

1 **Supplementary Material**

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

8

9 **Groundwater Sampling**

10 We sampled coastal groundwater and spring water along the NSCS shelf in
11 December 2008 and October 2010.

12 Groundwater was collected both from water-providing wells and in the intertidal
13 zone as close to the shoreline as possible using Push Point sampler (MHE Products,
14 Inc.). Sampling with a flojetTM pump was not initiated until stable readings of
15 salinity, pH and dissolved oxygen of the groundwater were recorded by a WTW 340i
16 Multi-Parameter Field Meter. The pump rate was maintained between 250-500 mL
17 min⁻¹ to minimize disturbance of the groundwater system. All of the groundwater
18 samples were collected at various depths within the unconfined surficial aquifer.

19

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

21 In 2008, there was no apparent spatial variation for the Ra quartet in fresh
22 groundwater with a mean of 13.6 ± 1.69 dpm 100 L⁻¹ for ²²³Ra and a mean of

1 427±6.58 dpm 100 L⁻¹ for ex ²²⁴Ra (Table S1). Saline springs contained very high
2 ²²³Ra (60.5±15.6 dpm 100 L⁻¹) and ex ²²⁴Ra (1195±35.1 dpm 100 L⁻¹) compared with
3 fresh groundwater. The activities of the long-lived Ra isotopes in the fresh
4 groundwater (182±21.2 dpm 100 L⁻¹ for ²²⁶Ra and 581±31.1 dpm 100 L⁻¹ for ²²⁸Ra)
5 and the saline spring (161±21.9 dpm 100 L⁻¹ for ²²⁶Ra and 422±31.0 dpm 100 L⁻¹ for
6 ²²⁸Ra) were similar (Table S1). Two possible reasons may explain the contrast
7 between fresh and saline groundwater and between the Ra isotopes with different
8 half lives. First, all the Ra isotopes would be desorbed from particles with increasing
9 ionic strength. Second, if the spring was exposed to the seawater long enough for ion
10 exchange process to complete, Ra would be diluted by the low Ra seawater. This
11 removal process can reduce the long-lived Ra but not the short-lived Ra isotopes due
12 to the latter's fast regeneration rate from the sediments.

13 In the 2010 sampling, the brackish groundwater had higher short-lived Ra isotopes
14 (512-1718 dpm 100 L⁻¹ for ex ²²⁴Ra and 11.0-60.5 dpm 100 L⁻¹ for ²²³Ra) relative to
15 the fresh groundwater (61.7-897 dpm 100 L⁻¹ for ex ²²⁴Ra and 3.63-31.4 dpm 100 L⁻¹
16 for ²²³Ra). Long-lived ²²⁸Ra in fresh groundwater revealed a broader spatial variation,
17 ranging from 30.2 to 396 dpm 100 L⁻¹, lower by a factor of 3 on average than that in
18 brackish groundwater (in the range from 419 to 872 dpm 100 L⁻¹) in 2010 (Table S1).

19 Comparing the Ra activities in these two years, saline spring in 2008 had comparable
20 high short-lived Ra with brackish groundwater in 2010. The ²²³Ra and ex ²²⁴Ra in
21 fresh groundwater were close in 2008 and 2010, but with larger spatial variability in
22 2010 (Table S1). As presented in Table S1 and Fig 6c, both fresh groundwater and

1 spring collected in 2008 had high ^{228}Ra comparable with that in brackish groundwater
2 sampled in 2010 (with averages of 462 versus 568 dpm 100 L⁻¹), which was higher
3 than fresh groundwater in 2010 (averaging 160 dpm 100 L⁻¹). The ^{228}Ra and ^{226}Ra
4 activities in groundwater along the NSCS fell into the general range of long-lived Ra
5 in various coastal monitor wells over the continental margins (10-1730 dpm 100 L⁻¹
6 for ^{228}Ra and 20-1740 dpm 100 L⁻¹ for ^{226}Ra ; Moore, 2010).

7 The $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio (AR) ranged 2.63-7.82 with an average of 4.09 in the
8 groundwater collected in 2008 along the NSCS shelf. The higher ^{228}Ra activity than
9 ^{226}Ra can be explained by different $^{232}\text{Th}/^{238}\text{U}$ ARs in the aquifer in view that ^{232}Th
10 (the parent of ^{228}Ra) can be preferentially adsorbed onto sediment than ^{238}U (the
11 parent of ^{226}Ra), and as such the sediment is a continuous ^{228}Ra source for the
12 groundwater and spring (Swarzenski et al., 2003). Ra-223 and ex ^{224}Ra in Fig. S1
13 showed good agreement in the $^{223}\text{Ra}/\text{ex } ^{224}\text{Ra}$ AR between the two years, indicating
14 the same ^{235}U (the parent of ^{223}Ra)/ ^{232}Th (the parent of ^{224}Ra) ratio in the aquifers
15 along the shoreline of the NSCS shelf.

16

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

18 Sodium and magnesium concentrations (Table S1) correlated linearly with salinity
19 (figures not shown), suggesting that the major ion composition was a result of the
20 mixing of seawater and fresh groundwater. Calcium showed slight addition from the
21 conservative mixing which may be explained by CaCO_3 dissolution and/or ion
22 exchange (Appelo, 1994; Harriet et al., 2004).

1 The fresh groundwater was the major source of DIN ($\text{NH}_4^+ + \text{NO}_3^- + \text{NO}_2^-$) and SiO_4^{4-}
2 (DSi) on the NSCS shelf as indicated by their distribution with salinity in both 2008
3 and 2010 (Table S1 and Fig. S2A to C). NH_4^+ concentration varied by three orders of
4 magnitude, from 0.3 to 318 $\mu\text{mol L}^{-1}$, in fresh groundwater (Table S1 and Fig. S2A)
5 with an average of 127 $\mu\text{mol L}^{-1}$. NH_4^+ was as high as 573 $\mu\text{mol L}^{-1}$ at salinity ~ 15 .
6 $\text{NO}_3^- + \text{NO}_2^-$ was in the range from 87.6 to 1612 $\mu\text{mol L}^{-1}$ in the fresh groundwater
7 (Table S1 and Fig. S2B) and decreased to 5.6 $\mu\text{mol L}^{-1}$ at salinity of 24.3, indicating
8 removal during mixing with seawater. SiO_4^{4-} was in the range from 83.0 to 702 μmol
9 L^{-1} in the fresh groundwater with average 292 $\mu\text{mol L}^{-1}$ and correlated positively with
10 salinity, as found elsewhere such as in the West Neck Bay STE (Beck et al., 2007).
11 However, PO_4^{3-} concentrations in most of the groundwater were low, averaging 1.0
12 $\mu\text{mol L}^{-1}$, except three samples with extremely high PO_4^{3-} concentrations of 17.2, 19.8
13 and 37.4 $\mu\text{mol L}^{-1}$, respectively. Note that, of the three exceptions, one was from a
14 freshwater well, and the other two were brackish groundwater (salinity ~ 15).
15 Generally speaking, nitrogen and phosphate concentrations in groundwater are low
16 when derived from natural sources, namely *in situ* organic matter decay and mineral
17 weathering (Slomp and Van Cappellen, 2004). The large spatial variation of DIN in
18 fresh groundwater suggests multiple N sources. High DIN concentrations might be
19 affected by anthropogenic activity such as fertilizer, manure and sewage, especially
20 aquaculture wastewater (Cao et al., 2007). Excess NH_4^+ and PO_4^{3-} but depletion of
21 $\text{NO}_3^- + \text{NO}_2^-$ during the mixing of seawater and groundwater (salinity ~ 15) is
22 evidence of the occurrence of denitrification or other organic degradation processes,

1 as also evidenced by extremely high DIC (7147-8757 $\mu\text{mol L}^{-1}$) and TAlk (7364-9009
2 $\mu\text{mol L}^{-1}$).

3

4 **CO₂ parameters in the NSCS subterranean estuary**

5 Figure S3 shows the distribution of DIC, TAlk, pH, and partial pressure of CO₂
6 ($p\text{CO}_2$) versus salinity in the NSCS STE sampled in 2008 and 2010. DIC mostly
7 ranged from 2300 to 6000 $\mu\text{mol L}^{-1}$ in fresh groundwater, with an average of 4002
8 $\mu\text{mol L}^{-1}$ (Fig. S3A). The brackish groundwater had DIC values ranged from 2866 to
9 8757 $\mu\text{mol L}^{-1}$, with an average of 5078 $\mu\text{mol L}^{-1}$, which was higher than that in
10 fresh groundwater (Fig. S3A). TAlk had a distribution pattern similar to DIC, except
11 that it was lower than DIC in fresh groundwater (average of 3301 $\mu\text{mol L}^{-1}$), but
12 higher in the high salinity zone (average of 6631 $\mu\text{mol L}^{-1}$; Fig. S3A and B).
13 Nevertheless, both DIC and TAlk in the groundwater were significantly higher than
14 those in the surface seawaters (DIC:~1909 $\mu\text{mol L}^{-1}$, TAlk:~2202 $\mu\text{mol L}^{-1}$), and the
15 overlying river waters (DIC:~1060 $\mu\text{mol L}^{-1}$, TAlk:~1007 $\mu\text{mol L}^{-1}$). High
16 concentrations of DIC and TAlk in groundwater but non carbonate dominant
17 sediments can be explained by strong bacterial activities. Aerobic organic matter
18 decomposition, denitrification, Mn and Fe oxide reduction, sulfate reduction, and
19 methanogenesis would produce ammonia and CO₂ simultaneously (Lovely and
20 Chapelle, 1995; Slomp and Van Cappellen, 2004; Chen et al., 2006). Good positive
21 relationship ($R^2=0.90$, $n=9$) between NH_4^+ and DIC in groundwater (Table S1, figure
22 not shown) provided evidence to support it. Another possible reason was that a great

1 number of liming additions has increased soil alkalinity in order to improve local
2 soil fertility and structure. The measured pH in the fresh groundwater ranged from
3 6.19 to 7.35, which was lower than saline groundwater (7.38 to 7.84; Fig. S3C).
4 Obviously, the STE has lower pH than seawater. Partial CO₂ pressure (*p*CO₂) in
5 groundwater was pronouncedly different from the surface waters, ranging from 1030
6 to 61040 μatm (Fig. S3D), and was 3-150 times higher than the atmospheric CO₂.
7 The extremely high *p*CO₂ level has been observed in many groundwater systems,
8 such as the wetlands and salt marshes in Georgia and South Carolina (Cai et al.,
9 2003; Moore et al., 2006), the Herbert aquifer in Great Barrier Reef (Gagan et al.,
10 2002), and the shallow groundwater in Konza Prairie (Macpherson et al., 2008).

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13 577-606, 2003.

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

Sample ID	Salinity	Temp (°C)	Na ⁺	Mg ²⁺	Ca ²⁺	DO	ex ²²⁴ Ra *	²²³ Ra	²²⁶ Ra	²²⁸ Ra	TAlk	DIC	pCO ₂	pH	Nutrient concentration (μmol L ⁻¹)			
			mmol kg ⁻¹			%	(dpm 100 L ⁻¹)				(μmol L ⁻¹)		(matm)		NH ₄ ⁺	NO ₃ ⁻ +NO ₂ ⁻	DIP	DSi
I [✕]	0.2	27.0	-	-	-	66	419.47±10.18	15.66±4.24	74.39±22.01	581.80±31.13	2925.4	3818.4	26.36	6.84	-	-	-	-
II [✕]	0.2	21.9	-	-	-	76	422.61±14.49	14.93±3.01	182.11±21.22	541.38±30.06	5025.7	5918.3	26.43	7.07	0.3	810.7	1.1	83
III [✕]	0.0	25.8	-	-	-	31	652.93±17.36	17.96±3.85	137.88±18.25	581.80±29.46	1579.2	3183.9	47.26	6.34	100.1	1009.7	0.7	194.1
IV [✕]	0.0	20.8	-	-	-	28	216.12±8.86	5.67±2.03	65.07±6.18	183.82±17.13	1764.7	2341.1	16.99	6.84	2.5	1612.5	37.4	360.2
Spring [✕]	17.2	-	-	-	-		1195.23±35.14	60.46±15.59	160.65±21.92	422.23±30.97	-	-	-	-	1.1	610.6	1.7	194.1
Xinxi [#]	8.5	28.2	5.1	14.7	3.5	19	1718.21±4.13	56.17±4.15	-	872.12±37.51	2663.0	2866.4	6.31	7.38	59.9	52.6	0.1	213.7
Dongshanhe [#]	0.5	26.7	2.3	0.7	2.4	13	271.35±14.41	6.57±1.16	-	79.60±10.83	7109.8	7523.6	14.45	7.35	436.7	-	-	701.5
Haimen 1 [#]	24.3	27.8	13.2	34.4	8.0	14	1368.13±2.33	56.13±6.55	-	585.51±29.64	3306.0	3203.4	1.03	7.82	89.3	5.56	0.8	75.6
Haimen 2 [#]	23.2	28.8	12.5	32.2	7.8	11	1072.26±73.58	41.59±5.79	-	523.35±24.53	3521.9	3414.2	1.10	7.84	50.6	6.84	0.2	80.6
Huilai [#]	0.0	27.8	0.3	0.1	0.2	45	61.71±5.17	3.63±1.14	-	30.16±12.55	380.7	900.8	15.46	6.19	1.6	87.64	0.1	243.3
Luyuanchun [#]	0.5	26.8	2.4	0.8	2.2	-	897.22±1.59	31.43±3.42	-	395.67±20.75-	5343.6	-		6.93	32.9	1043.9	0.1	273.6
Shajiaowei [#]	0.0	27.2	0.3	2.4	0.5	-	280.89±12.95	7.88±2.22	-	133.23±12.78-	2278.4	4329.9	61.04	6.27	318.2	148.6	0.2	185.6
Xiayang 1 [#]	15.6	28.3				-	521.22±29.23	11.01±2.2	-	439.32±23.65	7364.5	7147.2	2.19	7.73	573.5	5.24	19.8	169.2
Xiayang 2 [#]	16.6	27.6	8.9	26.5	7.1	-	512.25±36.39	20.32±2.71	-	418.87±20.64	9008.9	8757.1	2.72	7.69	572.2	7.08	17.2	180.6

3 Superscript ✕ groundwater taken in Dec. 2008; # groundwater collected in Oct. 2010.

4 *ex²²⁴Ra denotes excess ²²⁴Ra, corrected for the ingrowth from ²²⁸Th.

5 pCO₂ was calculated from DIC and TAlk using CO₂SYS.XLS 14th version ([HTTP:// www.ecy.wa.gov/programs/eap/models.html](http://www.ecy.wa.gov/programs/eap/models.html)).

Figures Captions in Supplementary Material

Fig S1. Correlation between ^{223}Ra and $\text{ex } ^{224}\text{Ra}$ (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 (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 ($p\text{CO}_2$) plotted versus salinity in the northern South China Sea subterranean estuary both in December 2008 and October 2010.

Figure S1

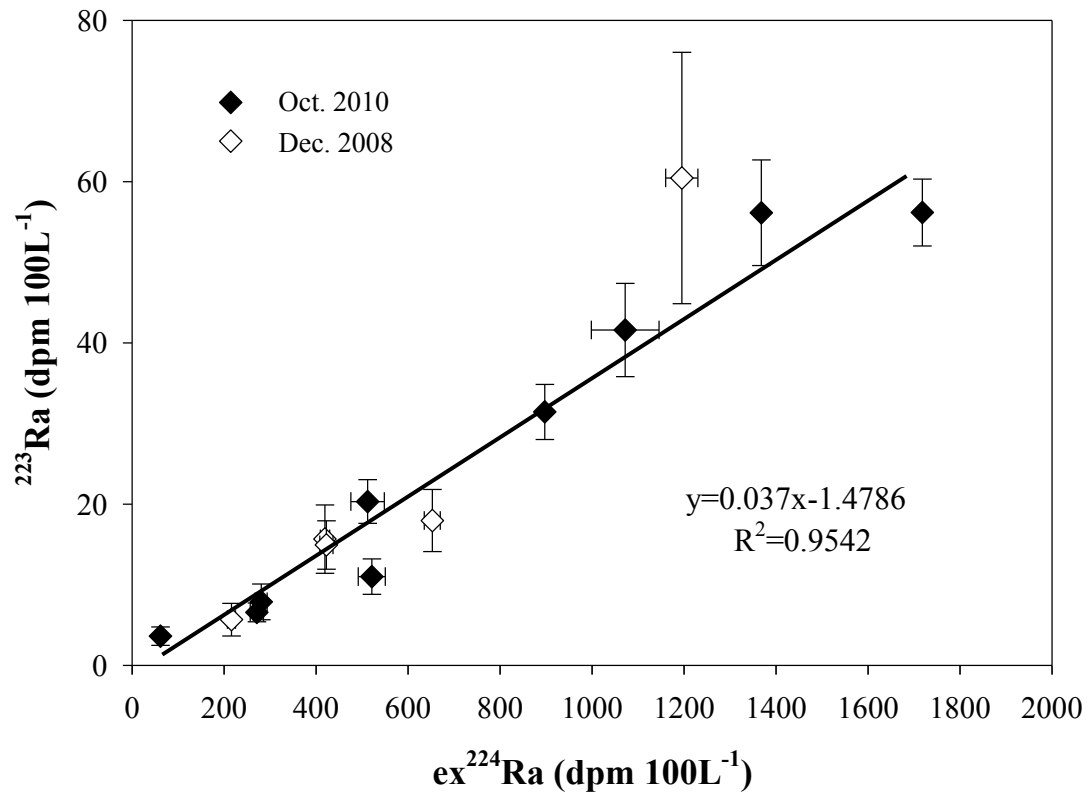


Figure S2

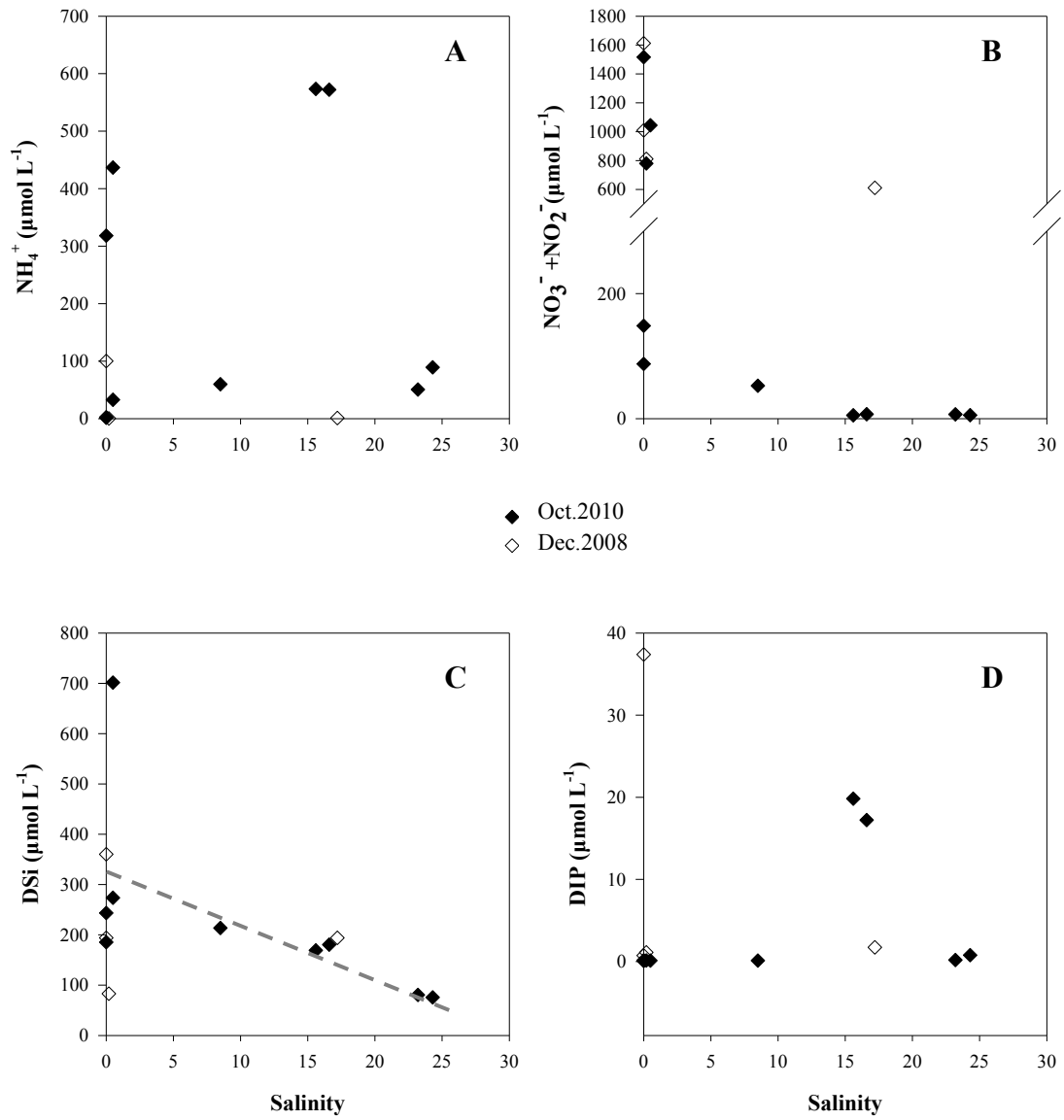


Figure S3

