Supplementary material

Seasonal variations in groundwater chemistry, quality, and associated health risks from domestic wells and crucial constraints in the Pearl River Delta

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Health risk assessment

The average daily dose (ADD) was estimated to calculate the hazard quotient and cancer risk via the following equations [1-3].

$$ADD_{ing} = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (5)$$

$$ADD_{dermal} = \frac{C \times SA \times Kp \times ET \times EF \times ED \times CF}{BW \times AT} \quad (6)$$

where, C is the elemental concentration, IR is the ingestion rate (L/day, 2.0 for adults and 0.64 for children); EF is the exposure frequency (360 days/year); ED is the exposure duration (years, 30 for adults and 6 for children); BW is the average body weight (kg, 63.5 for adults and 16.6 for children [4]; and AT is the average exposure time in days (ED×365 days/year, i.e., 10,950 for adults and 2190 for children). The additional parameters in equation (6) include the following: SA is the area of skin exposed (cm^2, 18,000 for adults and 6600 for children); Kp is the dermal permeability coefficient (cm/h, 0.001 for As, Cd, Cr, and Cu and 0.0001 for Pb); ET is exposure time (h/day, 0.58 for adults and 1 for children); and CF is the volumetric conversion factor for groundwater (1 L/1000 cm^3).

Noncarcinogenic health risk (health quotient, HQ) from groundwater through ingestion and dermal absorption was estimated via equation (7):

$$HQ = \frac{ADD_{ing/dermal}}{RfD} \quad (7)$$

where the RfD value is the reference dose (μg/kg/day). The RfD values for exposure through the mouth oral or skin are Fe (300/45), Cu (40/12), Pb (1.4/0.42), Ni (20/5.4), Cr (3/0.015), Cd (0.5/0.005), As (0.3/0.3), and NO_3^- (1600/1600) according to previous studies [5, 6].

The overall noncarcinogenic effects are summarized as HQ from all the contaminants and expressed as hazard indices (HI). Assuming that the risk is cumulative, the total noncarcinogenic risk after oral consumption or skin contact of contaminated

groundwater can be assessed using the total hazard index (THI) calculated according to $THI = HI_{ing} + HI_{dermal}$. If the HI or THI value is greater than 1, a potential noncarcinogenic health risk is likely present for local residents [5, 7].

The carcinogenic risk (cancer risk, CR) from exposure through ingestion was determined [6] via equation 8:

$$CR = ADD \times SF \quad (8)$$

where SF is the slope factor $(mg/kg/day)^{-1}$ for risk via ingestion and is 1.5 for As. Other potential carcinogenic metals like Cr, Pb, and Cd were not considered because they did not show elevated concentrations than the recommendation. Values of $CR < 10^{-6}$ suggest a very low cancer risk, $10^{-6} < CR < 10^{-4}$ suggests lower cancer risk, $10^{-4} < CR < 10^{-3}$ suggests moderate cancer risk, and $10^{-3} < CR < 0.1$ and $CR>0.1$ suggest a higher and strong higher cancer risk through prolonged exposure to the metals in groundwater [5].

Table S1 The values of coefficients (S_i, I_i, guideline value, and W_i) used in HPI computation.

Heavy Metal	S_i (µg/L)	I_i (µg/L)	W_i
As	10	-	0.100
Pb	10	-	0.100
Ni	70	20	0.014
Fe	300	-	0.003
Cu	1500	50	0.001
Cr	50	-	0.02
Cd	3	-	0.333

Table S2 Assigned weights of drinking water quality parameters

Chemical parameter (*i*)	**Drinking water quality standard (DWQS)**	**Weight assessment (AW)**	**Relative weight (RW)**
pH	8.5	4	0.095
TDS (mg/L)	500	5	0.119
TH (mg/L)	300	2	0.048
Ca^{2+} (mg/L)	75	2	0.048
Mg^{2+} (mg/L)	30	2	0.048
Na^{+} (mg/L)	200	4	0.095
K^{+} (mg/L)	12	2	0.048
HCO_3^{-} (mg/L)	300	1	0.023
Cl^{-} (mg/L)	250	5	0.119
SO_4^{2-} (mg/L)	200	5	0.119
NO_3^{-} (mg/L)	45	5	0.119
F^{-} (mg/L)	1.5	5	0.119
∑		42	1

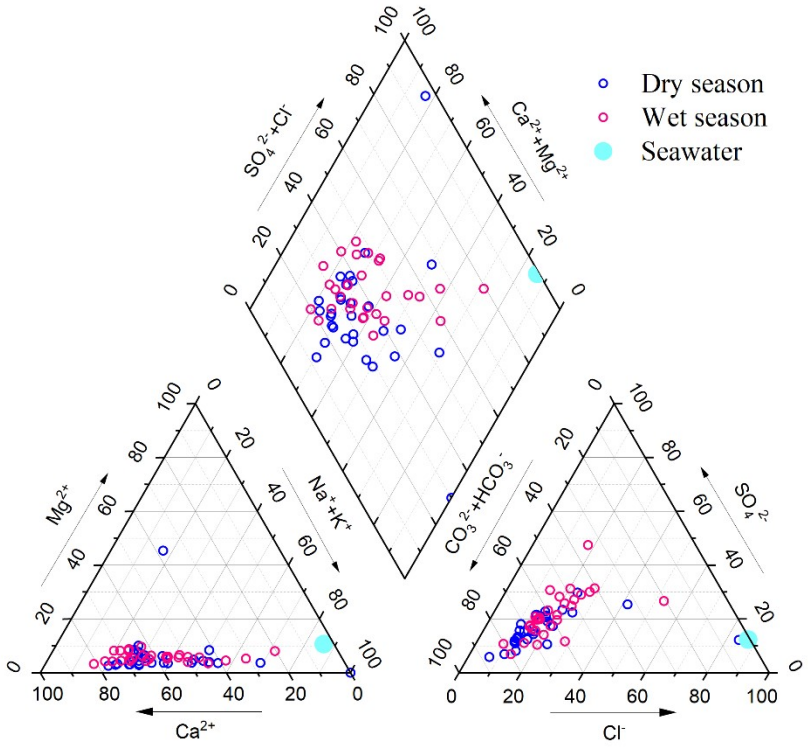

Fig. S1. Piper diagram for the main geochemical types of shallow groundwater in the wet and dry seasons from the Pearl River Delta. Seawater is also plotted as a blue filled circle [8].

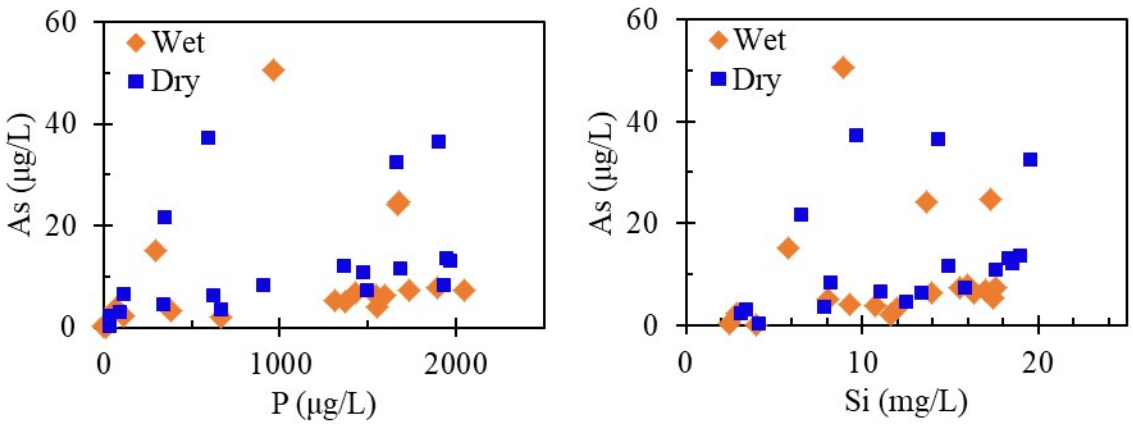

Fig. S2. Changing trend between As and P or Si in the groundwater.

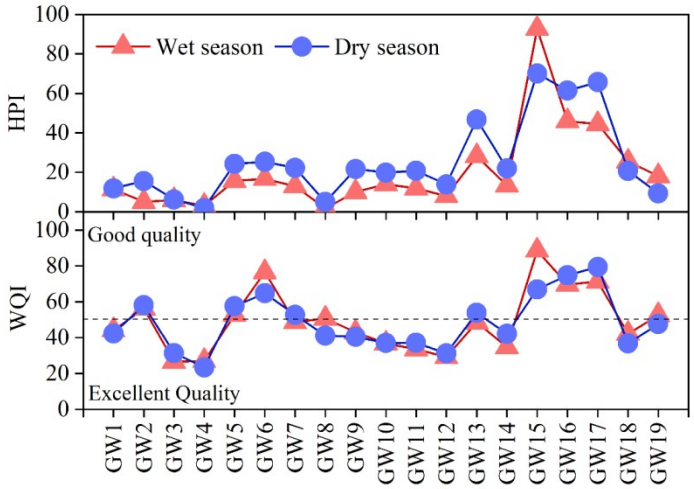

Fig. S3. Heavy metal pollution index (HPI) and water quality assessment (WQI) of shallow groundwater from domestic wells in the Pearl River Delta. Groundwater with a threshold HPI value below 100 is suitable for drinking [1]. The WQI value indicate that the water quality is excellent (< 50), good (50–100), poor (100–200), very poor (200–300), and unsuitable for drinking (>300) [9].

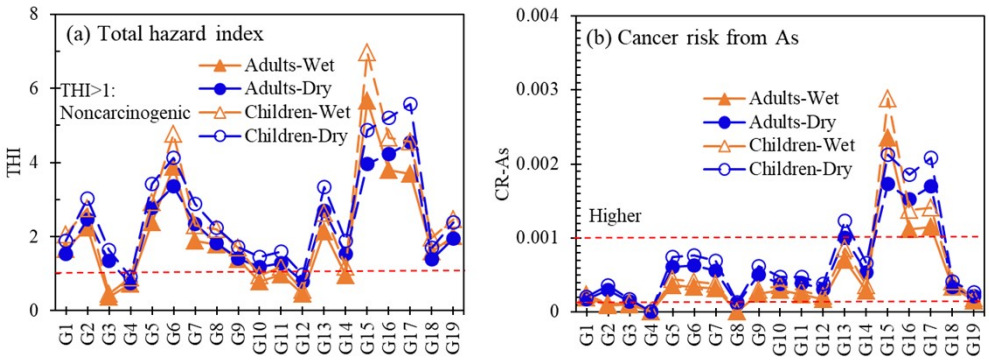

Fig. S4. Total hazard index (THI, a) and cancer risk from As (b) of groundwater samples from domestic wells in the Pearl River Delta in the dry and wet seasons. Except for As, no carcinogenic risk was estimated from other elements with permissible concentrations in groundwater in this work. A THI value greater than 1 represents a potential noncarcinogenic health risk, and cancer risk value: $10^{-6} < CR < 10^{-4}$ suggests lower cancer risk and $10^{-4} < CR < 10^{-3}$ suggests moderate cancer risk [5].

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