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Temporal-Spatial Evolution of Groundwater Nitrogen Pollution Over Seven Years in a Highly Urbanized City in the Southern China

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Abstract Understanding the temporospatial variation in nitrogen pollution in groundwater and the associated controlling factors is important to establish management practices that ensure sustainable use of groundwater. In this study, we analyzed inorganic nitrogen content (nitrate, nitrite, and ammonium) in 1164 groundwater samples from shallow, middle-deep, and deep aquifers in Zhanjiang, a highly urbanized city in the southern China. Our data span a range of 7 years from 2005 to 2011. Results show that shallow aquifers had been heavily contaminated by nitrate and ammonium. Temporal patterns show that N contamination levels remained high and relatively stable over time in urban areas. This stability and high concentration is hypothesized as a result of uncontrolled, illicit sewer discharges from nearby business facilities. Groundwater in urban land and farmland displays systematic differences in geochemical characteristics. Collectively, our findings demonstrate the importance of continuously monitoring groundwater quality and strictly regulating sewage discharges in Zhanjiang.

Keywords Nitrogen pollution · Temporo-spatial variation · Groundwater · Nitrate · Nitrite · Ammonium · Zhanjiang

Nitrogen pollution in groundwater is a severe environmental issue for many agricultural and urban areas around the world (Hiscock 1991; Luo and Jin 2002; Lu et al. 2010; Mario et al. 2014). A long-term intake of water at an elevated nitrate concentration above the safety level may lead to methemoglobinemia and high risk of cancer (Hill 1999; Roos et al. 2003; Knobeloch et al. 2000; Ash-Bernal et al. 2004). High nitrite concentration in drinking water also poses health risks (Joseph and James 2007). Worldwide, nitrogen accumulation in aquifers has been attributed mostly to agricultural and industrial fertilizer application and domestic and industrial sewage discharges (Nikolaidis et al. 1998; Ju et al. 2006; Qian et al. 2011; He et al. 2016).

In China, nitrogen contamination of groundwater is particularly concerning due to rapid agricultural and urban development as well as a large, concentrated population relying on groundwater as drinking water (Ma et al. 2012; Hu et al. 2017). Our study area, Zhanjiang city, is a highly urbanized area with a population of more than seven million, representing one of the coastal cities undergoing the most rapid economic growth in China. Over the past few decades, the city has transformed radically from an agriculture-dominated area to an industrial powerhouse. As the main source of drinking water, groundwater in this region is highly vulnerable to agricultural and industrial contamination. In fact, aquifer decreases have been reported in the Zhanjiang city. The cones of depression have appeared in areas with excessive groundwater exploitation (Zhou et al. 2007). However, data on groundwater quality remain limited. In particular, datasets spanning multiple years or encompassing a large geographic area are scarce, hindering a robust understanding of temporal development and spatial extent of groundwater nitrogen contamination.

In this paper, we presented temporal changes over 7 years (i.e., 2005–2011) in inorganic N pollutants in groundwater

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from an area of 1200 km^2 within an artesian basin in the Zhanjiang city. Through interpreting groundwater N data in relation to land use type, precipitation, and main ion chemistry of groundwater, we identified the main factor governing the spatiotemporal variation in nitrogen contamination of the aquifers in this rapidly urbanized region.

Materials and Methods

Zhanjiang is located in the south of the Guangdong Province in the southern China, and it has a population of 7,241,400 (as of 2016). It has a tropical monsoon marine climate with an annual mean temperature of 23 °C. The highest temperature occurs typically between June and August. The mean annual rainfall ranges between 1417 and 1802 mm, and the rainy season is from April to September. Our groundwater samples were collected from 31 wells distributed in the northwestern part of the Zhanjiang city (Fig. 1). Three of the wells are situated at the Donghai Island, a continental island separated from the mainland to the east by the Zhanjiang Bay. The elevation of the study area gradually decreases from the volcanic plateau (northwest) to the Zhanjiang Bay coast (southeast) (Fig. 1a). The terrain in the central part of the study area and the eastern part of the Donghai Island is mainly erosion platform, which is characterized by a strong terrain incision and a large elevation gradient.

Along the coast, accumulation plains and alluvial plains are overlaid by thick Quaternary loose sediment composed of sand and clayey soil, forming a considerably thick aquifer system with multiple layers. Overall, the aquifer system can be classified into three types according to burial depth, including shallow, unconfined aquifers (< 30 m), middle to deep aquifers (30–200 m), and deep, confined aquifer (200–500 m). In the Donghai Island, the shallow aquifer is isolated from aquifers on the mainland, but the middle-deep and deep aquifers are well connected to the mainland aquifers (Zhou et al. 2013). In the northwestern part of the study area, there are a large number of volcanic craters that lead to good hydraulic connectivity among various aquifers (Wen 2013).

We collected a time series dataset over the span of 7 years, i.e., from 2005 to 2011. Water level data were measured from 44 wells, of which, 9, 20, and 15 wells were from the shallow, middle to deep, and deep aquifers, respectively. Groundwater samples were collected from other 31 water quality monitoring wells (of which 1 is surface water, 7 are shallow, 11 are middle to deep, and 12 are deep) (Fig. 1a). Sample collection was performed twice a year, in dry (March) and rainy season (September), respectively. Basic water quality parameters including pH, total alkalinity (TA), total hardness (TH), and total dissolved solids (TDS)

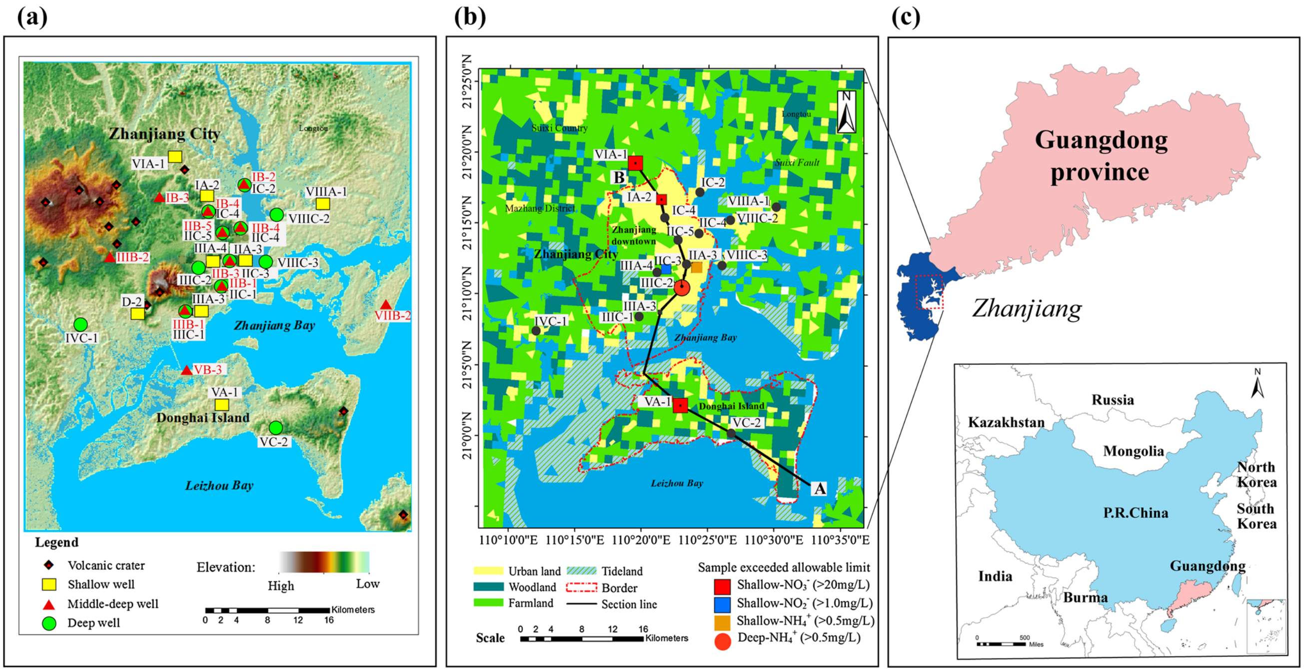

Fig. 1 **a** The study area showing the location of water quality monitoring wells; **b** land use of the study area and location of groundwater wells showing high levels of nitrogen contamination in September 2011. The cross-section line A–B is for the Kriging spatial interpolation analysis to understand spatial variation of N pollution in the study aquifers (see results in Fig. 4); **c** location of the study area relative to China

contents were determined following the standard DZ/T 0064 1993 by the Ministry of Land and Resources, P. R. China. The concentrations of nitrate, nitrite, and ammonium, as well as main ions, including Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, and HCO_3^-, were analyzed at the Guangdong Geological Survey, following the protocol described in the Technical Specifications for Environmental Monitoring of Groundwater, the Ministry of Environmental Protection, P. R. China (HJ/T 164-2004). Data accuracy was evaluated by the charge balance error (CBE) (Freeze and Cherry 1979), which was within 5%. The concentrations of inorganic nitrogen were compared to the Standard for Groundwater Quality, the Ministry of Land and Resources, P. R. China (DZ/T 0290-2015). The category III defined in DZ/T 0290-2015 indicates good water quality that is appropriate for drinking. Groundwater classified below this category is not suitable for drinking without proper treatment. Therefore, the criterion defined in the Category III (20.0 mg/L NO_3-N, 1.00 mg/L NO_2-N, and 0.50 mg/L NH_4-N) was taken as the upper limit concentrations to evaluate the extent to which N levels exceed in the study aquifers. We defined a parameter quantifying the proportions of contaminated samples (PCS) following the equation below:

$$PCS = n/m \times 100\%$$

where n denotes the number of the groundwater samples that have concentrations above the Category III values and m represents the number of the total groundwater samples from an aquifer or a time period of interest.

The spatial variation of nitrogen contamination was analyzed using the Ordinary Kriging method along one representative cross-section of the study area (A—B in Fig. 1b). The Kriging spatial interpolation method can generate a continuous surface from a number of discrete observation

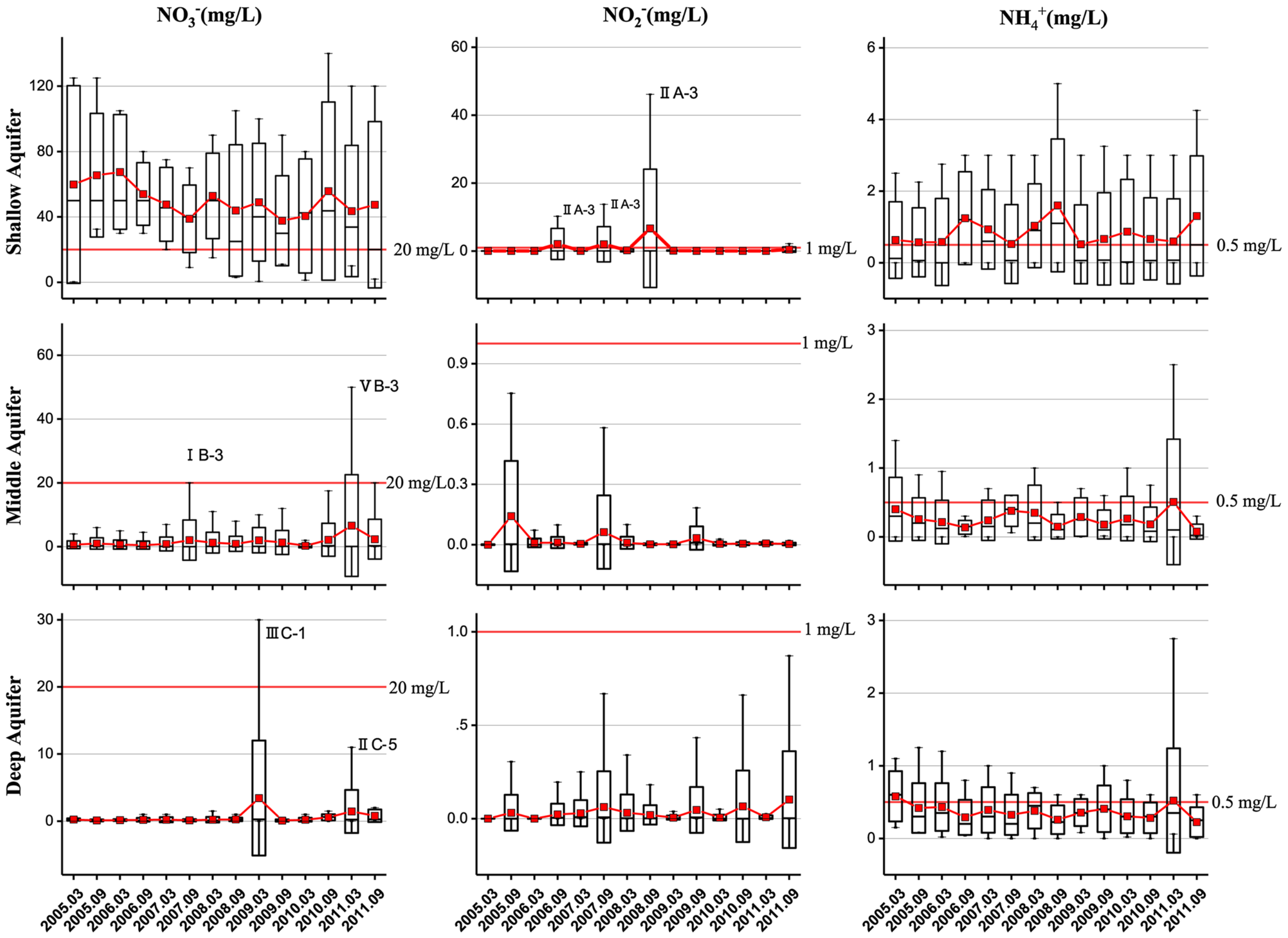

Fig. 2 Box plot comparisons of temporal variation in the concentration of nitrate, nitrite, and ammonium in the aquifers of Zhanjiang from 2005 to 2011. The red straight lines represent the upper limit concentrations of NO_3^--N, NO_2^--N and NH_4^+-N for Category III water defined in the Standard for Groundwater Quality DZ/T 0290-2015. The names of those severely contaminated wells are labeled above the corresponding boxes. The medians are shown as the black lines across the boxes, and the means denoted by the red dots within the boxes are connected by the red lines to describe the temporal trend. Boxes show the range of standard deviation and whiskers extend to the maximum and minimum values

points. This geostatistical method has been widely used in spatial analysis and decision-making research (Goovaerts 2000; Sampson et al. 2013; Hu and Shu 2015). Ten monitoring wells in September of 2007 and 2011 were used for this analysis, including seven wells located at downtown Zhanjiang and three on the Donghai Island. The land use map is provided by Data Center for Resources and Environmental Sciences, Chinese Academy of Sciences (RESDC) (http://www.resdc.cn).

Results and Discussion

The concentrations or PCSs of NO_3^-, NO_2^- did not show an evident temporal pattern from March, 2005 to September, 2011 in all three types of aquifers (Fig. 2). The PCS of NH_4^+, however, shows an overall declining trend (Fig. 3), which could indicate that ammonium pollution was decreasing. However, it must be acknowledged that ammonium is not a stable species and the variation could be due to changes in other factors such as oxygen levels and microbial community. Between dry versus wet seasons, no systematic differences were observed for all three N species, suggesting little influence of rainfall on the temporal variation in nitrogen contamination in the aquifers.

Overall, the concentrations of NO_2^- were mostly below the Category III value from 2005 to 2011 (Fig. 3). However, a shallow-aquifer well (IIA-3) showed abnormally high nitrite concentrations in the rainy season of 2006, 2007, and 2008 (Fig. 2). The values were 10.24, 13.76 and 46.14 mg/L, respectively, more than ten times higher than the upper limit of the Category III groundwater (1.0 mg/L). Given that IIA-3 was located near a restaurant, these particularly high NO_2^- values suggest direct wastewater discharge from the restaurant into soil without proper treatment, and rainfalls facilitate the infiltration into the shallow aquifer.

The mean concentrations of NO_3^-, NO_2^- and NH_4^+ of most of the shallow groundwater samples were beyond the upper limit concentrations for Category III groundwater (see the mean values that were mostly above the red straight lines in Fig. 2), demonstrating severe nitrogen contamination in the shallow aquifers. The mean concentration of NO_3^- was much higher in the shallow aquifer (49.53 mg/L) than in the middle-deep (1.57 mg/L) and deep aquifers (0.59 mg/L). Correspondingly, the PCS values were much higher in the shallow aquifer (76.5%) than in the other two aquifers (near 1%) (Table 1; Fig. 2). This observation shows that the shallow groundwater has been severely contaminated with nitrate, while the deeper aquifers have not been much impacted. Similar to nitrate, ammonium concentrations increased with depth (Table 1). The PCSs were high for all aquifers, averaging 34.5%, 20.9%, and 22.5% for shallow, middle-deep, and deep aquifers, respectively. In addition to the direct input of ammonium from fertilizers and urban discharges, ammonium accumulation in the deep aquifers points out two possible sources warranting further research attention—remineralization of organic N as well as dissimilatory reduction of nitrate to ammonium. By comparison, the PCSs of nitrite were consistently below 6% for all three types of aquifers (Table 1; Fig. 3). However, both ammonium and nitrate can be converted to nitrite by microbes, and hence a consistently elevated concentration of nitrate or ammonium may eventually lead to nitrite enrichment in these aquifers under suitable geochemical conditions.

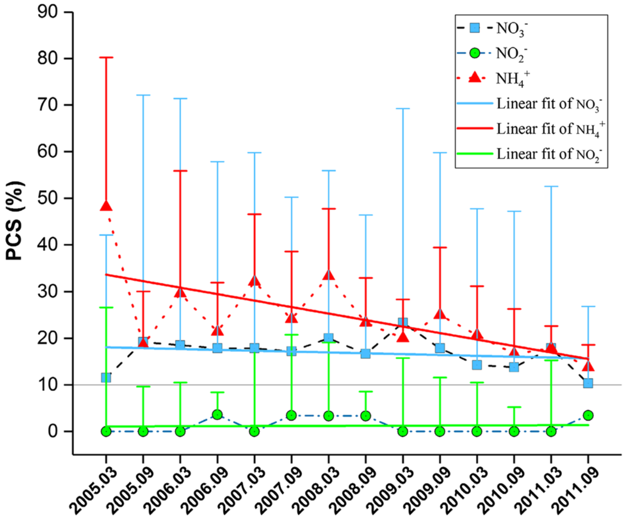

Fig. 3 Temporal trend of mean values of the proportion of contaminated samples (PCS), i.e., samples exceeding the safety standard of NO_3^-, NO_2^- and NH_4^+, in the aquifers in Zhanjiang from 2005 to 2011. Error bars represent plus standard deviation from multiple groundwater wells sampled in the same month

Overall, the spatial analysis from southeast to northwest of the study region (line A-B in Fig. 1) shows a similar spatial distribution pattern of groundwater N between September 2007 and September 2011 (Fig. 4). However, the maximum NO_3^- concentration in 2011 was higher than that in 2007, highlighting the need to continuously and closely monitor these wells. Furthermore, nitrate pollution was most severe in the shallow aquifer on the Donghai Island and in downtown Zhanjiang City, and ammonium pollution was most significant in downtown Zhanjiang (Fig. 4). In particular, two shallow-aquifer wells, IA-2 and VIA-1, stood out for the heavy NH_4^+ pollution (Fig. 4c, f). The land use of the Donghai Island comprises urban land (13.7%), farmland (48.3%) and woodland (38.0%), whereas downtown Zhanjiang comprises urban land (42.9%), farmland (43.1%) and woodland (14.0%) (Fig. 1c). This pattern suggests that both urban sewage and farmland fertilizers may be responsible for severe nitrate and ammonium pollution in the shallow

Table 1 The descriptive statistics of the concentrations of shallow, middle-deep, deep aquifers in Zhanjiang, China

Aquifer	Shallow			Middle-deep			Deep		
Nitrogen	NO_3^-	NO_2^-	NH_4^+	NO_3^-	NO_2^-	NH_4^+	NO_3^-	NO_2^-	NH_4^+
Maximum (mg/L)	140.0	46.14	5	50	0.753	2.50	30	0.87	2.75
Mean (mg/L)	49.53	0.890	0.85	1.57	0.02	0.286	0.59	0.03	0.366
Minimum (mg/L)	0.20	BD	BD	BD	BD	BD	BD	BD	BD
PCS (%)	76.5	5.8	34.5	0.7	0	20.9	0.63	0	22.5

PCS the proportions of contaminated samples, *BD* below detection

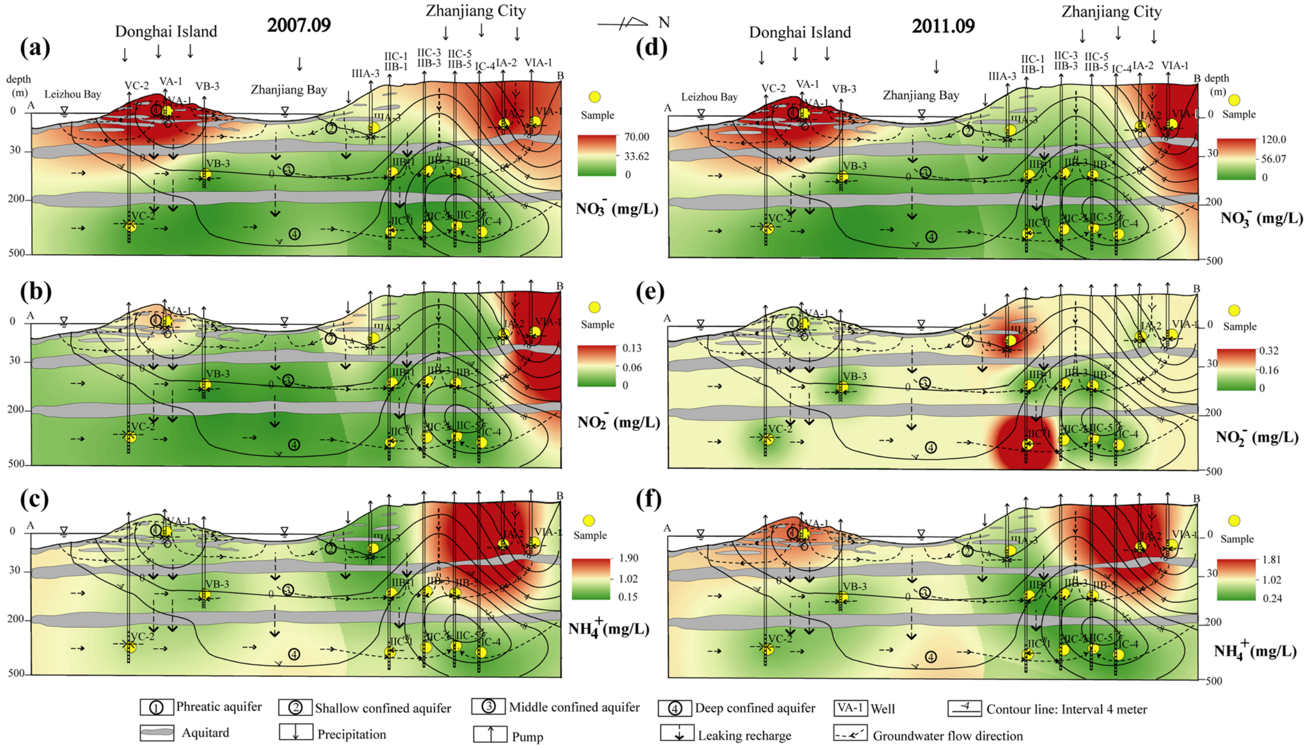

Fig. 4 Spatial distribution profiles of nitrogen contaminants of aquifers in Zhanjiang along a SE–NW cross-section (see line A-B in Fig. 1) in September of 2007 and 2011. The profiles were derived from the Kriging spatial interpolation analysis. Contour lines represent the groundwater water level

Table 2 The land use character and nitrogen contaminant statistics in shallow-aquifer wells in Zhanjiang, China

Well name		IA-2	IIA-3	VA-1	VIIIA-1	IIIA-3	IIIA-4	VIA-1
Land use of the sampling well location		Urban	Urban	Urban	Urban	Farmland	Farmland	Farmland
NO_3^-	PCS (%)	92.9	42.9	100	62.3	35.7	71.4	100
	Mean	42.23	22.25	96.79	27.37	22.65	56.18	71.32
	Standard deviation	13.14	14.57	21.27	21.44	13.44	39.92	37.7
NO_2^-	PCS (%)	0	28.6	0	0	0	14.3	0
	Mean	0.03	5.16	0.02	0.01	0.09	0.39	0.06
	Standard deviation	0.02	12.56	0.02	0.03	0.13	0.79	0.05
NH_4^+	PCS (%)	100	21.4	57.1	21.4	7.1	0	7.1
	Mean	2.84	0.8	1.06	0.22	0.23	0.13	0.13
	Standard deviation	0.35	1.65	1.08	0.44	0.35	0.11	0.26

aquifers. The PCSs of nitrate contamination were high in shallow wells from both urban lands and farmlands (i.e., 35.7%–100%, Table 2). By comparison, ammonium contamination was more prevalent in shallow wells from urban lands (PCSs: 21.4%–100%) than from farmlands (PCSs: 0%–7.1%) (Table 2).

In order to understand the geochemical and land use controls of N contamination, we plotted the shallow aquifer samples in the Piper diagram (Fig. 5) (Piper 1944). We compared the characteristics of nitrate-polluted samples (i.e., the concentration of NO_3-N > 20 mg/L) and more pristine samples from urban lands and farmlands. Most urban samples were plotted in zone A (except well IIA-3 in zone C) that is characterized by a high concentration of Cl^- and SO_4^{2-} (Table 3). In contrast, most farmland samples were plotted in zone B characterized by a high HCO_3^- concentration (Table 3). The shallow aquifer had a Cl + SO_4 type groundwater in urban land and a HCO_3^- type groundwater in farmland. These observations indicate that the groundwater geochemistry differed between urban lands versus farmlands. However, the polluted and more pristine groundwater samples were clustered together in the Piper diagram, suggesting that N pollution level did not vary as a function of groundwater geochemistry.

Table 3 The statistics of water quality parameters in shallow-aquifer wells in Zhanjiang, China

Well name	Statistics	pH	Na^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)
IA-2 (urban)	Mean	4.82	30.60	16.07	6.53	51.77	35.54	4.95
	SD	0.53	1.03	5.38	1.71	2.83	4.62	6.17
IIA-3 (urban)	Mean	7.11	26.94	42.02	6.38	27.61	30.62	142.18
	SD	0.26	10.57	16.12	3.65	11.01	11.53	47.63
VA-1 (urban)	Mean	5.04	71.19	38.50	20.33	134.04	70.72	5.23
	SD	0.56	24.81	15.39	22.16	41.29	22.83	4.90
VIIIA-1 (urban)	Mean	4.84	29.09	26.26	7.89	44.16	58.03	36.56
	SD	1.23	13.81	16.80	2.49	17.19	12.43	70.62
IIIA-3 (farmland)	Mean	6.75	26.85	33.06	5.46	32.49	44.60	93.74
	SD	0.41	10.99	10.56	2.56	17.75	23.74	40.53
IIIA-4 (farmland)	Mean	7.67	37.34	46.27	29.75	79.45	108.18	214.40
	SD	0.54	25.02	23.64	24.30	52.65	80.25	81.98
VIA-1 (farmland)	Mean	6.95	70.44	65.66	19.29	114.37	95.62	198.93
	SD	0.37	21.87	20.07	12.01	46.27	38.57	83.87

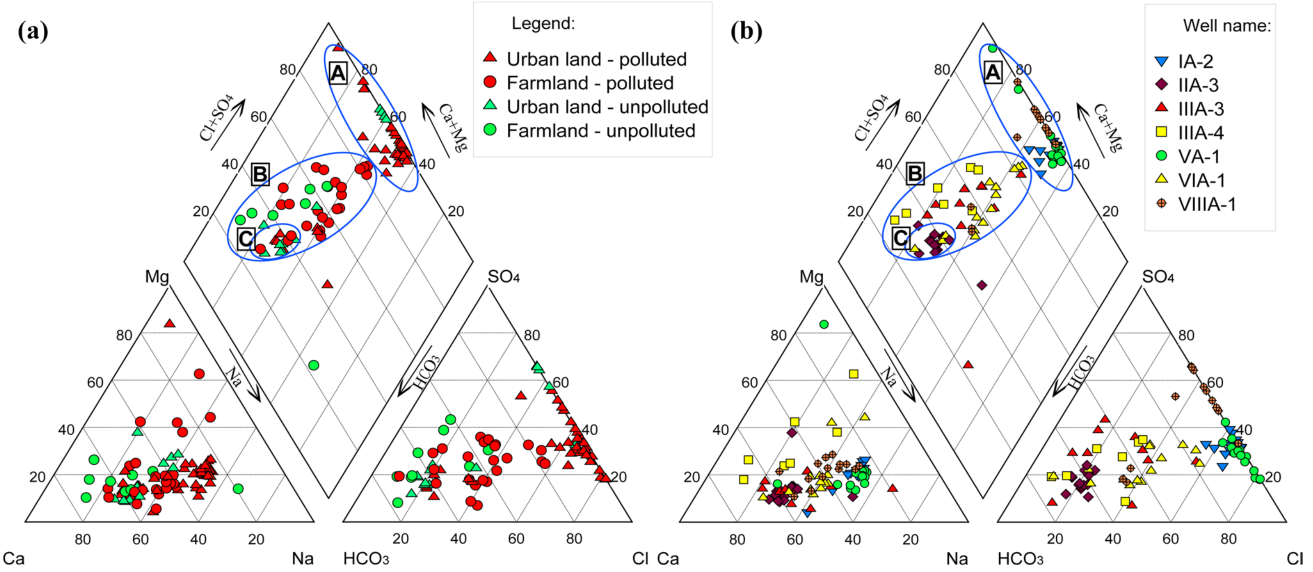

Fig. 5 Piper diagrams of the shallow-aquifer groundwater samples from Zhanjiang, China. **a** Distribution of the polluted samples (NO_3-N > 20 mg/L) versus more pristine samples; and **b** distribution of samples from various wells

Together, our data and spatiotemporal analyses show that the level of groundwater nitrogen pollution in Zhanjiang remained relatively stable from 2005 to 2011, while continuous monitoring remains critical, particularly given the rapid economic development and abundant urban and agricultural sources in the region. The contamination issue was most severe in the shallow aquifers in urban areas, suggesting that urban sewage was the main source of pollution. Although most business and industrial facilities in Zhanjiang treat sewage via sedimentation tank before the discharge into municipal sewers, a large number of small restaurants have been discharging untreated, raw sewage (Huang et al. 2006). Our results show the negative effects of such illicit practices, urging immediate, stricter measures of regulating sewage treatment and discharge in this highly urbanized area.

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