

Abnormally High Ammonium of Natural Origin in a Coastal Aquifer-Aquitard System in the Pearl River Delta, China

JIU JIMMY JIAO,^{*,†} YA WANG,[†]
JOHN A. CHERRY,[‡] XUSHENG WANG,[§]
BINGFA ZHI,^{||} HAIYAN DU,^{||} AND
DONGGUANG WEN[⊥]

Department of Earth Sciences, The University of Hong Kong, Hong Kong, P R China, School of Engineering, University of Guelph, Guelph, ON N1G 2W1, Canada, School of Water Resources & Environment, China University of Geosciences, 29 Xueyuan Road, Beijing, China, 100083, Guangdong Geological Survey, 739 East Dongfeng Road, Guangdong, China, 510080, and China Geological Survey, 45 Fuwai Street, Beijing, China, 100037

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High-nitrogen loadings of rivers and aquifers systems are a major concern because of potential effects on human health and water quality impacts such as eutrophication of lakes and coastal zones. This nitrogen enrichment is commonly attributed to anthropogenic sources such as sewage and agricultural and industrial wastes. The aims of this study were to delineate spatial distribution of groundwater ammonium in the coastal aquifer system in Pearl River Delta (PRD), China and to identify the origin of the abnormally high ammonium. A total of 40 boreholes were drilled to collect core samples of the aquitard and groundwater samples in the basal aquifer. The core samples were used for extraction of pore water for centrifugation and bulk chemical analyses in laboratory. Unlike previous studies which focused mainly on the aquifer, this study treated the aquifer-aquitard system as a hydrogeochemical continuum. The results show that the aquifer-aquitard system contains an exceptionally large total ammonium mass. Ammonium occurred at concentrations up to 390 mg/L in the basal sand Pleistocene aquifer 20–50 m deep, the largest concentration reported for groundwater globally. This ammonium was natural, areally extensive (1600 km²) and originated in the overlying Holocene–Pleistocene aquitard and entered the aquifer by groundwater transport and diffusion. Total ammonium in the aquifer (190×10^6 kg) was exceeded by total ammonium in the aquitard (8600×10^6 kg) by a factor of 45. Much organic nitrogen remained in the aquitard available for conversion to ammonium. This natural ammonium in the aquifer was slowly transported into the PRD river channels and the estuary of the South China Sea. The rate of this contribution will likely be greatly increased by sand dredging in the river channels and

estuary. Although the ammonium in PRD groundwater occurred in the largest concentrations and mass reported globally, the literature shows no reports of other delta aquitards having been examined for ammonium occurrence and therefore abundant ammonium formed in aquitards rich in organic matter may not be uncommon and this “geologic” source of ammonium may present a large and hitherto unappreciated source of nitrogen discharging to surface waters.

1. Introduction

In the Pearl River System, which is China’s third longest river (Figure 1A), there is much use of the abundant surface water resources in the multichannel river network. However, the groundwater beneath the delta is much less exploited and consequently groundwater studies are limited. The Pearl River Delta (PRD) has seen rapid population increase and economic growth particularly since 1980. Excess nitrogen loading in the river system (1–3) is a major concern because of its ecological and environmental impacts, such as deterioration of water quality and eutrophication in coastal areas. This nitrogen enrichment has been commonly attributed to anthropogenic sources such as sewage and agricultural and industrial wastes (1, 2), but there have been no studies on possible natural sources of nitrogen in the PRD.

In the 1970’s, local farmers were too poor to afford synthetic fertilizers. Instead, they found ammonium-rich water, locally known as “fertile water”, in the basal sand aquifer about 20–50 m below ground surface (3). This groundwater is fertile because, after being diluted significantly, it was used to fertilize agricultural fields. However, this practice did not last long because the fertile water is usually associated with high salinity, causing irrigated fields soon to become saline (3). In 1971, the Guangdong Hydrogeology Team confirmed that groundwater in the basal aquifer in a few counties in the PRD contained very high ammonium (3).

Natural nitrogen in the subsurface has been the target of several previous investigations. Aquifer with elevated ammonium contents of natural origin has been noted in aquifer systems in different parts of the world, such as Iowa (4) and Illinois (5, 6) in the U.S., La Laguna Region, Northern Mexico (7), the Bengal Basin in Bangladesh (8), West Bengal in India, the Hanoi area in Vietnam (9), Nepal, and Hungary (8). The maximum ammonium concentration among these sites is 48 mg/L (Hanoi), which is much less than the ammonium concentrations in the PRD.

The only study focused on the elevated natural ammonium (>2 mg/L) was done in the regional aquifer in Iowa and Illinois where aquifer wells were sampled (4–6). Different explanations were given on the sources of ammonium (4, 5), suggesting that the precise mechanisms for the elevated ammonium groundwater in Iowa and Illinois remain unclear. In a study examining the origin of nitrogen in rivers, geological source of nitrogen from bedrock has been recognized (10).

The aims of this study were to investigate spatial distribution of groundwater ammonium in the coastal aquifer system in Pearl River Delta and to explore the origin of the abnormally high ammonium. This study went beyond the investigation of high ammonium in the aquifer by including the overlying aquitard in the search for the origin of the ammonium. The study demonstrated that the aquitard-aquifer system in PRD formed a continuum of ammonium rich water and the high ammonium was from a natural geological source.

* Corresponding author phone: (852)2857 8246; fax: (852) 2517 6912; e-mail: jjiao@hku.hk.

† The University of Hong Kong.

‡ University of Guelph.

§ China University of Geosciences.

|| Guangdong Geological Survey.

⊥ China Geological Survey.

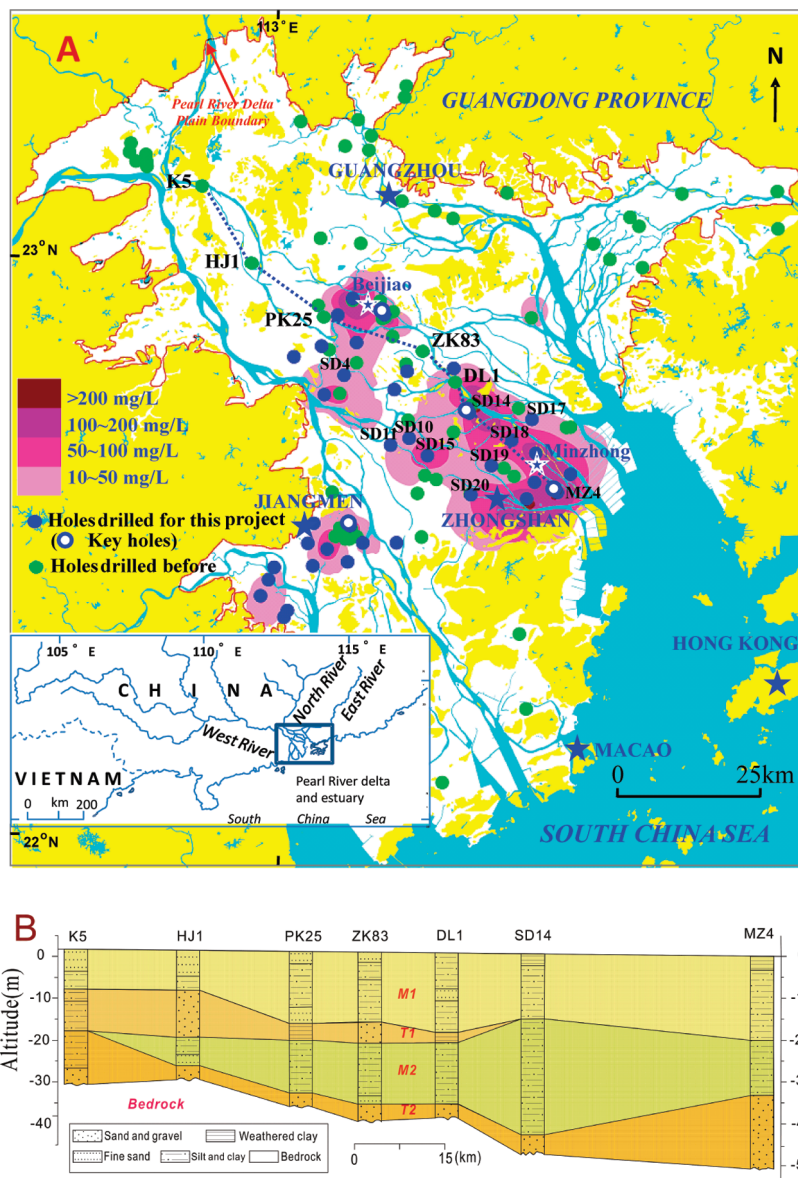


FIGURE 1. (A) The Pearl River Delta with ammonium-rich groundwater distribution ($\text{NH}_4^+ > 10 \text{ mg/L}$). The white area is a fluvial and alluvial platform about 5–10 m in elevation and the yellow areas are mountain areas with higher elevation. (B) Simplified geological section from K5 to MZ4. The part from K5 to DL1 is based on ref 15.

2. Site Background

The PRD is under a monsoonal climate. At present the annual average precipitation is between 1600 and 2000 mm. The annual average temperature is around 22 °C. The warm and humid conditions over the catchment support tropical to subtropical mixed evergreen and deciduous forests (11, 12).

The Quaternary of PRD and its evolutionary history were extensively studied (13–15). The delta deposits mainly consist of four stratigraphic units (Figure 1B): an old terrestrial unit (or hereafter called T2, which was formed prior to marine isotope stage (MIS) 5), an old marine unit (M2 in MIS 5), a younger terrestrial unit (T1 in MIS 4–2) and a younger marine unit (M1 in MIS 1). The younger marine unit was formed during the Holocene and the other three units were formed during the Pleistocene. T2 is dominated by sand and gravel and becomes the basal aquifer. T1 can be sandy fluvial deposits or clayed silt weathered from the in situ materials during the last glacial period (14) and becomes a local intermediate aquifer when it is sandy. In many places the old marine unit and the younger terrestrial unit are missing or decomposed into clay when the sea-level regressed during

the last glacial period. There is a thin layer of disturbed sandy sediments or agricultural soil near the ground surface, which is not shown in Figure 1B for simplification. A detailed discussion on the progradation of the delta can be found in (12).

At about 7000 years BP, the transgression reached its maximum and the coastline at this period was much farther north and was probably in the suburb of Guangzhou City (12). The younger Holocene marine deposits with thickness varying from 5 to 20 m, was mainly deposited between 7000 and 2000 yrs BP (12). During this period, the temperature first increased and then remained high (16), and the Asian Monsoon was relatively strong (17). The heavy ancient forests developed in the wetland around the then coastal areas at around 4000 yrs BP (16). As a result, the content of organic matter in the Holocene deposits is greater than modern sediments and the organic carbon, chloroform bitumen A and hydrocarbon in the Holocene sediments in PRD are greater than those in other areas in East China (18). The Holocene depositional environment in PRD was classified as deltaic progradation under stable sea level conditions and

the Holocene sediment ecology was dominated by brackish water diatoms and foraminifera (15).

Although much of the groundwater in the Pleistocene sand aquifer in areas southeast Beijiao (Figure 1A) is undrinkable because of salinity, nevertheless it is pumped for various other purposes. For example, farmers deliberately pump saline groundwater from the basal aquifer for fish and lobster aquaculture. The aquifer system may be also disturbed by large-scale sand dredging along major river channels for construction purposes and land reclamation in the past 20 years which shortens the flow path from groundwater to surface water and enhances groundwater circulation through the aquifer system.

3. Materials and Methods

3.1. Field Study and Sample Collection. This study acquired data from both the aquifer and overlying aquitard using wells and cores. Boreholes were drilled at 18 and 22 locations in 2007–2008 and 2008–2009, respectively. At each of these locations, cores were collected through the aquitard into the top of aquifer, and then, with temporary drill casing in the hole, groundwater samples were pumped from the aquifer. From the interior of cores, samples were collected for chemical analyses for two purposes: one for extraction of pore water by centrifugation and the other for bulk-chemical analyses. Four core holes subject to most comprehensive studies (key holes) were drilled using percussion method without drilling liquid. At Minzhong key hole site (Figure 1A), 8 drive-point piezometers were installed in a cluster to determine hydraulic head and provide groundwater samples for hydrogeochemical studies.

About 1000 sediment samples and 300 groundwater samples from the basal aquifer and the aquitard were collected for sediment and pore water chemical analyses. Sediment samples were placed in bags that were sealed. Water samples were filtered through 0.45 μm membrane filters. All samples for cation analysis were acidified to pH 2 with HNO_3 . Samples collected for anion analysis were not acidified. Some parameters such as TDS, pH, EC, and NH_4^+ were tested in situ using portable equipment. Both groundwater and sediment samples were preserved in coolers with frozen blue ice in the field and during sample transportation.

3.2. Laboratory Chemical Analyses. Ammonium was determined in both pore water and sediments. Milli-Q deionized water (18.2 M Ω) was used to extract water-soluble ammonium in the sediment samples taken from the aquitard at the sediment to water weight ratio of 1:10 (19). The sediment and water were mixed and sealed in baker, then shaken for 1 h, and centrifuged for 30 min at room temperature of about 25 $^{\circ}\text{C}$ to separate the sediment and the solution. Exchangeable NH_4^+ is defined as NH_4^+ that can be extracted at room temperature with a neutral 2 M KCl solution (20, 21). A mixture of 10 g sediment sample taken from the aquitard and 100 mL solution was shaken on a reciprocating shaker and then transferred into centrifuge tube. The ammonium measured from the solution after centrifuging represents the total ammonium, which includes water-soluble and exchangeable ammonium. Exchangeable ammonium was then calculated by the difference between the ammonium extracted by KCl solution and that by deionized water. For the key hole in Minzhong, pore water of core samples was directly obtained by centrifuging the samples to measure ammonium and other chemicals.

Cations were analyzed using by inductively coupled plasma-mass spectrometer (ICP-MS) (Model VG EXCELL) and anions were measured on an ion chromatography (Dionex LC25). Total nitrogen (TN) and total organic carbon (TOC) in sediment samples (HCl-treated sediment) were determined on ThermoQuest Italia SPA EA 1110 at State Key Laboratory of Marine Geology, Tongji University. Two M KCl

solution was used to extract exchangeable NH_4^+ , NO_3^- , and NO_2^- from deposits (20, 21). HANNA HI 93733 ammonia ion specific meter was employed to measure the concentrations of ammonium. This meter adopts the Nessler Method (22), which was approved by United States Environmental Protection Agency, to measure ammonium. Data quality control was done by the standard additional method, which showed recovery rates within 96.2–103.4%. Flow injection analysis was employed to determine nitrate plus nitrite nitrogen.

Water-soluble ammonium concentrations of the extractions from the sediment were converted into concentrations in the original pore water in the sediment using the following formula:

$$\text{NH}_4^+(\text{p})(\text{mg/L}) = (\text{NH}_4^+(\text{e})(\text{mg/L}) \times ((100 \text{ mL} + 10 \text{ g} \cdot \text{w}\%) / 1000 \text{ mL/L})) / (10 \text{ g} \cdot \text{w}\% / 1000 \text{ mL/L}) \quad (1)$$

where $\text{NH}_4^+(\text{p})$ indicates ammonium concentration in pore water; $\text{NH}_4^+(\text{e})$ indicates ammonium concentration in extraction; w% indicates measured water content.

4. Results and Discussion

4.1. Ammonium Distribution in the Basal Aquifer. The ammonium distribution in the basal aquifer was obtained and the ammonium concentration ranging from 10 to 390 mg/L was contoured, as shown in Figure 1. The total area of the aquifer where ammonium was greater than 10 mg/L was about 1600 km^2 . The ammonium distribution was not spatially continuous and there were four centers with ammonium >200 mg/L. Overall, ammonium concentration tended to increase toward the coast.

4.2. Geochemical Environment in Basal Aquifer. Ammonium concentrations in the basal aquifer were significantly correlated with the average total ammonium in the aquitard, with correlation coefficient of 0.79 at significant level of 0.01 (Figure 2A). Ammonium concentrations in the basal aquifer were also correlated with the thickness of the aquitard overlying the aquifer (Figure 2B). This suggested that the ammonium in the aquitard was probably the source of the ammonium in the aquifer.

There is a close correlation between TDS and ammonium in the groundwater in the basal aquifer (Figure 2D). Groundwater in the basal aquifer in most areas between Beijiao and the coastline has salinity >1 g/L (3), this high salinity is likely the result of paleo seawater, or residual seawater which intruded into the system during the Holocene transgression, rather than modern seawater intrusion because groundwater in this area has been only minimally exploited. High ammonium is typically associated with high salinity, suggesting a salty water environment is favorable for the release of ammonium in the sediments to groundwater. Similar results were observed previously (23, 24). For example, ammonium was found to be the dominant nitrogen species in saline groundwater beneath an Atlantic coastal estuary (23). This is probably because some major cations in seawater with relatively stronger affinity than NH_4^+ exchange for adsorbed NH_4^+ in the sediments and cause the release of exchangeable NH_4^+ from sediments to water (24).

Iodine concentration and NH_4^+ in the groundwater in the basal aquifer are highly correlated (Figure 2C), suggesting that they both were originated from organic matter. Iodine from the residual seawater alone cannot lead the elevated concentration observed in these samples because the average concentration of iodine in seawater is only 0.06 mg/L (25), which is much less than that of iodine in the groundwater.

When the concentration of ammonium is great, the concentrations of dissolved oxygen, nitrate, and nitrite are almost zero (data not shown). Local geotechnical engineers occasionally find methane in boreholes (3). The geochemistry

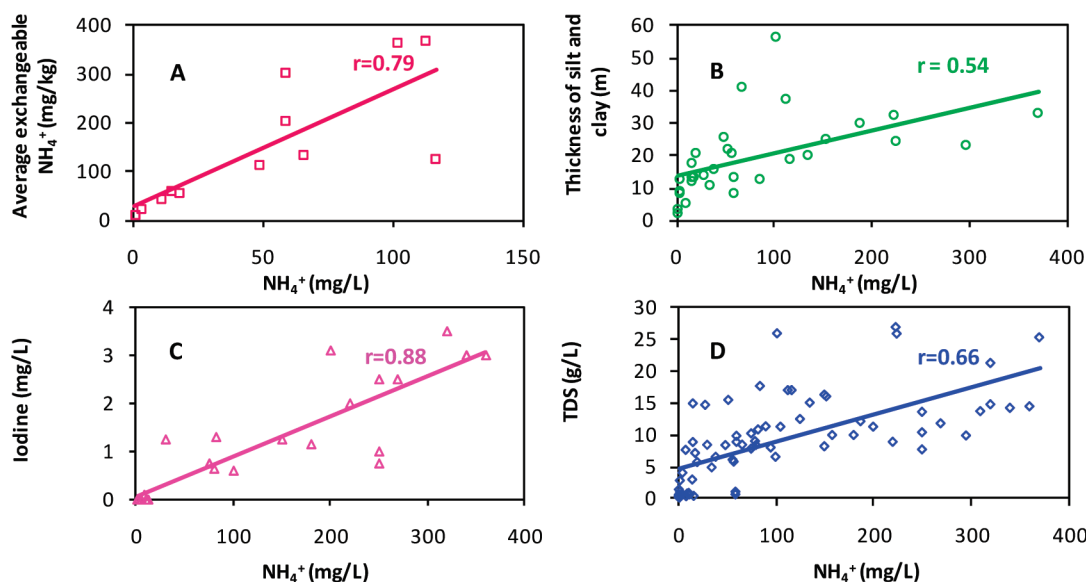


FIGURE 2. Relations between NH_4^+ in the pore water in the basal aquifer and (A) average total NH_4^+ in the aquitard; (B) thickness of aquitard over the aquifer; (C) iodine in aquifer; and TDS in aquifer. r is the correlation coefficient and the correlation is significant at the 0.01 level.

of the fertile water indicates that extremely reducing conditions conducive for ammonium preservation exists in the aquifer.

4.3. Vertical Geochemical and Hydraulic Profiles in Aquitards. **4.3.1. Ammonium Profiles.** Nine boreholes were studied for water-soluble ammonium in the pore water of the aquitard. The water-soluble ammonium concentrations of the extractions from the samples were then converted into concentrations in the original pore water in the samples using eq 1. The results indicate that the ammonium concentration in the pore water of the aquitard is on average 3.5 times (range 1.4–6 times) greater than in the basal aquifer (Figure 3). The aquitard pore water from SD14 had the greatest ammonium concentration at ~ 810 mg/L. Overall correlations between TOC, TN, and ammonium in the aquitard sediments are strong (e.g., in SD14; Figure 3J). Although both TOC and TN were variable, they were consistently greater than 10 g/kg and 1 g/kg, respectively, between depths of 15 and 30 m. In this zone, the total ammonium (water-soluble plus exchangeable) is also great, with concentrations up to ~ 0.6 g/kg as N.

4.3.2. Hydraulic and Geochemical Profiles through the Aquitard at MZ4. NH_4^+ concentrations measured from pore water extracted by centrifugation (Figure 4D; red line with dots) and from piezometers (triangles) indicated overall increases with depth. The generally higher NH_4^+ concentrations in the piezometer pore water relative to the centrifuge samples were attributed to the pore water in the piezometer being in equilibrium with exchangeable ammonium. In the deep zone in the aquitard, the incremental increase in ammonium was smaller, TDS was almost constant, and both pH and TDS were similar to seawater (Figure 4C–E).

The hydraulic profile in Figure 4B indicated downward flow through the aquitard into the aquifer. The average total vertical head difference between the water table and the bottom of the aquitard was about 1.5 m, most of which was dissipated between 17 and 30 m, indicating this deep aquitard zone had much lower bulk vertical hydraulic conductivity than the zone above it. Horizontal hydraulic conductivity of the shallow and deep zones was estimated based on slug tests at 1.5×10^{-9} and 3.7×10^{-10} m/s, respectively. The vertical hydraulic conductivity was expected to be much lower. When piezometers were installed, a hand-held electric hammer could only drive the piezometers down to 17 m.

Therefore piezometer installation below 17 m required use of a hammer mounted in a drilling rig.

These observations indicate the Pleistocene marine sediment had consolidated to some degree and its permeability was less than that of Holocene marine sediment. Consequently, the migration of constituents was slow and likely diffusion-controlled, as concluded from previous studies of other Holocene and late Pleistocene aquitards of similar thickness (26, 27). This may explain why paleo seawater has not yet flushed from the aquitard despite exposure to the present hydrologic regime. Furthermore, production of ammonium likely began soon after sediment deposition at TOC and TN concentrations much higher than at present.

4.4. Estimation of Ammonium Inventory in Pore Water in Aquitard-Aquifer System. Using the stratigraphic information from the 40 boreholes drilled for this study and 303 boreholes from previous geological studies, the spatial distribution and thickness of the aquifer and aquitard were estimated. The aquifer area was divided into 1×1 km² cells. Total ammonium storage (M) was calculated as

$$M = \phi \Delta x \Delta y \sum_{i=1}^N C_i D_i$$

where ϕ is the porosity, and C_i and D_i are ammonium concentration and aquifer thickness, respectively, for the i -th cell. Ammonium concentrations were obtained from Figure 1A. The porosity of the basal aquifer was taken to be 0.3 based on its physical characteristics. The total water-soluble ammonium in the aquifer based on areas with measured ammonium concentrations >10 mg/L is estimated at 190×10^6 kg. This estimate is conservative because the large areas with concentrations <10 mg/L are not included; furthermore, areas with high ammonium but thus far not intercepted by the holes drilled are also highly possible.

Using an average porosity of 0.55 (28), and the same equation as above, the total water-soluble ammonium in the aquitard was estimated at 3600×10^6 kg. Seventeen boreholes were studied for exchangeable ammonium (data not shown). Water-soluble ammonium and exchangeable ammonium in the aquitard were closely related, with a correlation coefficient of 0.83. Based on an average ratio between exchangeable and water-soluble ammonium of 1.44, the exchangeable ammonium in the aquitard was estimated

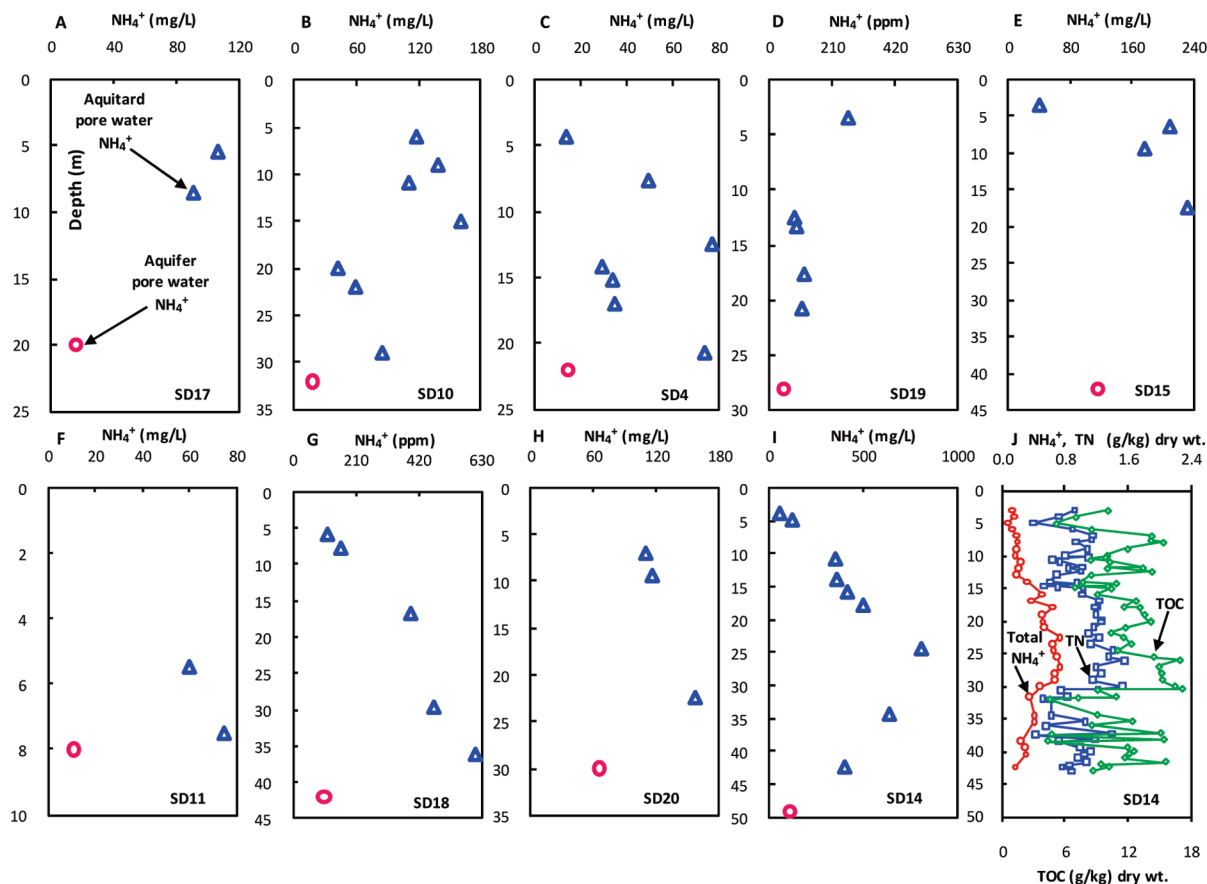


FIGURE 3. (A-I) NH_4^+ in the aquitard pore water in aquitard (triangle) and NH_4^+ in the aquifer (circle). (J) Total ammonium (soluble and exchangeable $\text{NH}_4^+\text{-N}$), TOC, and TN concentrations in aquitard sediments at SD14.

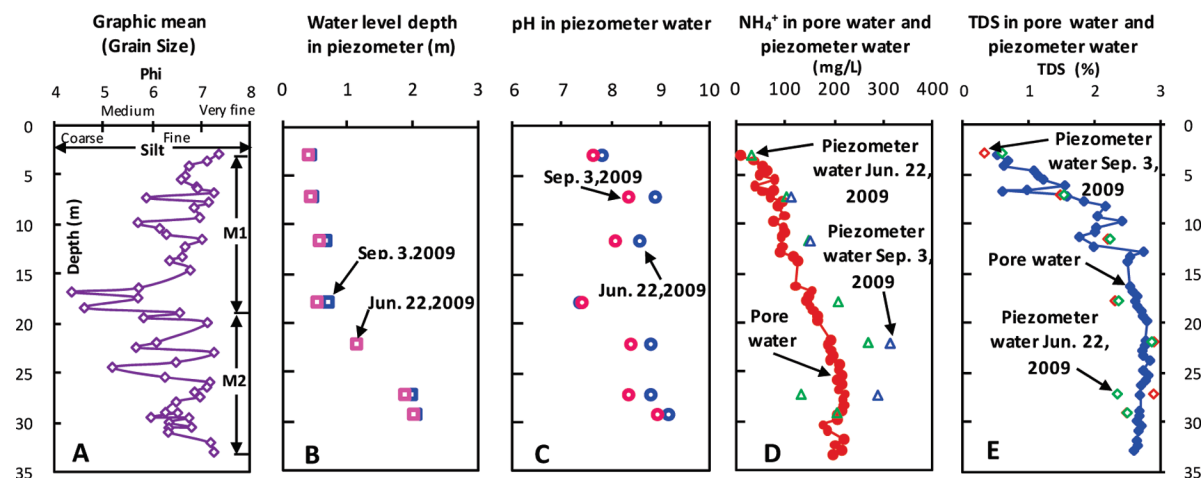


FIGURE 4. Vertical hydraulic and geochemical profiles through the aquitard at MZ4. (A) Phi diameter vs depth and simplified stratigraphy. (B) Water level depth. (C) pH of piezometer water. (D) NH_4^+ of pore water from centrifuge samples and piezometer water. The ammonium concentration in the basal aquifer at this location is 223 mg/L. (E) TDS of pore water from centrifuge samples and piezometer water. Piezometer data were measured on June 22 and September 3, 2009.

to be $\sim 5000 \times 10^6$ kg. Therefore, the total ammonium (water-soluble plus exchangeable) in the aquitard was $\sim 8600 \times 10^6$ kg, which exceeded the ammonium in the aquifer by a factor of 45.

The large amounts of TOC and TN remaining in situ in the aquitard (Figure 3J) indicated the potential for the production of much more ammonium in the future. Conversion to nitrogen was very limited because the low permeability of the aquitard severely restricted oxygen invasion, and it was expected the residual TOC and TN would gradually further mineralize into

ammonium, then migrate to the aquifer because of downward groundwater flow, diffusion, and pore water squeezing due to gradual consolidation.

4.5. Possible an Unrecognized but Large Natural Nitrogen Source to Receiving Waters. The aquifer-aquitard system is a hydrological continuum with connections to surface waters. There remains much organic N in the low-permeability aquitard not yet converted to NH_4^+ , indicating a slow continuous supply of NH_4^+ to the aquifer for a long time.

Given the gentle topographic slope southeaster ward toward the coast and shallow water table everywhere in the delta following the topography, the general direction of flow in the sand aquifer is also toward the coast. The ammonium-rich groundwater must migrate to the surface waters via various pathways, potentially causing impacts to surface waters, such as deterioration of river water quality and eutrophication in coastal areas (1, 2, 29). The rate of input of ammonium from the groundwater environment to the surface water environment may increase because of the ongoing human activities in the delta system. For example, increasingly large-scale sand dredging has occurred along major river channels and in the shallow sea near the coast for construction purposes and land reclamation. These activities reduce the thickness of the river or sea beds, shorten the flow path from deep groundwater to surface waters, which could enhance the release of ammonium to surface waters. Anthropogenic sources of ammonium are commonly considered in the PRD, however, this study suggests that the contribution of groundwater ammonium to nitrogen budgets and cycles and its ecological influence on receiving waters should be evaluated. This discovery of the large inventory of geological ammonium in this deltaic aquitard-aquifer system may be relevant to other coastal river plains, such as West Bengal in India and the Hanoi area in Vietnam.

Acknowledgments

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