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Origin of groundwater salinity and hydrogeochemical processes in the confined Quaternary aquifer of the Pearl River Delta, China

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SUMMARY

The Pearl River Delta (PRD), located in the coastal area of South China, contains a large confined Quaternary aquifer. This aquifer has been identified to have high concentrations of total dissolved solids–ranging from 1 g/l in the inland area to 26.8 g/l near the southeast shoreline. This work aims to investigate the origin of groundwater salinity and the major hydrogeochemical processes controlling the groundwater evolution in the confined basal aquifer of the PRD. A total of 40 boreholes were drilled in the PRD during 2007–2009, and groundwater samples were collected for major ion (Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, Cl^-, SO_4^{2-} and HCO_3^-) and isotope ($\delta^{18}O$, δ^2H, ^3H, $\delta^{13}C$ and ^{14}C) analyses. These analyses demonstrate that groundwater in the confined basal aquifer is recharged by local rainwater and seawater, and seawater is the major salinity source for groundwater. The contribution of seawater varies from less than 1% in the inland areas to 74% near the shoreline. SO_4^{2-} reduction and methanogenesis occur in this reducing confined aquifer. The results of ion exchange show that Mg^{2+} exchanges mainly with the NH_4^+ ion, which is derived from the mineralization of sedimentary organic matter. Ion exchange between Na^+ and Ca^{2+} and groundwater facies suggest that the brackish aquifer in the northwest inland area is undergoing freshening. ^3H analysis suggests that infiltrated rainwater is younger than seawater. ^{14}C analysis indicates that the seawater most likely infiltrated into the confined basal aquifer during the Holocene transgression period.

1. Introduction

Groundwater salinization occurs in many coastal aquifers (Louvat et al., 1999; Edmunds and Milne, 2001; de Montety et al., 2008; Somay and Gemici, 2009). The origin of groundwater salinity in coastal aquifers has been studied by many researchers, and various sources of groundwater salinity have been identified, including wastewater (Ghabayen et al., 2006), fossil seawater (Tijani, 2004), and modern seawater induced by excessive groundwater pumping (Kim et al., 2003). Groundwater salinity in coastal aquifers has been studied in parts of Southeast Asia (Samsudin et al., 2008; Praveena et al., 2011), but the contribution of paleo-seawater intrusion to groundwater salinization in these areas is not clear.

Seawater intrusion is frequently observed in both confined and unconfined coastal aquifers (Groen et al., 2000; Jorgensen, 2002; Kim et al., 2003; Bouchaou et al., 2009; El Yaouti et al., 2009; Somay and Gemici, 2009), but few studies have investigated the hydrogeochemical processes in confined coastal aquifers that are intensively influenced by paleo-seawater intrusion. Understanding the processes and factors that control the evolution of brackish groundwater in subsurface system is of scientific and practical importance. Confined aquifers overlain by organic matter-rich aquitards, with groundwater having a long residence time, can experience complex hydrogeochemical processes that control the groundwater evolution.

The plain of the Pearl River Delta (PRD) has an area of 6932.5 km^2 (excluding the area of Hong Kong) (Huang et al., 1982). This region has seen rapid population increase and economic growth particularly since the 1980s. The water supply of this region relies almost entirely on surface water due to abundant rainfall and the well-developed river network. However, rapid population and economic growth have led to the deterioration of surface water quality through pollution and declining river discharge (Cheung et al., 2003; Lu et al., 2009). Surface water alone can no longer meet the needs of the region, and people are looking to groundwater as an alternative supply. However, groundwater in many areas of the southern part of the PRD has been found to have total dissolved solids (TDS) of over 10 g/l (GHT, 1981). The recent increase in groundwater exploitation in the PRD has necessitated an evaluation of the origin of the salinity and an understanding of the chemical evolution of the groundwater resources in this region.

This research project was undertaken to determine the source(s) of salinity of brackish groundwater and to identify the hydrogeochemical processes related to groundwater evolution in the confined coastal aquifer of the PRD. To accomplish these goals, the spatial distribution of the brackish groundwater was mapped, and the origins of its salinity were investigated using hydrochemical

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and isotopic techniques. The major ion compositions and $\delta^{13}C$ values of inorganic carbon in groundwater were used to determine the hydrogeochemical processes, and Pearson's correlation analysis (Davis, 2002) was used to evaluate the ion exchange behaviour of the major cations. Radiocarbon dating was carried out to estimate the residence time of the brackish groundwater in the confined basal aquifer.

This study concerns the impact of sea-level changes during a period of paleo-intrusion on coastal aquifer systems, with an emphasis on naturally-occurring high salinity groundwater. Although NH_4^+ is not generally regarded as a main component of either seawater or fresh groundwater, it exists in significant amounts in many coastal aquifers (Correll et al., 1999; Berg et al., 2001; Bratton et al., 2004; Santos et al., 2008). Naturally occurring NH_4^+, deriving from mineralization of sedimentary organic matter, has been identified as one of the major ions (concentrations up to 390 mg/l) in most of the confined basal aquifer of the PRD (Jiao et al., 2010). Unlike many other studies that only focus on the ion exchange of major cations of seawater (Ca^{2+}, Mg^{2+}, Na^+, K^+) in coastal aquifers (Martinez and Bocanegra, 2002; Appelo and Postma, 2005; Capaccioni et al., 2005), this investigation examines the ion exchange behaviour of naturally occurring NH_4^+ with the major cations of seawater. The findings should be useful for understanding the salinity processes of other coastal aquifers and other major estuaries in which sedimentary settings are largely influenced by transgressions, such as in the coastal aquifers of Malaysia (Samsudin et al., 2008) and the Netherlands (Post et al., 2003). Also, the major hydrogeochemical processes identified in the confined basal aquifer in this research can help to understand the groundwater evolution in other anoxic coastal aquifers, for example, the Gangetic plain in West Bengal and the Hanoi area in Vietnam (Berg et al., 2008; Chetia et al., 2011), which also contain abundant sedimentary organic matter in the sediments.

2. Geological and hydrogeological settings

Geologically, the Pearl River drainage basin (Fig. 1) was formed by the Tibetan Plateau uplifting during the Tertiary and Quaternary periods (Aitchison et al., 2007). The Pearl River Delta is largely covered with Quaternary sediments, and has an elevation ranging from 6 to 9 m above sea level in the north to 1–2 m near the coast (GHT, 1981). Bedrocks of Cambrian to Tertiary age crop out around and within the delta (Fig. 1).

During the Holocene period, the PRD experienced large-scale transgression. Studies on diatoms and radiocarbon dates by Zong et al. (2009b) suggest that the rapid sea level rise between 9000 and 7000 calibrated years before present (cal. yr BP) initiated the formation of deltaic sequence. The most landward shoreline (6800 cal. yr BP) occurs around the apex of the deltaic plains (Zong et al., 2009b), and a paleo-shoreline estimated to have formed 2000 cal. yr BP (Li et al., 1991) is located in the center of the PRD (Fig. 1A). Therefore, the PRD plain was inundated by the sea for several thousand years, providing a long period of interaction between paleo-seawater and groundwater in the Quaternary aquifer system.

The formation and evolution of the PRD during the late Quaternary period have been extensively studied (Huang et al., 1982; Wu et al., 2007; Yim et al., 2008; Zong et al., 2009a). The Late Quaternary stratigraphic sequence consists mainly of two terrestrial (T1 and T2) and two marine (M1 and M2) units (Zong et al., 2009a) (Fig. 1B). The oldest terrestrial unit of sand and gravel (T2) is widely distributed in paleo-valleys prior to the last transgression in the late Pleistocene period and forms the basal confined aquifer in the region. The oldest marine unit of silt and clay (M2), formed during the last transgression in the late Pleistocene period, rests on T2. During the last glacial period, the upper part of M2 was extensively weathered due to the low sea level. During this time, a younger terrestrial unit of sand and gravel was laid down along paleo-river channels. Both the weathered clay and the young terrestrial unit constitute T1. Beginning at 8.2 cal. ka BP, a rapid postglacial rise in sea level resulted in the deposition of unit M1, with a thickness of 5–20 m (Zong et al., 2009a). Because they consist of very fine-grained silt and clay, M1 and M2 are effective aquitards in the PRD groundwater system. The calibrated ^{14}C ages available from studies on the PRD (Huang et al., 1982; Li et al., 1991; Zong et al., 2009a,b), are shown in Fig. 1B. Rainwater locally infiltrates through the thick aquitard, or enters the aquifer through the recharge areas near the west and north boundaries of the delta, where the marine deposits are in contact with coarse colluvial and alluvial deposits, and flows laterally through the basal aquifer to the sea. The general direction of regional groundwater flow in the sand and gravel basal aquifer of the PRD is southeast toward the coast (Jiao et al., 2010).

3. Field and laboratory studies

A total of 40 boreholes were drilled in the PRD in the dry season (from December to March) during 2007–2009 (Fig. 1A). After drilling, steel pipes with diameter of 110 mm were emplaced to make temporary wells, and the open intervals were screened in the basal aquifer. Well development was carried out, and groundwater was sampled after the pumped water from the borehole became clean. Enough groundwater was collected from each site to fill two 125 ml, high density polyethylene bottles after filtering by passing the water through 0.45 μm filter paper. One bottle that was used for major cation (Ca^{2+}, Mg^{2+}, Na^+, K^+) measurements was treated with double distilled nitric acid until the pH was below 2; the untreated water from the other bottle was used for major anion (Cl^- and SO_4^{2-}) analyses. These samples were preserved in coolers with frozen blue ice and analyzed within two weeks of sampling. Groundwater samples from 21 boreholes were collected in 250 ml Pyrex glass bottles for $\delta^{18}O$, δ^2H and ^3H analyses. In addition, groundwater of seven boreholes was sampled for measurement of inorganic ^{14}C using the sampling system designed by the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences. One to five 25 l samples were collected in plastic barrels at each site depending on the concentrations of dissolved inorganic carbon (DIC) in groundwater samples. Variable amounts of $FeSO_4$, saturated NaOH solution (carbonate-free), and polyacrylamide solution were added to each barrel, and the DIC was precipitated with $BaCl_2$ as $BaCO_3$. The sampling system was designed to prevent any atmospheric CO_2 contamination. Raw groundwater was placed directly in 1 l plastic sampling bottles for $\delta^{13}C$ of DIC analysis. The samples were kept at 4 °C before analysis.

After groundwater sampling, YSI 6-Series Multiparameter Water Quality Sondes (6920V2) (YSI, 2006) were placed in each well at the middle of the basal aquifer to measure pH, temperature, TDS and the oxidation–reduction potential (ORP) of the groundwater. Several readings were taken after equilibrium was achieved between the sondes and the groundwater, and stable values were used. The sondes were checked before every use adopting standard solutions and calibration was carried out if necessary. Hach Digital Titrator Kits and HANNA HI 93733 Ammonia Ion Specific Meters were used to measure alkalinity and NH_4^+, respectively, in the field immediately after water sampling. Concentrations of HCO_3^- were calculated after Rounds (2006). The method of standard addition (Harris, 2003) was used to ensure data quality.

$\delta^{18}O$, δ^2H and ^3H were analyzed at the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological