Factors Controlling Natural Background Levels of Ammonium and Iodide in Shallow Groundwater of Coastal Aquifers, South China

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Abstract: Assessing natural background levels (NBLs) in groundwater is crucial for evaluating groundwater pollution and the use of groundwater resources in coastal areas. This study assessed NBLs of iodide and ammonium in the shallow groundwater of the Pearl River Delta (PRD) by using a preselection method with Grubbs' test, and discussed factors controlling NBLs in various groundwater units. Here, the preselection method consists of Cl/Br mass ratios versus Cl concentrations and the oxidation capacity, and the PRD is divided into four groundwater units. Results showed that NBL-iodide in groundwater unit A was 0.14 mg/L and >2 times greater than that in other groundwater units. Similarly, NBL-ammonium in groundwater unit A was 0.32 mg/L and also >2 times greater than that in other groundwater units. The release of iodide from both of organic-iodine in the vadose zone and iodine-rich minerals in aquifer sediments were the two main sources for the higher NBL-iodide in groundwater unit A compared to other units. By contrast, the occurrence of ammonium from organic-nitrogen in the vadose zone was the major source for the higher NBL-ammonium in groundwater unit A compared with the other units. Soluble iodide resulted from the mineralization of organic-iodine in Quaternary marine formation, and the release of iodide accompanied with reductive dissolution of iodide-loaded Fe (oxyhydr) oxides in aquifer sediments was the main driving force controlling the higher NBL-iodide in groundwater unit A compared with the other units. By contrast, the release of soluble ammonium from the mineralization of organic-nitrogen in marine formation entering into groundwater was the main driving force controlling the higher NBL-ammonium in groundwater unit A relative to the other units. These results enhance the knowledge on groundwater NBLs in coastal areas and improve groundwater resources management in coastal areas such as the PRD.

Keywords: natural background levels; iodide; ammonium; shallow groundwater; coastal areas

1. Introduction

More than 80% of countries in global have coastlines, and areas located at coastlines have been centers of human activity for long time. For example, China has a long coastline with more than 18,000 km, and the population of coastal areas accounted for >20% of total population in China [1]. Groundwater in coastal aquifers is often a very important water resource for human beings in coastal areas because of the ever-increasing water demand resulting from the increase in population and the development of economy [2–4]. For instance, groundwater is being used to supplement the available surface water for water demand in the Pearl River Delta (PRD) adjacent to the South China Sea owing to the large scale urbanization and industrialization, resulting in the growth of the population and shortage of available surface water [5]. However, Zhang et al. reported that a significant portion of groundwater in the PRD is unsuitable for drinking, agricultural, or industrial

purposes due to the contamination of several contaminants such as iodide (I^-), ammonium (NH_4^+), nitrate (NO_3^-), etc [6]. This limits the use of groundwater in coastal aquifers such as the PRD. Therefore, it is necessary to understand natural background levels (NBLs) and their geogenic factors of contaminants in groundwater for assessing the status of groundwater contamination and quality in coastal areas, and to thereby support the reference basis for groundwater resource management. Here, groundwater NBL represents the concentration of a certain component in groundwater derived from natural sources [7].

NBLs as part of anthropogenic pollutants in the groundwater of the PRD have already been assessed. For example, Huang et al. used a new preselection method to evaluate NBLs of groundwater Cl^- and NO_3^- in the PRD [8]; moreover, Bi et al. used an oxidation capacity method in combination with Grubbs' test to assess groundwater PO_4^{3-} NBL in various aquifers in the PRD [9]. By contrast, NBLs and the geogenic factors of some of their main contaminants, such as I^- and NH_4^+ in groundwater of the PRD, have received little attention, although a few of studies have reported on the spatial distributions and origins of I^--rich and NH_4^+-rich groundwaters in the PRD [10,11].

Therefore, this study aims to evaluate the NBLs of groundwater I^- and NH_4^+ in various aquifers of the PRD by using a new preselection method established by [8], and thereby to discuss factors controlling these NBLs in various aquifers. Unlike the levels of pollutants such as Cl^- and NO_3^-, high levels of I^- and NH_4^+ in the shallow groundwater of the PRD are not only affected by human activities but are also influenced by geogenic factors [10,11]. The results will enhance the knowledge on groundwater NBLs in coastal areas and improve groundwater resources management in coastal areas such as the PRD.

2. Study Area

2.1. Geographical and Land-Use Conditions

The PRD (111°59′–115°25′ E, 21°17′–23°55′ N) is located in Guangdong Province of China and is adjacent to the South China Sea in the south (Figure 1). It is a compound delta formed by sediments brought by water flows of three major rivers (i.e., Xijiang River, Beijiang River, Dongjiang River) and their tributaries (i.e., Tanjiang River, Suijiang River, and Zengjiang River), with nearly half of the area dotted with hills, platforms, and residual hills. The southern coastline is 1059 km long. The average annual precipitation and temperature are 1800–2200 mm and 21.4–22.4 °C, respectively. The majority of precipitation falls in the wet season between April and September [12,13]. Land use in the PRD can be divided into four types including urbanized area (UA), peri-urban area (PUA), agricultural area (AA), and the remaining area (RA) [14]. The remaining area consists of woodlands, grasslands, small villages, and uncultivated lands.

2.2. Hydrogeological Conditions

Bi et al. reported that the PRD has four types of aquifers and can be divided into four groundwater units (Figure 1) [9]. Briefly, groundwater unit A is mainly distributed in the central-southern part of the PRD and consists of coastal-alluvial plains where continental and marine formations are interbedded with each other [15]. Continental formations are dominated by sandy fluvial deposits or gravel and compose aquifer-I. The vadose zone in unit A consists of marine sediments and is predominantly silt/clay with low permeability. Groundwater unit B is outside of unit A, where valley and interhill plains are distributed, but marine formations are missing. Continental formations in this unit compose aquifer-II. Compared to groundwater unit A, vadose zone in unit B is dominated by coarser media (e.g., sandy clay) with higher permeability. Groundwater unit C is mainly distributed in hilly areas where fractured bedrocks compose aquifer-III. Groundwater unit D is related to karst aquifers (aquifer-IV) where carbonate rocks aged from the Devonian to the Permian are common. Incomplete weathering of bedrocks overlying aquifer-III and aquifer-IV result in vadose zones in groundwater units C and D being composed predominantly of coarse media (e.g., sand, gravel). In general, groundwater in the PRD is mainly recharged by

precipitation and agricultural irrigation [16,17]. The direction of groundwater flow in the PRD is from groundwater units B and C to unit A [6].
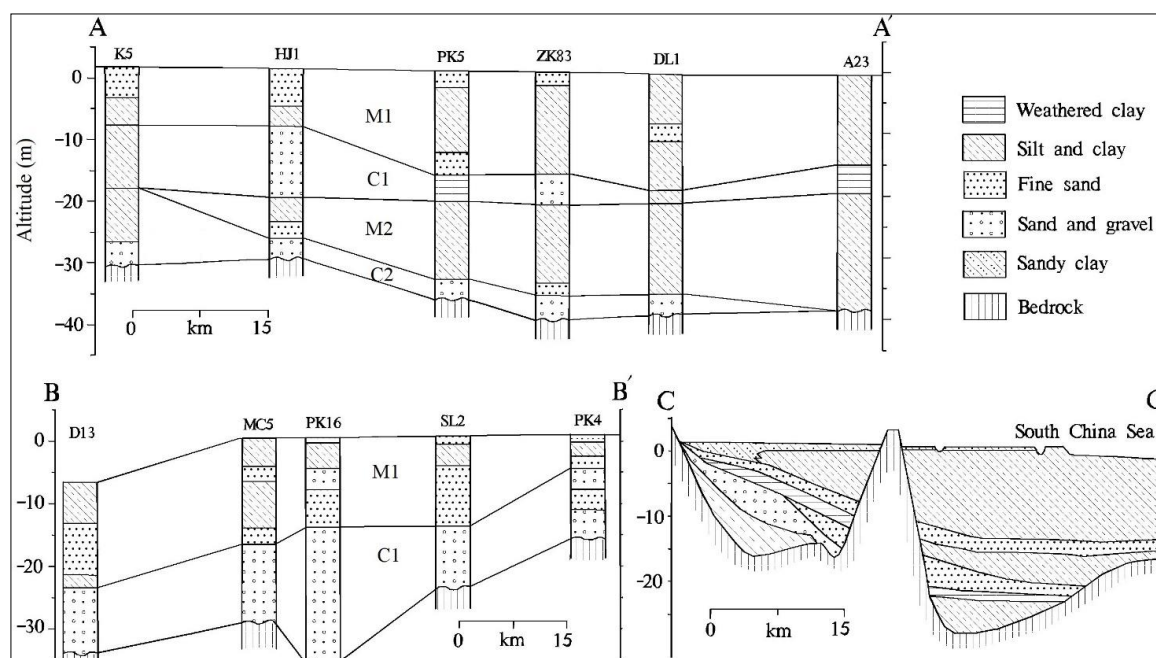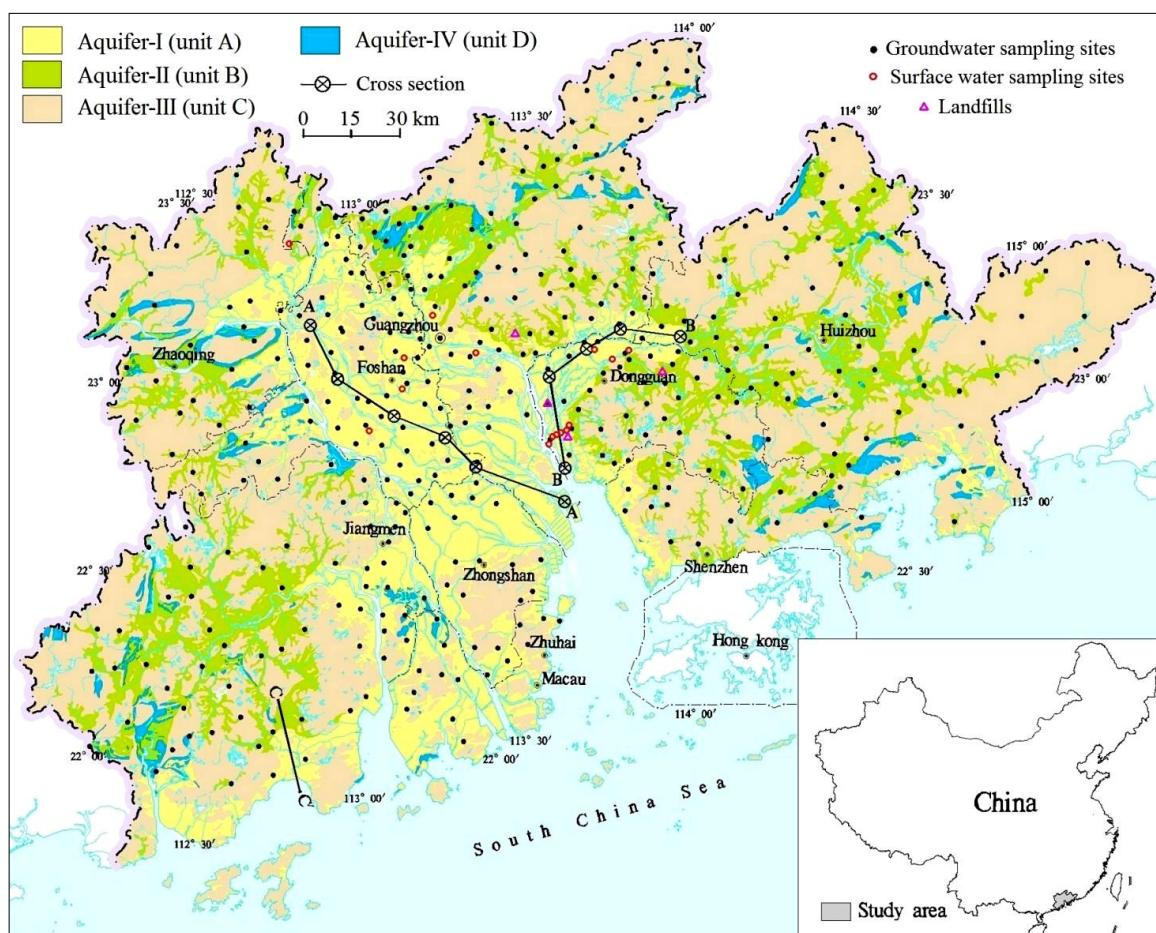

Figure 1. Hydrogeological units and sampling sites in the Pearl River Delta.

3. Materials and Methods

3.1. Sampling and Analysis

In one session, 399 groundwater samples, 15 surface water samples, and 4 leachate samples were collected in the wet season from the PRD. Among them, 124, 134, 132, and 9 sampling sites for groundwater were distributed in groundwater units A to D, respectively. Groundwater samples were collected in situ at the depth of 0.5 m below groundwater level and filtered (0.45 μm membrane) on site. Three physicochemical parameters including pH, redox potential (Eh), and dissolved oxygen (DO) were determined by a multiparameter instrument on site, and multiparametric probes in this instrument were calibrated before measurement. Another 18 parameters including total dissolved solids (TDS), chemical oxygen demand (COD), 5 cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, and NH_4^+), 8 anions (HCO_3^-, NO_3^-, SO_4^{2-}, Cl^-, Br^-, NO_2^-, PO_4^{3-}, and I^-), and 3 heavy metals (Fe, Mn, and Pb) in water samples were measured in the laboratory. Details of the analytical methods have already been described in previous works [8,10].

3.2. NBL Assessment

The method for NBL assessment used in this study was recently established by Huang et al. [8]. It consists of indicators of the oxidation capacity and Cl/Br ratios versus Cl concentrations combined with contamination markers. Briefly, this method included four steps (Figure S1). In step one, eight chemical components including NO_3^-, NO_2^-, PO_4^{3-}, Pb, TDS, Na, NH_4^+, and COD were selected as the candidate contamination markers in groundwater in the PRD owing to the anthropogenic contamination, and contamination markers in various groundwater units were selected by using a hierarchical cluster analysis (HCA) (Figure S2). In step two, contaminated groundwaters were identified from original datasets by using plots of Cl/Br mass ratios versus Cl concentrations combined with contamination markers, and the remaining datasets were denoted as CBM datasets (Figure S3). In step three, groundwaters remaining in the CBM datasets were removed by using the oxidation capacity method, and the remaining datasets after this step were denoted as the PS datasets (Figure S4). In step four, outliers in the PS datasets were deleted by Grubbs' test, and the maximum values in various groundwater units in residual datasets were denoted as NBLs. The details of the above method are shown in Section 3.2 of the Supplementary Materials.

3.3. Principal Components Analysis

Principal component analysis (PCA) is often used to reduce high-dimensional hydrochemical datasets, extract the main factors that control groundwater chemistry, and thereby deduce the geochemical processes indicated by these factors [18–20]. The present study used PCA with SPSS® version 23.0 software to extract PCs that control NBL-I and NBL-NH_4 from residual datasets in various groundwater units. Varimax method was used for rotation of PCs, and eigenvalues > 1 of PCs were retained for analyses. The terms of strong, moderate, and weak refer to the absolute PC loadings of >0.75, 0.75–0.5, and 0.5–0.3, respectively [10].

4. Results

4.1. NBLs of Groundwater I^- and NH_4^+ in the PRD

More than 60% of contaminated groundwaters in the PRD were excluded according to their oxidation capacities and Cl/Br mass ratios versus Cl concentrations (Figures S3 and S4). Then, groundwater NBL-I^- and NBL-NH_4^+ in various units were identified by the Grubbs' test ($\alpha = 0.01$). As shown in Figure 2, the groundwater NBL-I^- in unit A was 0.14 mg/L and was 2.5 times, 3.3 times, and 5.6 times greater than that in units B to D, respectively. Note that the NBL-I^- in groundwater unit A was significantly higher than the allowable limit (0.08 mg/L) of I^- in groundwater recommended by the Chinese government [10], while the NBLs-I^- in other groundwater units were not. This indicates that I^- is likely a more common geogenic contaminant in groundwater unit A rather than it is in other units in the

PRD. Similarly, the groundwater NBL-NH_4^+ in unit A was 0.32 mg/L and was also more than 2 times greater than that in other units. Note that groundwater NBLs-NH_4^+ in all units of the PRD were below the allowable limit (0.5 mg/L as N) of NH_4^+ in groundwater recommended by the Chinese government [11].
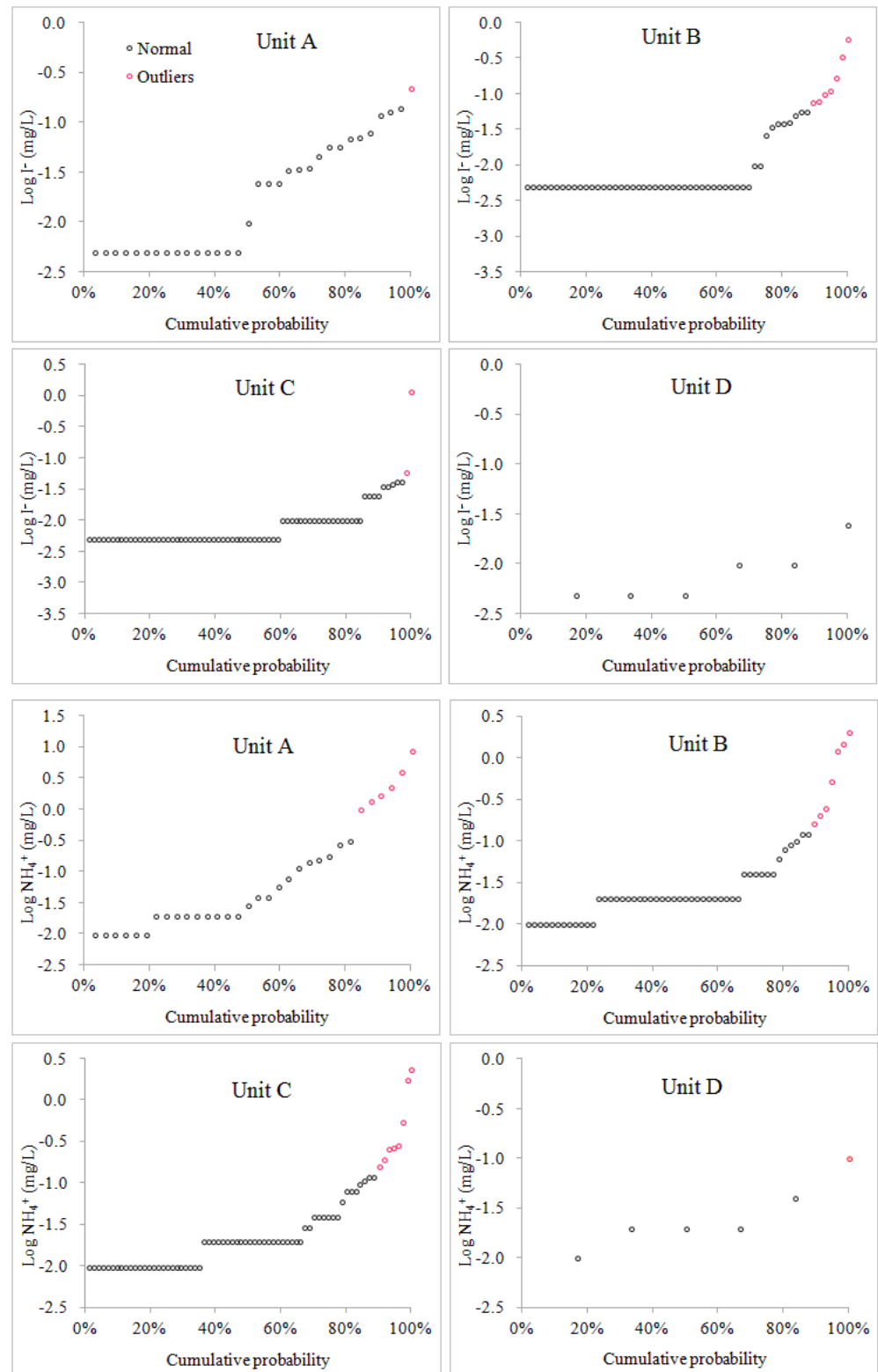

Figure 2. Outliers in the OXC datasets in various groundwater units tested by Grubbs' test.

4.2. Hydrogeochemical Characteristics in Residual Datasets in Various Aquifers

In this study, we focused on the differences of the hydrogeochemical characteristics between unit A and other units because of the much higher NBL-I^- and NBL-NH_4^+ in aquifer-I than in the other aquifers (Figure 2). In the residual datasets for both of NBL-I^- and NBL-NH_4^+, the mean pH values in groundwater unit A were higher than those in other units (Table 1), indicating that the groundwater in unit A had less acidic conditions than did the other units. Mean values of oxidation indicators including Eh, DO, and NO_3^- in groundwater unit A were significantly lower than those in the other units (Table 1). On the contrary, the mean concentrations of reduction indicators including NO_2^-, Fe, and Mn in groundwater unit A were more than 2 times those of other units (Table 1). These results indicate that the groundwater in unit A was a relatively reducing environment in comparison with that in other units. Moreover, the mean concentrations of Na^+, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, Cl^-, and PO_4^{3-} in groundwater unit A were also about 2 or more times greater than those in the other units (Table 1). This indicates that the groundwater in unit A was enriched with Na^+, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, Cl^-, and PO_4^{3-} in comparison with the other units.

Table 1. Mean concentrations of physicochemical parameters in residual datasets in various groundwater units.

NBL Datasets		NH_4^+				I^-			
		Unit A	Unit B	Unit C	Unit D	Unit A	Unit B	Unit C	Unit D
pH		6.21	5.89	5.78	5.79	6.37	5.96	5.84	5.87
Eh	mV	70	92	91	103	67	86	83	92
DO		3.62	3.92	4.26	3.77	3.74	3.87	4.24	3.45
COD		1.40	1.17	1.17	1.00	1.62	1.25	1.33	1.13
TDS		286	159	103	94	339	164	108	127
K^+		9.0	7.3	4.3	3.2	9.8	7.3	4.1	5.3
Na^+		22.2	10.5	6.2	5.5	22.5	11.0	6.2	7.0
Ca^{2+}		39.5	21.1	12.8	14.1	48.4	21.6	13.8	18.4
Mg^{2+}		6.2	2.9	1.7	1.8	7.6	2.9	1.8	2.6
HCO_3^-		134.2	65.4	41.5	36.0	176.5	69.6	44.5	55.9
Cl^-	mg/L	38.4	18.1	10.2	10.1	37.4	17.9	9.9	12.0
SO_4^{2-}		16.5	6.8	2.9	6.6	16.1	6.3	3.5	7.4
NO_3^-		8.7	14.3	10.0	10.5	7.1	13.8	10.1	10.3
NO_2^-		0.11	0.01	0.01	0.02	0.38	0.04	0.02	0.02
I^-		0.031	0.022	0.004	0.005	0.031	0.007	0.004	0.004
PO_4^{3-}		0.55	0.07	0.06	0.13	0.54	0.11	0.07	0.11
NH_4^+		0.05	0.02	0.02	0.02	0.66	0.11	0.10	0.03
Fe		0.24	0.10	0.11	0.06	0.60	0.15	0.22	0.07
Mn		0.30	0.08	0.04	0.03	0.50	0.10	0.07	0.06
Pb		0.001	0.002	0.002	0.001	0.001	0.002	0.003	0.006

4.3. Relationships between I^-/NH_4^+ and Other Components in Groundwater Unit A in the Residual Datasets

Correlations between groundwater I^-/NH_4^+ and other components in unit A were investigated because of the higher NBL-I^- and NBL-NH_4^+ in groundwater unit A than those in the other units (Figure 2). As shown in Table 2, in the residual dataset of unit A, the groundwater I^- concentrations had significantly positive correlations with concentrations of Na^+, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, Cl^-, TDS, NH_4^+, Fe, and Mn, but negative correlations with values of DO and NO_3^-. By contrast, groundwater NH_4^+ concentrations in the residual dataset of unit A had positive correlations with concentrations of NO_2^- and Fe (Table 2). The relationships between I^-/NH_4^+ and other components in groundwater unit A were further investigated by the PCA. As shown in Table 3, in the residual dataset for NBL-I^-, 17 variables were combined to produce 5 significant PCs with eigenvalues > 1, which explained 85.15% of the variance in the hydrochemical dataset. Both PC1 and PC3

were related to I^-. Specifically, the PC1 had strong positive loadings with Cl^-, Na^+, Mg^{2+}, COD, and TDS; a moderate positive loading with HCO_3^-; a weak positive loading with I^-; and a weak negative loading with DO. The PC3 demonstrated strong positive loadings with NH_4^+ and Fe, a moderate positive loading with I^-, and weak negative loadings with NO_3^- and DO. By contrast, in the residual dataset for NBL-NH_4^+, four PCs with eigenvalues > 1 were extracted from the PCA, and the cumulative variance by the four PCs was 80.55% (Table 3). The PC3 was related to NH_4^+. It had strong positive loadings with NH_4^+ and Fe, and a weak negative loading with NO_3^-.

Table 2. Correlation coefficients of concentrations of I^-/NH_4^+ and other chemicals in groundwater unit A.

NBL Datasets	I^-	NH_4^+	NBL Datasets	I^-	NH_4^+
pH	0.283	0.334	NO_3^-	−0.369 *	−0.371
DO	−0.412 *	−0.068	PO_4^{3-}	−0.001	0.043
Eh	−0.236	−0.222	Pb	−0.181	−0.060
K^+	0.173	−0.049	NO_2^-	−0.090	0.610 **
Na^+	0.480 **	0.257	COD	0.309	0.356
Ca^{2+}	0.518 **	0.305	Fe	0.386 *	0.844 **
Mg^{2+}	0.566 **	0.362	TDS	0.588 **	0.314
HCO_3^-	0.561 **	0.288	Mn	0.388 *	0.042
Cl^-	0.471 **	0.251	NH_4^+	0.514 **	1
SO_4^{2-}	0.078	0.367	I^-	1	0.064

*: significance level at $p < 0.05$; **: significance level at $p < 0.01$.

Table 3. Principal component (PC) loadings for groundwater physicochemical parameters in unit A in the residual datasets.

Physicochemical Parameters	PCs—Residual Dataset for I^-					Physicochemical Parameters	PCs—Residual Dataset for NH_4^+			
	PC1	PC2	PC3	PC4	PC5		PC1	PC2	PC3	PC4
Cl^-	*0.974*	0.052	−0.024	0.018	0.014	Cl^-	*0.969*	0.097	0.052	0.082
Na^+	*0.973*	0.129	−0.030	0.012	0.011	Na^+	*0.965*	0.150	0.046	0.029
Mg^{2+}	*0.840*	0.458	0.088	0.182	−0.034	Mg^{2+}	*0.856*	0.424	0.152	0.000
COD	*0.820*	0.214	−0.012	0.102	0.318	COD	*0.851*	0.347	0.181	0.146
TDS	*0.720*	0.616	0.149	0.181	0.133	TDS	*0.721*	0.671	0.072	−0.001
Ca^{2+}	0.417	*0.807*	0.159	0.253	0.101	I^-	*0.567*	−0.035	−0.062	−0.074
SO_4^{2-}	0.035	*0.791*	−0.277	−0.109	0.341	DO	*−0.482*	−0.370	0.036	0.419
Eh	−0.172	*−0.767*	−0.067	0.353	0.343	SO_4^{2-}	−0.042	*0.876*	0.217	−0.139
HCO_3^-	0.504	*0.738*	0.238	0.245	0.110	pH	0.119	*0.871*	0.222	0.086
pH	0.137	*0.714*	0.038	0.424	0.304	Ca^{2+}	0.395	*0.862*	0.093	−0.064
NO_3^-	−0.152	*−0.484*	−0.351	−0.168	−0.065	HCO_3^-	0.507	*0.815*	0.074	−0.051
DO	−0.455	*−0.472*	−0.353	0.348	−0.178	K^+	0.135	*0.691*	−0.204	0.430
NH_4^+	−0.040	0.026	*0.955*	0.130	0.048	NO_3^-	−0.161	*−0.431*	−0.415	0.069
Fe	−0.069	0.020	*0.925*	−0.012	0.207	Fe	−0.101	0.059	*0.939*	0.026
I^-	0.476	0.250	*0.573*	0.211	−0.188	NH_4^+	0.187	0.149	*0.932*	−0.041
Mn	0.189	0.143	0.197	*0.902*	0.010	Mn	0.205	0.283	0.009	*0.829*
K^+	0.173	0.225	0.219	0.021	*0.868*	Eh	−0.186	−0.515	−0.055	*0.732*
Eigenvalue	4.80	4.17	2.63	1.54	1.34		5.00	4.89	2.15	1.66
Explained variance (%)	28.23	24.51	15.46	9.07	7.87		29.40	28.75	12.64	9.76
Cumulative % of variance	28.23	52.75	68.21	77.28	85.15		29.40	58.15	70.79	80.55

Bold and italic numbers—maximum absolute PC loading of one parameter.

4.4. Effectiveness of the Used Method

In original datasets, the differences between the maximum values of groundwater I^- and NH_4^+ at different land-use types were significant (Table S1). For example, the maximum value of I^- in unit A at UA was 3 times that at AA, and the maximum values of I^- in unit B at UA and PUA were more than 2 times that at RA (Table S1). Similarly, the maximum values of NH_4^+ in unit B at UA and PUA were more than 2 times that at AA and more than 10 times that at RA (Table S1). These findings indicate that groundwater I^- and NH_4^+ concentrations at various land-use types were influenced by human activities.

By contrast, if the used method has utility, in residual datasets, the differences between the maximum values of groundwater I^- and NH_4^+ at different land-use types within a same unit would be insignificant in comparison with those in the original datasets because groundwaters impacted by anthropogenic inputs are excluded via the method used [8,14].

Correspondingly, in the residual datasets, the differences between maximum values of I^- at various land-use types in both the A and B units were all within 0.4 times. Similarly, the differences between maximum values of NH_4^+ at various land-use types in both the A and B units were all within 0.8 times (except RA in unit B). These findings indicate that the differences of maximum values at various land-use types in residual datasets are more insignificant than those in the original datasets and that human activities have little impact on groundwater I^- and NH_4^+ concentrations at different land-use types in residual datasets in comparison with those in the original datasets. Therefore, the preselection method used in this study is effective in evaluating the NBLs of groundwater I^- and NH_4^+ in urbanized areas.

5. Discussion

In this study, we focused on factors controlling groundwater NBLs of I^-/NH_4^+ in unit A rather than in other units due to the much higher NBLs-I^-/NH_4^+ in groundwater unit A relative to those in the other units (Figure 2).

5.1. Main Sources for NBLs-I^-/NH_4^+ in Groundwater Unit A

Generally, after the removal of anthropogenic sources, chemical components in groundwater are from the precipitation, the natural release of sediments in vadose zones and aquifers, and the interaction with other water bodies [21]. Firstly, the iodine in rainfall is commonly at low levels of <0.01 mg/L and is less than one-tenth of groundwater NBL-I^- in unit A (Figure 2) [22]. This indicates that the precipitation has little contribution to the higher NBL-I^- in groundwater unit A compared to other units. By contrast, the precipitation may be an important source for groundwater NBL-NH_4^+ because nitrogen deposition is one of the major components in the rainfall in the PRD [23]. However, in the residual datasets, groundwaters with high levels of NH_4^+ (>0.2 mg/L) were distributed in areas where acid rain pH is relatively high and acid rain frequency is relatively low (representing low nitrogen deposition) (Figure 3). Thus, the contribution of the precipitation for higher NBL-NH_4^+ in groundwater unit A compared to that in other units is also negligible. Secondly, the natural release from the iodine/nitrogen-rich organic matter in the vadose zone is likely to be the major source for the higher NBLs-I^-/NH_4^+ in groundwater unit A compared to those in other units because the vadose zone overlaying aquifer-I consists of marine sediments where organic-iodine and organic-nitrogen are abundant and the mineralization of organic-iodine/nitrogen results in the release of I^-/NH_4^+, whereas iodine/nitrogen-rich marine sediments are missing in the vadose zones overlaying other aquifers [24,25]. Thirdly, the natural release from iodine-rich minerals (e.g., iodine-loaded Fe/Mn oxides) in aquifer sediments is also probably another major contributor to the higher NBLs-I^-/NH_4^+ in groundwater unit A compared to those in the other units because Fe/Mn (oxyhydr) oxides are often the primary reservoirs for coastal sediment iodine owing to their high adsorption capacities for iodine [26], and I^- concentration was positively correlated with concentrations of Fe and Mn in groundwater unit A (Table 2). Fourthly, the interaction with other water bodies may be another important source for shallow groundwater I^-/NH_4^+ in unit A. This is can be explained by two phenomena. One is that deep groundwater in unit A is often enriched with high concentrations of geogenic I^-/NH_4^+ and salinity [24], and these I/NH_4-rich deep groundwaters in coastal areas are sometimes pumped out for farming marine animals (e.g., shrimp), thereby contaminating the shallow groundwater via infiltration [12]. Another is that groundwaters with high levels of NH_4^+ (>0.2 mg/L) in the residual datasets were distributed in the river network areas where surface water was enriched with NH_4^+ (Figure 3) [11], and the interaction between shallow groundwater and surface water often occurs in river network areas of the PRD [12]. By contrast, groundwaters with high levels of I^- (>0.08 mg/L) in residual the datasets were independent of the river network area (Figure 4), and uncontaminated surface water was commonly at low levels of I^- (<0.01 mg/L) [12]. Furthermore, other natural water bodies (e.g., sea water) that interact with the shallow groundwater of the PRD are generally poor in

I^- (<0.02 mg/L) and NH_4^+ (<0.1 mg/L) [10,12]. This suggests that I-rich deep groundwater is a more important source for the higher NBLs-I^- in groundwater unit A relative to other units, but it is not the main one; meanwhile, NH_4-rich deep groundwater and surface water are two important sources for the higher NBL-NH_4^+ in groundwater unit A compared with other units.

5.2. Main Driving Forces for NBLs-I^-/NH_4^+ in Groundwater Unit A

A few studies reported that the mineralization of organic matter in marine sediments is one of the major factors controlling the occurrence of I/NH_4-rich shallow groundwater in the PRD [10,11]. This is also probably the major geogenic force for the higher NBLs-I^-/NH_4^+ in groundwater unit A compared with the other units, which can be explained by the following. Firstly, as mentioned above, the Quaternary marine formation overlaying aquifer-I is enriched with organic matter such as organic-iodine and organic-nitrogen, whereas the Quaternary marine formation is missing in other units (Figure 1) [24]. Secondly, groundwater unit A was shown to be a more reducing environment in both the vadose zone and aquifer in comparison with other units because the vadose zone in unit A consists of marine sediments dominated by silt/clay with low permeability, whereas the vadose zones in other units are dominated by coarser media (e.g., sandy clay, sand) with higher permeability. Similarly, reduction indicators (e.g., NO_2^-, Fe, and Mn) in aquifer-I were shown to have higher concentrations than in the other aquifers, and oxidation indicators (e.g., Eh, DO, and NO_3^-) in aquifer-I had lower values than those in the other aquifers (Table 1). Thirdly, Cl^-, Na^+, Mg^{2+}, TDS, NH_4^+, Fe, HCO_3^-, and I^- in groundwater unit A had the same source or similar geochemical behaviors because the PC1 had positive loadings of Cl^-, Na^+, Mg^{2+}, TDS, HCO_3^-, and I^-, while PC3 had positive loadings of NH_4^+, Fe, and I^- (Table 3). Similarly, NH_4^+ and Fe in groundwater unit A had the same source or similar geochemical behaviors because the PC1 had positive loadings of NH_4^+ and Fe (Table 3). Fourthly, fine-grained marine sediments in Asian deltas often contain trapped seawater enriched with Cl^-, Na, Mg, and TDS [27]. Therefore, the major driving forces controlling higher NBLs-I^-/NH_4^+ in groundwater unit A compared to other units can be outlined as follows. In a reducing environment, HCO_3^- and soluble I^- result from the mineralization of organic-iodine in the Quaternary marine formation, and then Cl^-, Na^+, and Mg^{2+} in trapped seawater accompanied with HCO_3^- and soluble I^- in the marine formation enter into aquifer-I via water flow. This induces the reductive dissolution of I-loaded Fe (oxyhydr) oxides and is accompanied by the release of I^- in aquifer sediments due to the influx of water with reducing conditions. Finally, groundwater in unit A is enriched with I^- and related components, such as Cl^-, Na^+, Mg^{2+}, Fe, and HCO_3^- (Table 1). This is also supported by the evidence that groundwater I^- concentration was positively correlated with concentrations of Cl^-, Na^+, Mg^{2+}, Fe, and HCO_3^- (Table 2). Similarly, the mineralization of organic-nitrogen in the marine formation also leads to an increase in soluble NH_4^+, which enters into aquifer-I and is accompanied by the infiltrated water with reducing conditions. This triggers the reductive dissolution of Fe (oxyhydr) oxides and the denitrification in aquifer sediments because the PC3 has positive loading with NH_4^+ but negative loading with NO_3^- (Table 3). Finally, groundwater in unit A is enriched with NH_4^+ and Fe but is NO_3^- poor (Table 1).
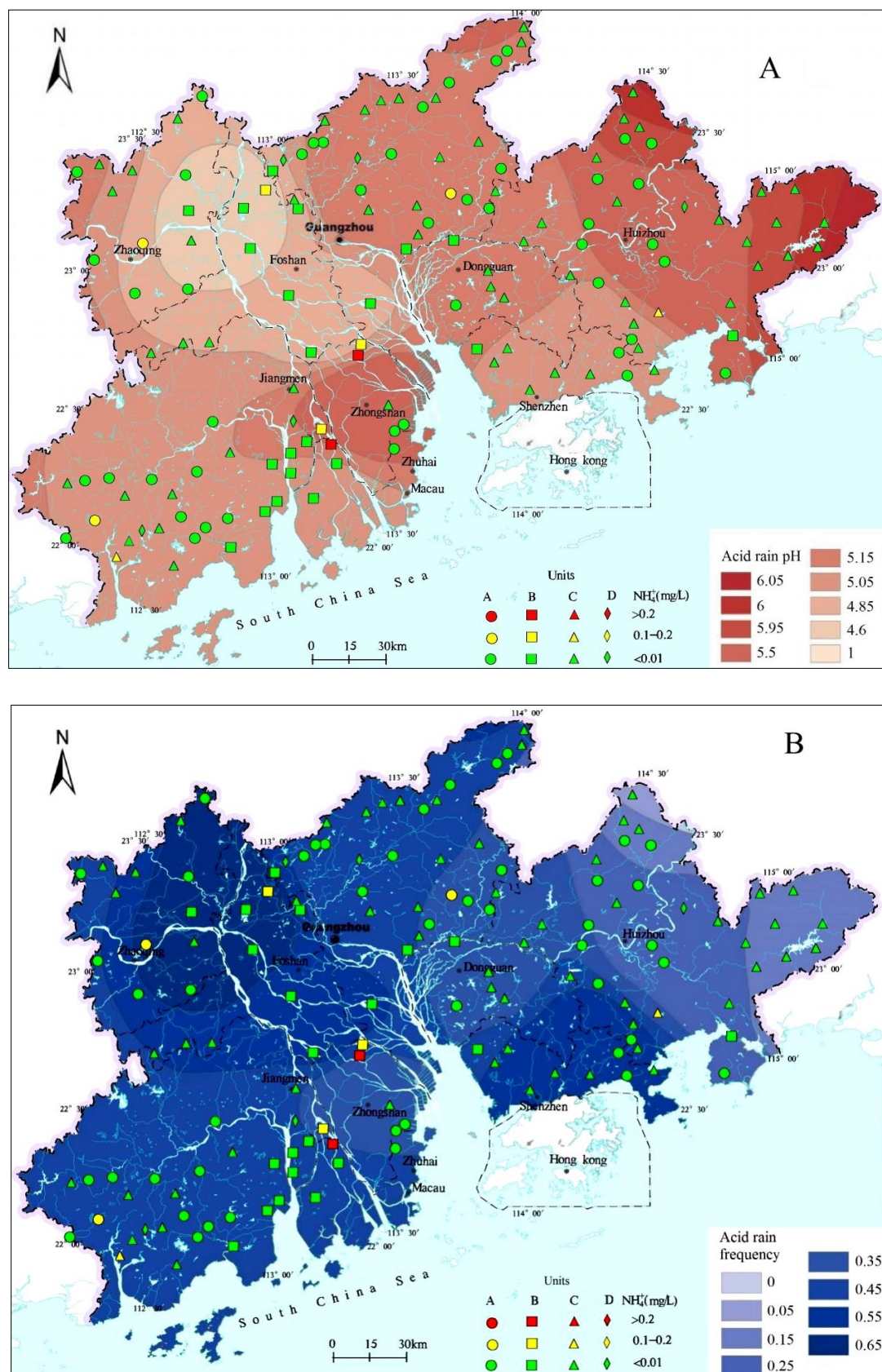
Figure 3. Distribution of NH$_4^+$ in various groundwater units in residual datasets and acid rain data for the Pearl River Delta (data of acid rain from Liu et al. [23]). (**A**) is acid rain pH, and (**B**) is acid rain frequency.
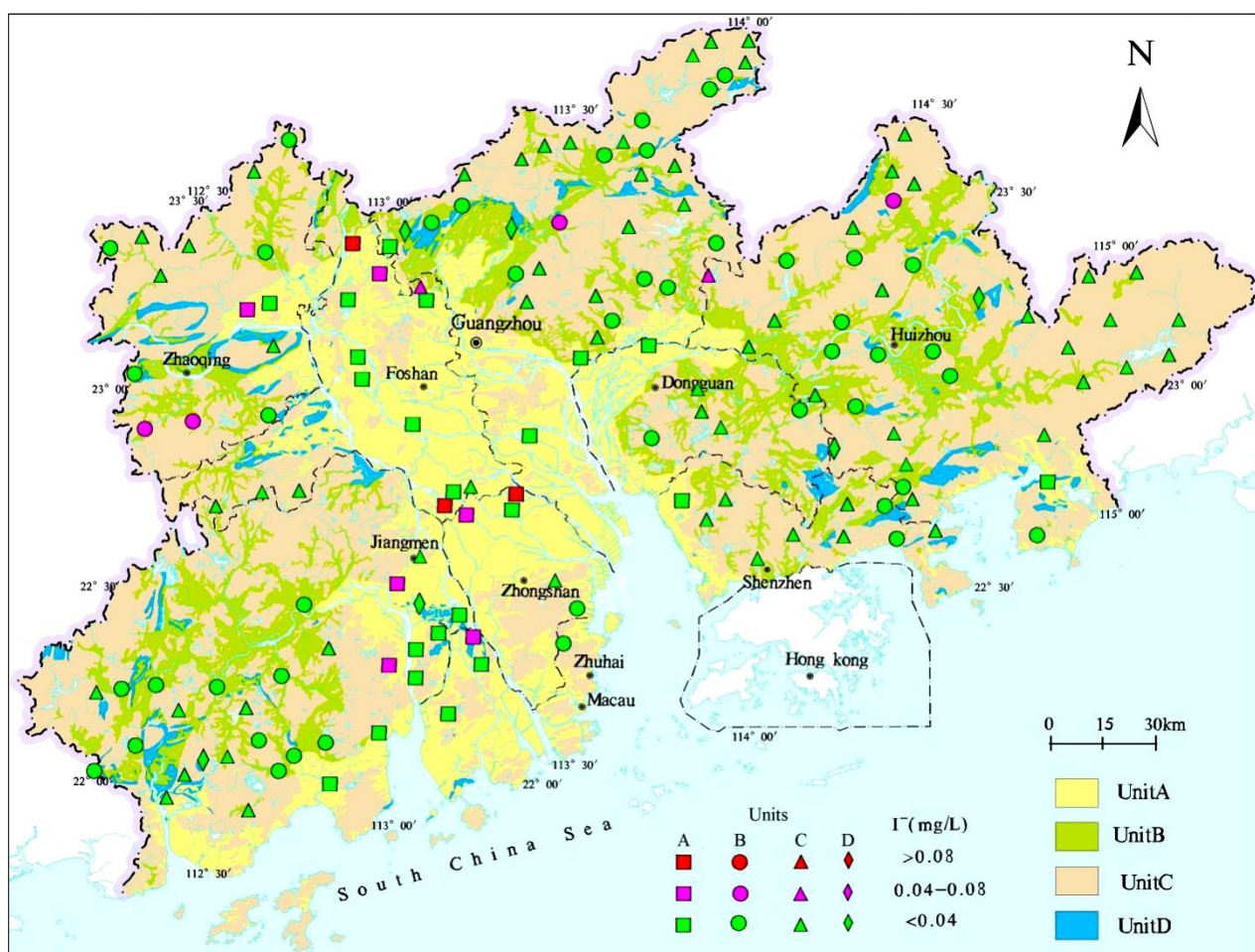
Figure 4. Distribution of I⁻ in various groundwater units in the residual datasets.

6. Conclusions

The NBLs of I⁻ and NH_4^+ in the shallow groundwater of the PRD was assessed by a preselection method with Grubbs' test. Here, the preselection method consisted of Cl/Br mass ratios versus Cl concentrations and the oxidation capacity. In the evaluation of four groundwater units, NBL-I⁻ in groundwater unit A was 0.14 mg/L, which is nearly 2 times greater than the allowable limit of I⁻ in groundwater recommended by the Chinese government, and was 2.5 times, 3.3 times, and 5.6 times higher than those in groundwater units B to D, respectively. The NBL-NH_4^+ in groundwater unit A was 0.32 mg/L, which was also 2 times greater than that in the other groundwater units.

The natural release of I⁻ from both of organic matter in the vadose zone and iodine-rich minerals (e.g., iodine-loaded Fe/Mn oxides) in aquifer sediments are two major sources for the higher NBLs-I⁻ in groundwater unit A compared to other units. Additionally, I-rich deep groundwater is another important source but is not the main one. Rather, the occurrence of NH_4^+ from organic matter in the vadose zone is the major source for the higher NBLs-NH_4^+ in groundwater unit A compared to other units. In addition, NH_4-rich deep groundwater and surface water are two other important sources for the higher NBL-NH_4^+ in groundwater unit A.

Soluble I⁻ results from the mineralization of organic-iodine in the Quaternary marine formation, and the release of I⁻ accompanied by reductive dissolution of I⁻-loaded Fe (oxyhydr) oxides in aquifer sediments is the main driving force controlling the higher NBL-I⁻ in groundwater unit A relative to other units. By contrast, soluble NH_4^+ resulting from the mineralization of organic-nitrogen in marine formation entering into aquifer-I is

the main driving force controlling the higher NBL-NH_4^+ in groundwater unit A relative to other units.

In the future, we will use these NBLs to evaluate the I^- and NH_4^+ pollution status in groundwater of the PRD and to provide suggestions for the prevention of groundwater I^- and NH_4^+ pollution. In addition, we will monitor groundwater quality once again and verify these NBLs by using new hydrochemical data.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14223737/s1, Table S1: Maximum concentrations of groundwater I- and NH4+ in units A and B at different land use in original and residual datasets; Figure S1: Procedure of the NBL assessment from [8]; Figure S2: Cl/Br mass ratios and candidate contaminated-markers in various groundwater units in the Pearl River Delta was grouped by the hierarchical cluster analysis (Ward's method and Euclidean distance); Figure S3: Plots of Cl/Br mass ratios versus Cl concentrations combining with concentrations of contaminated-markers in various groundwater units in the Pearl River Delta [8]; Figure S4: Concentrations of NO_3 and SO_4 as well as oxidation capacity in groundwaters in CBM datasets [8].

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