 135 F_m is the flux out of the system by mixing

A site in Plover Cove was selected for ²²²Rn analysis in July 2005. ²²²Rn in coastal 136 137 waters was monitored continuously by a commercially available radon-in-air monitoring 138 system called RAD7 produced by Durridge Co., Inc. for four days, with 48 hours during 139 the neap tide (14-16 July) and 48 hours during the spring tide (21-23 July). In the 140 meantime, water depth was estimated from the iron framework where a height indicator 141 was made. Water samples were collected bihourly for ²²⁶Ra analysis. Sediments were collected from the sea bottom to estimate ²²²Rn in porewater. Wind speed, salinity, air and 142 water temperatures were measured manually every 10 minutes. At the same time, a 143 144 continuous heat-type automated seepage meter (Taniguchi and Iwakawa, 2001) was also deployed for direct SGD measurement. It was pushed into the sea bottom and 145 programmed to take readings every 6 s. During the sampling period, monitoring of ²²²Rn 146 in coastal waters was suspended twice: from 00:23, July 16 onwards to measure ²²²Rn in 147 ambient air, and from 05:00, July 22 onwards because of a storm. ²²²Rn in groundwater 148

from two private wells (Po Sum Pai and Chim Uk) was collected and measured in March
2006. Po Sum Pai private well is situated on Quaternary deposits of volcanic rocks with a
depth of 2.7 m, while Chim Uk private well is situated on granitic rocks with a depth of
3.3 m.

153 Continuous Monitoring of ²²²Rn

In order to monitor ²²²Rn in coastal waters continuously, an iron framework was 154 placed on the sea bottom on which the submersible pump was fastened so that it was 155 156 fixed at 0.5 m above the sea bottom. Seawater was pumped out and filtered through a 1 157 um cartridge filter to screen out the particulates. It was then sparged into an air-water 158 exchanger where radon was distributed from the running flow of water to a closed air 159 loop until the two phases reached equilibrium. The air stream was then fed to the RAD7 for measurement, which was converted to ²²²Rn in the water by the following equation 160 161 (Durridge Co., Inc., 2001),

162

163

$$\alpha = 0.105 + 0.405e^{-0.0502T} \tag{2}$$

164

165 where α is the partition coefficient (concentration ratio of water to air)

166 T is the water temperature in °C, which was measured by a temperature probe 167 inserted into the air-water exchanger

168 The RAD7 was programmed to integrate counts every hour.

169 ²²⁶Ra analysis

170 The water from the air-water exchanger was fed into a 50 L water tank for radium 171 extraction. After 50 L of the water had been collected, it was forced to flow through 30 g 172 of Mn-fiber described by Moore (1976) to extract the radionuclide. The flow rate was 173 controlled below 1 L/min so that sufficient time was allowed for the adsorption. In the 174 laboratory, ²²⁶Ra was extracted from the Mn-fiber by refluxing with HCl, and the filtrate was co-precipitated with 10 mL of saturated $Ba(NO_3)_2$ and 25 mL of 7 M H₂SO₄. The precipitate [Ba(Ra)SO₄]] was then filtered out by 0.45 µm glass-fiber filter and washed with 3 M HCl and water to remove the Mn remains. Finally the precipitant was air-dried, stored in a small vial for 3-4 weeks for equilibrium, and measured by gamma ray spectrometer (Rutgers van der Loeff and Moore,1999).

180 **Determination of ²²²Rn in Groundwater**

Groundwater samples were pumped out from two private wells (Figure 1) and collected in 250 mL collection vials. As radon in groundwater can be quickly distributed into air, narrow tubing was attached to the pump and inserted into the bottom of the collection vial which was placed inside a 1 L plastic beaker. The vial was filled from bottom with fresh sample until the water overflowed into the beaker and the water in the beaker rose well above the vial. In this way, the vial was flushed with fresh sample without exposure to air and it was capped while still under the water.

The samples were then measured by RAD7 with the RAD-H₂O accessory. RAD-H₂O aerates the sample for 5 minutes to deliver 222 Rn to the RAD7. The system will wait a further 5 minutes for the equilibrium between 222 Rn and 218 Po. The air stream is then measured by RAD7 in 4 runs of five-minute period and the result is given as the average of the 4 runs.

193 **Determination of ²²²Rn in Porewater**

194 Concentration of ²²²Rn in porewater was determined by sediment equilibration 195 experiment which was described by Corbett et al. (1998). Sediments from the sea bottom 196 and seawater were collected for the experiment. In the laboratory, 85 g sediments were 197 mixed with 300 mL seawater in a 500-mL Erlenmeyer flask. The flask was sealed and 198 agitated for 1 month until ²²²Rn in head space, water and sediments reach equilibrium. 199 The water was then pumped out and transferred into a 40 mL collection vial, with the special sampling technique employed to prevent air contact. The sample was then
measured by RAD7 with the RAD-H₂O accessory.

202 **Determination of Nutrients in Porewater**

Wet sediment at a depth of 0.5 m was collected along the foreshore during lowest tide. It was immediately brought to the laboratory where the porewater was separated from the sediment by centrifuge. Nutrients in porewater (NO₂-N, NO₃-N, NH₃-N, PO₄-P and silica) were then analyzed by a spectrophotometer.

207

208 Result and Discussion

The results of the continuous ²²²Rn measurements in the water column, together with 209 210 the observed water depth, during the neap and spring tides are shown in Figures 3 and 4, respectively. The concentrations of ²²²Rn were high during low tide, and low during high 211 tide, which fluctuated between 110 and 688 Bq/m³ with an average of 222 Bq/m³. Tidal 212 period cyclicity of the ²²²Rn data was generally accepted to reflect dilution of offshore 213 214 waters at flood tide, mixing offshore and most importantly, SGD variation (Kim and 215 Hwang, 2002; Burnett and Dulaiova, 2003; Lambert and Burnett, 2003). At low tide, 216 recirculated seawater drains out due to tidal pumping. Simultaneously the hydrostatic 217 pressure is lowered and the hydraulic gradient between seawater and groundwater is 218 increased, which contributes to a larger SGD flux. At high tide, recirculated seawater 219 seeps into the seabed sediments due to tidal pumping. Simultaneously the hydrostatic 220 pressure is increased and the hydraulic gradient between seawater and groundwater is 221 decreased, which contributes to a smaller SGD flux.

222 Tidal Effects

In order to account for the dilution effect during flood tide, Lambert and Burnett (2003) introduced the concept of excess ²²²Rn inventory to eliminate the effect. Excess

²²²Rn inventory is defined as the product of excess ²²²Rn in water (Concentration of ²²²Rn – Concentration of ²²⁶Ra) and the water depth (*h*). During flood tide, a larger *h* is multiplied so that the dilution effect can be compensated. Apart from that, ²²⁶Ra which is about 6 Bq/m³ was also subtracted from ²²²Rn in excess ²²²Rn inventory so that the radon supported by ²²⁶Ra was also corrected.

Excess ²²²Rn inventory can actually be interpreted as the excess ²²²Rn in a water 230 column within an area of 1 m^2 . From this definition, it is deduced that inventory is still 231 subject to changes in tidal height: ²²²Rn is removed from the water column with the 232 outgoing waters on the ebb tide (F_0) while extra ²²²Rn is added to the water column with 233 234 the incoming waters on the flood tide (F_i). Correction is required to remove this tidal effect. The excess ²²²Rn inventory is corrected by an addition of the removed ²²²Rn 235 inventory (Δh x concentration of ²²²Rn in the study domain) at low tide or a subtraction of 236 the extra ²²²Rn inventory (Δh x concentration of ²²²Rn in offshore waters) at high tide, 237 238 where Δh is the difference between the two successive tidal heights.

239 Atmospheric Loss

²²²Rn is slightly soluble gas in water, exchange across the air-water interface is
 possible if ²²²Rn in the two phases are in disequilibrium. At equilibrium,

242 243

$$C_w = \alpha C_a \tag{3}$$

244

245 where C_w is the concentration of ²²²Rn in water

- 246 C_a is the concentration of ²²²Rn in air
- 247 α is the partition coefficient

248 When $C_w > \alpha C_a$, ²²²Rn will diffuse across the air-water interface and according to 249 MacIntyre et al. (1995), the diffusive flux is,

250

$$F_{atm} = k(C_w - \alpha C_a) \tag{4}$$

252

251

253 where F_{atm} is the diffusive flux across the air-water interface

254

k is the gas transfer velocity

255 Considerable effort has gone into determining empirical relationship between the gas 256 transfer velocity and wind speed, which was based on five experiments on lakes with 257 deliberate tracers SF_6 (MacIntyre et al., 1995; Lambert and Burnett, 2003),

258

259
$$k_{600} = \begin{cases} 0.45\mu^{1.6}(\frac{Sc}{600})^{-0.5} & \text{for } \mu > 3.6 \ m/s \\ 0.45\mu^{1.6}(\frac{Sc}{600})^{-0.6667} & \text{for } \mu \le 3.6 \ m/s \end{cases}$$
(5)

260

261 where μ is the measured wind speed (m/s)

262 *Sc* is the Schimidt number

263 k_{600} is the gas transfer velocity normalized to the Schimidt number of CO₂ at 20 264 °C in freshwater (cm/hr)

At wind speeds of less than 1.5 m/s, the value for k is assumed to be 0.91 cm/hr (Lambert and Burnett, 2003). This value is calculated based on the k value for CH₄ (0.75

 267 ± 0.54 cm/hr) measured by Happell et al. (1995) at zero wind speed.

The Schmidt number for ²²²Rn in seawater is given by Pilson (1998) as a function of the water temperature.

Five measurements were made from 23:40, July 15 to the end of neap tide period for ²²²Rn in air and the average (30 Bq/m³) is used for calculation (Table 1). Figures 5 and 6 show the temporal variations of wind speed and the diffusive flux of ²²²Rn across the airwater interface during the two sampling periods.

Diffusive Flux from Seabed Sediments

275	Similar to the air-water interface, exchange across the sediment-water interface is			
276	possible if concentration of ²²² Rn in porewater is greater than that in the overlying water			
277	The diffusive flux across the sediment-water interface is given by Martens et al. (1980),			
278 279	$F_{sed} = (\lambda D_s)^{0.5} (C_{eq} - C_o) $ (6)			
280 281	where F_{sed} is the diffusive flux across the sediment-water interface			
282	λ is the decay constant of ²²² Rn, which is 0.181 day ⁻¹			
283	D_s is the effective wet bulk sediment diffusion coefficient			
284	C_{eq} is the concentration of ²²² Rn in porewater			
285	C_o is the concentration of ²²² Rn in the overlying water			
286	Ullman and Aller (1981) pointed out that the effective wet bulk sediment diffusion			
287	coefficient is approximately equal to the product of porosity and the molecular diffusivit			
288	coefficient of ²²² Rn. Molecular diffusivity coefficient was described by Peng et al. (1974			
289	as a function of temperature,			
290				
291	$D_o = 10^{-\left\lfloor \left(\frac{980}{T+273}\right) + 1.59 \right\rfloor} $ (7)			
292 293	where D_o is the molecular diffusivity coefficient			
294	T is the temperature in $^{\circ}C$			
295	Particle size analysis classified the seabed sediments as loose uniform sand. The			
296	porosity estimated from soil analysis is around 0.41.			
297	Concentration of ²²² Rn in porewater was determined by sediment equilibration			
298	experiment. From the experiment, the activity of ²²² Rn released from the wet sediments is			

299 0.6 Bq/kg. Concentration of ²²²Rn in porewater is calculated by,

300

301
$$C_{eq} = \frac{{}^{222}\text{Rn released from the wet sediment} \times \rho_{wet}}{n}$$
(8)

302 where n is the porosity (0.41)

303 ρ_{wet} is the wet bulk density, which is measured as 2086 kg/m³, which is based on 304 excavation method and sand displacement test.

From the sediment equilibration experiment, concentration of 222 Rn in porewater is estimated to be 3052 Bq/m³. Concentration of 222 Rn in overlying water was monitored continuously during the two sampling periods. The diffusive flux of 222 Rn across the sediment-water interface is calculated to be 0.4 Bq/m²·hr, which is insignificant in comparison to the total flux.

310 Mixing Loss

Figures 7 and 8 show the net ²²²Rn flux after correcting for atmospheric loss and sediment diffusion, which should be a balance between supply from SGD and mixing loss to the open sea. Burnett and Dulaiova (2003) and Lambert and Burnett (2003) chose the negative net ²²²Rn fluxes as conservative estimates of the mixing loss. Indeed a larger mixing loss is possible to be balanced by a larger supply from SGD, but the conservative estimates of the mixing loss provide a good guess for the minimum SGD flux. It is represented by the dashes line shown in Figures 7 and 8.

The estimated mixing losses are between 29.4 to 89.0 $Bq/m^2 \cdot hr$ during neap tide and between 64.0 to 125.0 $Bq/m^2 \cdot hr$ during spring tide.

320 SGD Flux

As mentioned, the net ²²²Rn flux is a balance between supply from SGD and mixing loss to the open sea. After correcting for mixing loss, the ²²²Rn flux is solely attributed to SGD. The average ²²²Rn flux solely attributed to SGD is 52.8 Bq/m²·h r, which is about 130 times larger than the flux diffused from sediment. Although Hu et al. (2001) and Xu et al. (2004) suggested that significant amount of nutrients was diffused from seabed
sediments and supplied to the phytoplankton in Tolo Harbour, nutrients discharged with
SGD are conceived to be much more significant than diffusion from sediment in Plover
Cove.

In order to convert ²²²Rn fluxes to SGD fluxes, the ²²²Rn fluxes solely attributed to 329 SGD have to be divided by the concentration of ²²²Rn in the SGD fluid. Determination of 330 the SGD fluid requires an understanding of the discharge characteristic: If slow seepage 331 through sediment is dominant, ²²²Rn in porewater will be a good guess of that in SGD; 332 otherwise ²²²Rn in groundwater will be more representative if fast groundwater flow is 333 dominant. ²²²Rn in porewater was determined by sediment equilibration experiment to be 334 3052 Bq/m³. Groundwater was collected from two private wells near Plover Cove, the 335 concentrations of ²²²Rn are 6858 Bq/m³ (n = 28; σ = 3728) for Po Sum Pai private well 336 337 and 16790 Bq/m³ (n = 5; σ = 4188) for Chim Uk private well.

The SGD fluxes are plotted on Figures 9 and 10 and summarized in Table 2. The inverse relationship between tidal height and SGD is verified. Precisely the peaks of SGD coincide with the transitions from flood tide to ebb tide. With porewater being selected to represent the SGD fluid, the mean SGD fluxes are 30.3 and 63.0 cm/day for neap and spring tides respectively. The mean SGD fluxes are 7.8 and 16.3 cm/day for neap and spring tides with groundwater from the two wells averaged to represent the SGD fluid.

The SGD fluxes based on terrestrial groundwater are chosen for calculating the nutrient loading to Plover Cove through SGD so as to obtain the most conservative estimates of SGD and the corresponding nutrient loading to Plover Cove. These values are also comparable to the mean SGD fluxes measured directly by seepage meter, which are 8.0 and 9.3 cm/day for neap and spring tides respectively. The width of the seepage face is difficult to estimate. During the field studies, neap tide, the exposed sandy beach face during neap tide is about 30 m from the high water mark. In the following calculation, it is assumed that the width of the seepage face is 30 m. With the length of the shoreline approximately about 3.5 km, the amount of SGD should be around 8,000 m³/day for neap tide and 17,000 m³/day for spring tide. Result in nutrient analysis and nutrient loading to Plover Cove through SGD are given in Table 3.

355 **Conclusion**

Within Tolo Harbour, Plover Cove has been selected for SGD study. SGD flux has been estimated via continuous ²²²Rn measurements and seepage meter. ²²²Rn flux attributed to SGD has been obtained after correcting for tidal effect, atmospheric loss, sediment diffusion and mixing loss to the open sea. With terrestrial groundwater being selected, the amount of SGD is 8,000 m³/day during neap tide and 17,000 m³/day during spring tide. It has to point out that the estimated SGD include both components of terrestrial groundwater discharge as well as recirculated seawater.

363 Management of algal blooms has emphasized on external nutrient loading from rivers. 364 Even most of the nutrient loading from rivers has been removed through the Tolo 365 Harbour Action Plan, the total phytoplankton densities are still the highest among Hong 366 Kong waters. In this study, nutrients discharged with SGD are conceived to be much 367 more significant than all the other pathways in Plover Cove. Taking the width of the 368 seepage area to be 30 m, nutrient loading on Plover Cove through SGD during neap tide 369 and spring tide are: Total inorganic nitrogen 1,241 and 2,599 mol/day; Orthophosphate 370 phosphorus 27.8 and 58.2 mol/day; Silica 185.9 and 388.5 mol/day. In terms of nutrient 371 loadings per unit area, the amount of nitrate-nitrite nitrogen loading through SGD is about 372 twice of that released from sediment diffusion obtained by Hu et al. (2001). 373 Transformation along the groundwater flow path in the sediments may attenuate nutrient

15

composition in the SGD fluid but still, based on the result from this study, the current
practice for the management of algal blooms in Tolo Harbour has to be reviewed and the
control measures of groundwater contamination are obviously required.

377

378 Acknowledgments

This study was partially supported by a grant from the Research Grants Council of Hong Kong (HKU 7028/06P) and the Seed Funding within the Faculty of Science in The University of Hong Kong. The authors wish to thank staff from Department of Physics, HKU who helped in ²²⁶Ra measurement, staff from Department of Civil Engineering, HKU who helped in the nutrients analysis. The authors also appreciate students who assisted in the boat trips in the Tolo Harbour.

References

Addison, R. (1986), *Geology of Sha Tin: 1:20000 sheet 7*, Geotechnical Control Office, Civil Engineering Services Department, Hong Kong.

Braja, M. D. (1999), Principles of foundation engineering, PWS Pub, Pacific Grove.

- Burnett, W. C., and H. Dulaiova (2003), Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements, *Journal of Environmental Radioactivity*, 69, 21-35.
- Church, T. M. (1996), An underground route for the water cycle, Nature, 380, 579-580.
- Corbett, D. R., W. C. Burnett, P. H. Cable, and S. B. Clark (1998), A multiple approach to the determination of radon fluxes from sediments, *Journal of Radioanalytical and Nuclear Chemistry*, 236(1-2), 247-252.

Durridge Co., Inc. (2001), Manual for RAD AQUA, Durridge Company.

- Dzhamalov, R. G. (1996), A conceptual model of subsurface water exchange between the continent and the sea, *Water Resources*, 23(2), 124-128.
- Environmental Protection Department (1994), *Marine Water Quality in Hong Kong in* 1994, Environmental Protection Department, Hong Kong.
- Environmental Protection Department (2004), *Marine Water Quality in Hong Kong in 2004*, Environmental Protection Department, Hong Kong
- Gallardo, A., and A. Marui (2006), Submarine groundwater discharge: an outlook of recent advances and current knowledge, *Geo-marine letters*, *26*, 102-113.
- Geotechnical Control Office, Civil Engineering Services Department (1987), *Central New Territories*, Government Printer, Hong Kong.
- Geotechnical Control Office, Civil Engineering Services Department (1988), North New Territories, Government Printer, Hong Kong.

- Grant, C. J. (1989), *Permeability study Lam Tsuen and Tolo Harbour Areas*, Environmental Protection Department, Hong Kong Government.
- Griggs, E. M., L. R. Kump, and J. K. Bohlke (2003), The fate of wastewater-derived nitrate in the subsurface of the Florida Keys: Key Colony Beach, Florida, *Estuarine*, *Coastal & Shelf Science*, 58, 517-539.
- Happell, J. D., J. P. Chanton, and W. J. Showers (1995), Methane transfer across the airwater interface in stagnant wooded swamps of Florida: Evaluation of mass-transfer coefficients and isotopic fractionation, *Limnology and Oceanography*, 40(2), 290-298.
- Hodgkiss, I. J., and B. S. S. Chan (1986), Studies on four streams entering Tolo Harbour,
 Hong Kong in relation to their impact on marine water quality, *Archiv für Hydrobiologie*, 108(2), 185-212.
- Hodgkiss, I. J., and K. C. Ho (1997), Are changes in N:P ratios in coastal waters the key to increased red tide blooms?, in *Asia-Pacific Conference on Science and Management of Coastal Environment*, edited by Y. S. Wong and Y. T. Fung, pp. 141-147, Kluwer Academic Publishers, Belgium.
- Hodgkiss, I. J., and W. W. S. Yim (1995), A case study of Tolo Harbour, Hong Kong, in *Eutrophic shallow estuaries and lagoons*, edited by A. J. McComb, pp. 41-57, CRC Press, Inc.
- Holmes, P. R. (1988), Tolo Harbour the case for integrated water quality management in a coastal environment, *Journal of Institution of Water and Environmental Management*, 2, 171-179.
- Hu, W. F., W. Lo, H. Chua, S. N. Sin, and P. H. F. Yu (2001), Nutrient release and sediment oxygen demand in a eutrophic land-locked embayment in Hong Kong, *Environmental International*, 26, 369-375.

- Jiao, J. J., X. S. Wang, and S. Nandy (2005), Confined groundwater zone and slope instability in weathered igneous rocks in Hong Kong, *Engineering Geology*, 80, 71-92.
- Jiao, J. J., X. S. Wang, and S. Nandy (2006), Preliminary assessment of the impacts of deep foundations and land reclamation on groundwater flow in a coastal area in Hong Kong, China, *Hydrogeology Journal*, 14, 100-114.
- Johannes, R. E. (1980), The ecological significance of the submarine discharge of groundwater, *Marine Ecology Progress Series*, *3*, 365-373.
- Kohout, F. A. (1966), Submarine springs: a neglected phenomenon of coastal hydrology, *Hydrology*, *26*, 391-413.
- Lai, K. W., S. D. G. Campbell, and R. Shaw (1996), *Geology of the Northeastern New Territories:* 1:20000 sheets 3 & 4, Geotechnical Engineering Office, Civil Engineering Department, Hong Kong.
- Lambert, M. J., and W. C. Burnett (2003), Submarine groundwater discharge estimates at a Florida coastal site based on continuous radon measurements, *Biogeochemistry*, 66, 55-73.
- LaRoche, J., R. Nuzzi, R. Waters, K. Wyman, P. G. Falkowski, and D. W. R. Wallace (1997), Brown tide blooms in Long Island's coastal waters linked to international variability in groundwater flow, *Global Change Biology*, *3*, 397-410.
- Lee, J. H. W., and F. Arega (1999), Eutrophication dynamics of Tolo Harbour, Hong Kong, *Marine Pollution Bulletin*, 39(1-12), 187-192.
- Lee, K. M., and P. C. C. Ng (1999), A geotechnical investigation of marine deposits in a nearshore seabed for land reclamation, *Canadian Geotechnical Journal*, 36(6), 981-1000.
- Li, H., and J. J. Jiao (2003), Tide-induced seawater–groundwater circulation in a multilayered coastal leaky aquifer system, *Journal of Hydrology*, 274, 211-224.

- MacIntyre, S., R. Wanninkhof, and J. P. Chanton (1995), Trace gas exchange across the air-water interface in freshwater and coastal marine environments, in *Biogenic trace gases: Measuring emission from soil and water*, edited by P. A. Matson and R. C. Harriss, pp. 52-97, Blackwell Science, USA.
- Martens, C. S., G. W. Kipphut, and J. V. Klump (1980), Sediment-water chemical exchange in the coastal zone traced by in situ radon-222 flux measurements, *Science*, 208(4441), 285-288.
- Miller, D. C., and W. J. Ullman (2004), Ecological consequences of ground water discharge to Delaware Bay, United States, *Ground Water*, *42*(7): 959-970.
- Moore, W. S. (1976), Sampling radium-228 in the deep ocean, *Deep-Sea Res.*, 23, 647-651.
- Moore, W. S. (1996), Large groundwater inputs to coastal waters revealed by ²²⁶Ra enrichments, *Nature*, *380*, 612-614.
- Moore, W. S. (1999), The subterranean estuary: a reaction zone of ground water and sea water, *Marine* Chemistry, *65*, 111-125.
- Peng, T. H., T. Takahashi, and W. S. Broecker (1974), Surface radon measurements in the North Pacific station Papa, *Journal of Geophysical Research*, *79*, 1772-1780.
- Pilson, M. E. Q. (1998), An introduction to the chemistry of the sea, Prentice Hall, Upper Saddle River, New Jersey.
- Rutgers van der Loeff, M. M., and W. S. Moore (1999), Determination of natural radioactive tracers, in *Methods of seawater analysis*, edited by K. Grasshoff et al., pp. 365-398. Wiley-VCH, Weinheim, Germany.
- Ruxton, B. P., and L. Berry (1957), *Weathering of granite and associated erosional features in Hong Kong*, Geological Society of America, New York.

- Shum, K. T., and B. Sundby (1996), Organic matter processing in continental shelf sediments the subtidal pump revisited, *Marine Chemistry*, *53*, 81-87.
- Tam, S. W. (1980), *Environmental geological mapping of the Shatin Valley*, Department of Geography, Chinese University of Hong Kong, Hong Kong.
- Taniguchi, M., and H. Iwakawa (2001), Measurements of submarine groundwater discharge rates by a continuous heat-type automated seepage meter in Osaka Bay, Japan, *Journal of Groundwater Hydrology*, 43(4), 271-277.
- Taniguchi, M., W. C. Burnett, J. Christoff, C. F. Smith, R. J. Paulsen, D. O'Rourke, and S. Krupa (2003), Spatial and temporal distributions of submarine groundwater discharge rates obtained from various types of seepage meters at a site in northeastern Gulf of Mexico, *Biogeochemistry*, 66, 35-53.
- Tse, K. C. (2006), Estimation of submarine groundwater discharge into Tolo Harbour,M.Phil. Thesis, 106 pp., The University of Hong Kong, Hong Kong, 31 August.
- Ullman, W., and R. Aller (1981), Diffusion coefficients in nearshore marine sediments, *Limnology and Oceanography*, 27, 552-556.
- Webster, I. T., S. J. Norquay, F. C. Ross, and R. A. Wooding (1996), Solute exchange by convection within estuarine sediments, *Esturaine, Coastal and Shelf Science*, 42, 171-183.
- Whiteside, P. G. D (1984), Pattern of Quaternary sediments revealed during piling works at Sha Tin, Hong Kong, in *Geology of surficial deposits in Hong Kong*, edited by W. W. S. Yim, pp. 153-159, Geological Society of Hong Kong, Hong Kong.
- Xu, F. L., K. C. Lam, R. W. Dawson, S. Tao, and Y. D. Chen (2004), Long-term temporal-spatial dynamics of marine coastal water quality in the Tolo Habor, Hong Kong, China, *Journal of Environmental Sciences*, 16(1), 161-166.

- Yim, W. W. S., and Q. Y. Li (1983), Sea-level changes and sea-floor surficial deposits off
 Chek Lap Kok, in *Geology of Surficial Deposits in Hong Kong: residual soil, colluvium, alluvium and marine deposits: programme, abstracts and excursion guide,*edited by W. W. S. Yim and A. D. Burnett, pp. 48-59, Geological Society of Hong
 Kong, Hong Kong.
- Yin, K. (2003), Influence of monsoons and oceanographic processes on red tides in Hong Kong waters, *Marine Ecology Progress Series*, 262, 27-41.
- Yung, Y. K., C. K. Wong, M. J. Broom, J. A. Ogden, S. C. M. Chan, and Y. Leung (1997), Long-term changes in hydrography, nutrients and phytoplankton in Tolo Harbour, Hong Kong, in *Asia-Pacific Conference on Science and Management of Coastal Environment*, edited by Y. S. Wong and Y. T. Fung, pp. 107-115, Kluwer Academic Publishers, Belgium.

List of Tables

- Table 1 Measurements of 222Rn in ambient air on 16th July 2005
- Table 2 Estimated SGD fluxes
- Table 3 Nutrients in porewater and nutrient loading to Plover Cove through SGD

List of Figures

- Figure 1 Map of Tolo Harbour
- Figure 2 Sources and sinks of 222Rn in coastal waters (modified from Lambert and Burnett, 2003)
- Figure 3 Temporal variation of 222Rn during neap tide
- Figure 4 Temporal variation of 222Rn during spring tide
- Figure 5 Wind speeds and atmospheric losses of 222Rn during neap tide
- Figure 6 Wind speeds and atmospheric losses of 222Rn during spring tide
- Figure 7 Net 222Rn flux during neap tide (The dashed line represents the mixing loss)
- Figure 8 Net 222Rn flux during spring tide (The dashed line represents the mixing loss)
- Figure 9 SGD fluxes during neap tide
- Figure 10 SGD fluxes during spring tide

Tables

Tuble 1 Micubal ements of the mainstene an on 10th bary					
Time	Conc. of 222 Rn (Bq/m ³)				
01:23	47.73				
02:23	14.80				
03:23	29.23				
04:23	18.50				
05:23	37.37				
Average	29.53				

Table 1 Measurements of ²²²Rn in ambient air on 16th July 2005

Table 2Estimated SGD fluxes

During neap tide period

Approach	SGD fluxes	Mean (cm/day)
²²² Rn (SGD fluid represented by)		
• Porewater	0-67.5	30.3
• Groundwater from nearshore wells	0-17.4	7.8
Seepage meter	0.9-40.1	8.0
During spring tide period		
Approach		
²²² Rn (SGD fluid represented by)		
• Porewater	0-236	63.0
• Groundwater from nearshore wells	0-60.8	16.3
Seepage meter	1.0-144	9.3

Table 3 Nutrients in porewater and nutrient loading to Plover Cove through SGD

Nutrients	Concentration (µmol/L)	Nutrient Loading to Plover Cove through SGD (mol/day)	
		Neap Tide	Spring Tide
Nitrite Nitrogen	0.8	6.6	13.7
Nitrate Nitrogen	78.6	643.7	1345.2
Ammonia Nitrogen	72.1	590.5	1234.0
Orthophosphate Phosphorus	3.4	27.8	58.2
Silica	22.7	185.9	388.5

Figures



Figure 1 Map of Tolo Harbour



Figure 2 Sources and sinks of ²²²Rn in coastal waters (modified from Lambert and Burnett 2003)





Figure 4 Temporal variation of ²²²Rn during spring tide







 Time

 Figure 7 Net ²²²Rn flux during neap tide (The dashed line represents the mixing loss)



Time Figure 8 Net ²²²Rn flux during spring tide (The dashed line represents the mixing loss)



Figure 9 SGD fluxes during neap tide



Figure 10 SGD fluxes during spring tide