Supplementary Material

In order to better define the variability of the end-members of the groundwater discharged into the northern South China Sea (NSCS), we adopted the definition of Moore (1999) regarding subterranean estuary (STE), which emphasized that similar to a surface river estuary, the discharge of groundwater is as a matter of fact through a STE before its export to the shelf. This appendix provided additional description for the sampling and distribution of the dissolved constituents in the NSCS STE.

Groundwater Sampling

We sampled coastal groundwater and spring water along the NSCS shelf in December 2008 and October 2010. Groundwater was collected both from water-providing wells and in the intertidal zone as close to the shoreline as possible using Push Point sampler (MHE Products, Inc.). Sampling with a flojet™ pump was not initiated until stable readings of salinity, pH and dissolved oxygen of the groundwater were recorded by a WTW 340i Multi-Parameter Field Meter. The pump rate was maintained between 250-500 mL min⁻¹ to minimize disturbance of the groundwater system. All of the groundwater samples were collected at various depths within the unconfined surficial aquifer.  

Spatial variations of salinity and Ra isotopes in the NSCS subterranean estuary

In 2008, there was no apparent spatial variation for the Ra quartet in fresh groundwater with a mean of 13.6±1.69 dpm 100 L⁻¹ for $^{223}$Ra and a mean of
427±6.58 dpm 100 L\(^{-1}\) for ex\(^{224}\)Ra (Table S1). Saline springs contained very high \(^{223}\)Ra (60.5±15.6 dpm 100 L\(^{-1}\)) and ex\(^{224}\)Ra (1195±35.1 dpm 100 L\(^{-1}\)) compared with fresh groundwater. The activities of the long-lived Ra isotopes in the fresh groundwater (182±21.2 dpm 100 L\(^{-1}\) for \(^{226}\)Ra and 581±31.1 dpm 100 L\(^{-1}\) for \(^{228}\)Ra) and the saline spring (161±21.9 dpm 100 L\(^{-1}\) for \(^{226}\)Ra and 422±31.0 dpm 100 L\(^{-1}\) for \(^{228}\)Ra) were similar (Table S1). Two possible reasons may explain the contrast between fresh and saline groundwater and between the Ra isotopes with different half lives. First, all the Ra isotopes would be desorbed from particles with increasing ionic strength. Second, if the spring was exposed to the seawater long enough for ion exchange process to complete, Ra would be diluted by the low Ra seawater. This removal process can reduce the long-lived Ra but not the short-lived Ra isotopes due to the latter’s fast regeneration rate from the sediments.

In the 2010 sampling, the brackish groundwater had higher short-lived Ra isotopes (512-1718 dpm 100 L\(^{-1}\) for ex\(^{224}\)Ra and 11.0-60.5 dpm 100 L\(^{-1}\) for \(^{223}\)Ra) relative to the fresh groundwater (61.7-897 dpm 100 L\(^{-1}\) for ex\(^{224}\)Ra and 3.63-31.4 dpm 100 L\(^{-1}\) for \(^{223}\)Ra). Long-lived \(^{228}\)Ra in fresh groundwater revealed a broader spatial variation, ranging from 30.2 to 396 dpm 100 L\(^{-1}\), lower by a factor of 3 on average than that in brackish groundwater (in the range from 419 to 872 dpm 100 L\(^{-1}\)) in 2010 (Table S1). Comparing the Ra activities in these two years, saline spring in 2008 had comparable high short-lived Ra with brackish groundwater in 2010. The \(^{223}\)Ra and ex\(^{224}\)Ra in fresh groundwater were close in 2008 and 2010, but with larger spatial variability in 2010 (Table S1). As presented in Table S1 and Fig 6c, both fresh groundwater and
spring collected in 2008 had high $^{228}\text{Ra}$ comparable with that in brackish groundwater sampled in 2010 (with averages of 462 versus 568 dpm 100 L$^{-1}$), which was higher than fresh groundwater in 2010 (averaging 160 dpm 100 L$^{-1}$). The $^{228}\text{Ra}$ and $^{226}\text{Ra}$ activities in groundwater along the NSCS fell into the general range of long-lived Ra in various coastal monitor wells over the continental margins (10-1730 dpm 100 L$^{-1}$ for $^{228}\text{Ra}$ and 20-1740 dpm 100 L$^{-1}$ for $^{226}\text{Ra}$; Moore, 2010).

The $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio (AR) ranged 2.63-7.82 with an average of 4.09 in the groundwater collected in 2008 along the NSCS shelf. The higher $^{228}\text{Ra}$ activity than $^{226}\text{Ra}$ can be explained by different $^{232}\text{Th}/^{238}\text{U}$ ARs in the aquifer in view that $^{232}\text{Th}$ (the parent of $^{228}\text{Ra}$) can be preferentially adsorbed onto sediment than $^{238}\text{U}$ (the parent of $^{226}\text{Ra}$), and as such the sediment is a continuous $^{228}\text{Ra}$ source for the groundwater and spring (Swarzenski et al., 2003). Ra-223 and ex $^{224}\text{Ra}$ in Fig. S1 showed good agreement in the $^{223}\text{Ra}/\text{ex}^{224}\text{Ra}$ AR between the two years, indicating the same $^{235}\text{U}$ (the parent of $^{223}\text{Ra}$)/$^{232}\text{Th}$ (the parent of $^{224}\text{Ra}$) ratio in the aquifers along the shoreline of the NSCS shelf.

### Major ions (Na$^+$, Mg$^{2+}$, and Ca$^{2+}$) in the NSCS subterranean estuary

Sodium and magnesium concentrations (Table S1) correlated linearly with salinity (figures not shown), suggesting that the major ion composition was a result of the mixing of seawater and fresh groundwater. Calcium showed slight addition from the conservative mixing which may be explained by CaCO$_3$ dissolution and/or ion exchange (Appelo, 1994; Harriet et al., 2004).
The fresh groundwater was the major source of DIN (NH$_4^+$ + NO$_3^-$ + NO$_2^-$) and SiO$_4^{4-}$ (DSi) on the NSCS shelf as indicated by their distribution with salinity in both 2008 and 2010 (Table S1 and Fig. S2A to C). NH$_4^+$ concentration varied by three orders of magnitude, from 0.3 to 318 μmol L$^{-1}$, in fresh groundwater (Table S1 and Fig. S2A) with an average of 127 μmol L$^{-1}$. NH$_4^+$ was as high as 573 μmol L$^{-1}$ at salinity ~15.

NO$_3^-$ + NO$_2^-$ was in the range from 87.6 to 1612 μmol L$^{-1}$ in the fresh groundwater (Table S1 and Fig. S2B) and decreased to 5.6 μmol L$^{-1}$ at salinity of 24.3, indicating removal during mixing with seawater. SiO$_4^{4-}$ was in the range from 83.0 to 702 μmol L$^{-1}$ in the fresh groundwater with average 292 μmol L$^{-1}$ and correlated positively with salinity, as found elsewhere such as in the West Neck Bay STE (Beck et al., 2007).

However, PO$_4^{3-}$ concentrations in most of the groundwater were low, averaging 1.0 μmol L$^{-1}$, except three samples with extremely high PO$_4^{3-}$ concentrations of 17.2, 19.8 and 37.4 μmol L$^{-1}$, respectively. Note that, of the three exceptions, one was from a freshwater well, and the other two were brackish groundwater (salinity ~15).

Generally speaking, nitrogen and phosphate concentrations in groundwater are low when derived from natural sources, namely in situ organic matter decay and mineral weathering (Slomp and Van Cappellen, 2004). The large spatial variation of DIN in fresh groundwater suggests multiple N sources. High DIN concentrations might be affected by anthropogenic activity such as fertilizer, manure and sewage, especially aquaculture wastewater (Cao et al., 2007). Excess NH$_4^+$ and PO$_4^{3-}$ but depletion of NO$_3^-$ + NO$_2^-$ during the mixing of seawater and groundwater (salinity ~15) is evidence of the occurrence of denitrification or other organic degradation processes,
as also evidenced by extremely high DIC (7147-8757 μmol L⁻¹) and TAlk (7364-9009 μmol L⁻¹).

CO₂ parameters in the NSCS subterranean estuary

Figure S3 shows the distribution of DIC, TAlk, pH, and partial pressure of CO₂ (pCO₂) versus salinity in the NSCS STE sampled in 2008 and 2010. DIC mostly ranged from 2300 to 6000 μmol L⁻¹ in fresh groundwater, with an average of 4002 μmol L⁻¹ (Fig. S3A). The brackish groundwater had DIC values ranged from 2866 to 8757 μmol L⁻¹, with an average of 5078 μmol L⁻¹, which was higher than that in fresh groundwater (Fig. S3A). TAlk had a distribution pattern similar to DIC, except that it was lower than DIC in fresh groundwater (average of 3301 μmol L⁻¹), but higher in the high salinity zone (average of 6631 μmol L⁻¹; Fig. S3A and B).

Nevertheless, both DIC and TAlk in the groundwater were significantly higher than those in the surface seawaters (DIC:~1909 μmol L⁻¹, TAlk:~2202 μmol L⁻¹), and the overlying river waters (DIC:~1060 μmol L⁻¹, TAlk:~1007 μmol L⁻¹). High concentrations of DIC and TAlk in groundwater but non-carbonate dominant sediments can be explained by strong bacterial activities. Aerobic organic matter decomposition, denitrification, Mn and Fe oxide reduction, sulfate reduction, and methanogenesis would produce ammonia and CO₂ simultaneously (Lovely and Chapelle, 1995; Slomp and Van Cappellen, 2004; Chen et al., 2006). Good positive relationship (R²=0.90, n=9) between NH₄⁺ and DIC in groundwater (Table S1, figure not shown) provided evidence to support it. Another possible reason was that a great
number of liming additions has increased soil alkalinity in order to improve local
soil fertility and structure. The measured pH in the fresh groundwater ranged from
6.19 to 7.35, which was lower than saline groundwater (7.38 to 7.84; Fig. S3C).
Obviously, the STE has lower pH than seawater. Partial CO₂ pressure (pCO₂) in
groundwater was pronouncedly different from the surface waters, ranging from 1030
to 61040 μatm (Fig. S3D), and was 3-150 times higher than the atmospheric CO₂.
The extremely high pCO₂ level has been observed in many groundwater systems,
such as the wetlands and salt marshes in Georgia and South Carolina (Cai et al.,
2003; Moore et al., 2006), the Herbert aquifer in Great Barrier Reef (Gagan et al.,
2002), and the shallow groundwater in Konza Prairie (Macpherson et al., 2008).
References in supplementary material


Table S1. The location, temperature, salinity, major cations, dissolved oxygen (DO), radium activities, CO₂ parameters and nutrient concentrations for subterranean estuaries along the NSCS collected in 2008 and 2010. Sampling sites are shown in Fig 1.

<table>
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<th>Sample</th>
<th>Salinity (℃)</th>
<th>Temp (℃)</th>
<th>Na⁺ (mmol kg⁻¹)</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>DO (dpm 100 L⁻¹)</th>
<th>ex²²⁴Ra⁺</th>
<th>²²⁴Ra (μmol L⁻¹)</th>
<th>²²⁶Ra (μmol L⁻¹)</th>
<th>TAlk (matm)</th>
<th>DIC (μmol L⁻¹)</th>
<th>pCO₂ (μmol L⁻¹)</th>
<th>pH</th>
<th>Nutrient concentration (μmol L⁻¹)</th>
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*ex²²⁴Ra denotes excess ²²⁴Ra, corrected for the ingrowth from ²²⁴Th.

¹ CO₂ was calculated from DIC and TAlk using CO₂SYS.XLS 14th version (HTTP:// www.ecy.wa.gov/programs/eap/models.html).
Figures Captions in Supplementary Material

Fig S1. Correlation between $^{223}$Ra and ex $^{224}$Ra (excess $^{224}$Ra, corrected for the ingrowth from $^{228}$Th) activities in the northern South China Sea subterranean estuary collected in December 2008 and October 2010.

Fig S2. Concentrations of (A) ammonia ($\text{NH}_4^+$), (B) Nitrate and nitrite ($\text{NO}_3^- + \text{NO}_2^-$), (C) dissolved silicate (DSi) and (D) dissolved inorganic phosphate (DIP) plotted versus salinity in the northern South China Sea subterranean estuary both in December 2008 and October 2010.

Fig S3. Concentrations of (A) dissolved inorganic carbon (DIC), (B) total alkalinity (TAlk), (C) pH, (D) partial CO$_2$ pressure ($p$CO$_2$) plotted versus salinity in the northern South China Sea subterranean estuary both in December 2008 and October 2010.
Figure S1

![Graph showing the relationship between $^{224}$Ra and $^{223}$Ra activity levels from October 2008 to October 2010. The graph includes data points for Oct. 2010 and Dec. 2008. The regression line is given by $y = 0.037x - 1.4786$ with $R^2 = 0.9542$.](image_url)
Figure S2

A

B

C

D

Oct.2010
Dec.2008
Figure S3

- **DIC (μmol L$^{-1}$)**
- **TAlk (μmol L$^{-1}$)**
- **pH**
- **pCO$_2$ (μatm)**

Data points are differentiated by year:
- Dec. 2008
- Oct. 2010