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Importance of surface geologic condition in regulating As concentration of groundwater in the alluvial plain

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ABSTRACT

The arsenic (As) concentrations in the groundwater of alluvial plains generally show high spatial variability. We geochemically explore the factors causing the spatial variability in an alluvial plain that is mainly used for rice cultivation, the commonest land-use pattern in alluvial plains of Asia. We investigate the chemical processes, sources of chemicals that affect the behavior of As, and their relationships with the geologic conditions at seven multilevel sampler sites. All sites showed As concentrations that increased with depth at shallow levels and decreased at greater depths, which is the typical vertical pattern in alluvial aquifers where Fe-(hydr)oxide reduction is the major As release mechanism. Data show that NO_3 and SO_4 originating from the land surface play important roles in suppressing the increase in As concentration by buffering the redox potential at shallow depths and by precipitating As with sulfide minerals at deep depths, respectively. The As concentration in the intermediate depth range was also low in the presence of SO_4, because its reduction can occur together with Fe-(hydr)oxide reduction in a wide range of redox potentials. As a result, the maximum As concentrations at the sites where the land was covered with a thick silt layer (~5 m) were 3- to 5-times higher than those at other sites due to the supply of NO_3 and SO_4 from land surface being largely limited by the silt layer. This indicates that the surface geology could be an important indicator for the As concentration in alluvial groundwater.

1. Introduction

The seriousness of arsenic in groundwater was first recognized in Taiwan during the 1960s (Tseng et al., 1961). The severe As contamination later observed in Bangladesh and West Bengal of India has aroused world-wide concern over arsenic pollution in groundwater and triggered As investigations in groundwater in many countries.

Occurrences of As-rich groundwater are diverse, ranging from geothermal to mining areas and from bedrock to alluvial aquifers. However, the As problem in alluvial aquifers is accepted as the most serious and extensive. The As problem in Bangladesh and West Bengal of India is also mostly concentrated in the flood plain formed by the Ganges, Meghna, and Brahmaputra Rivers (GMB Plain). Groundwaters with As concentrations >100 $\mu g\ L^{-1}$ are very common in the GMB Plain (Nickson et al., 1998; Chakraborti et al., 2004). The general mechanism of arsenic release in the GMB Plain is via the desorption of As by the reductive dissolution of Fe (hydr)oxides (Nickson et al., 2000; McArthur et al., 2001; Harvey et al., 2002; Chauhan et al., 2009). This mechanism is also commonly observed in alluvial aquifers in many other Asian countries, including Taiwan (Chen and Liu, 2005), China (Guo et al., 2008), Vietnam (Postma et al., 2007), and Cambodia (Quicksall et al., 2008).

Arsenic concentrations in alluvial aquifers are characterized by high spatial variability. Many studies have suggested organic carbon as one of the main reasons for the variability (Harvey et al., 2002; McArthur et al., 2004; Lin et al., 2008; Papacostas et al., 2008; Quicksall et al., 2008). Recently, some studies suggested that the young organic carbon content in the sediment and the As concentration in groundwater are controlled by geomorphological and/or sedimentological processes (Papacostas et al., 2008; Quicksall et al., 2008). Others suggested the importance of hydrological condition such as recharge rate (Stute et al., 2007; Aziz et al., 2008). However, the processes causing the spatial variability of As concentration are still poorly understood.

In this study, we investigate the factors causing the spatial variation of As concentrations in an alluvial aquifer by inspecting the vertical variations in chemical distribution, chemicals affecting As concentrations and their sources, and geologic conditions at seven locations using multilevel samplers. This study was performed in a

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point bar area formed by the meandering of the Mankyeong River, Korea. The study area has a similar land-use setting to that of the GMB Plain, in that it is predominantly used for rice cultivation. Therefore, we believe that the findings of this study provide valuable insights into the occurrence of As-rich groundwaters in the GMB plain.

2. Study area and geology

The Mankyeong River flows westward toward the Yellow Sea and has formed a wide flood plain in the mid-western part of Korea (Fig. 1). The alluvial plain of the Mankyeong River, including the point bar area where this study was performed, is mainly used for the flooded cultivation of rice. Geologic logging carried out by Kim (2006) during the installation of multilevel samplers at six locations, showed that 10–15 m of alluvial sediments, consisting of silty clay, silty sand, sand, and gravel sand layers, covers the paleosol and saprolite layers in the study area (Fig. 1). A 5- to 6 m-thick gravel sand layer, which unconformably overlies the paleosol layer, acts as the main aquifer. The monthly average temperature is 0.6 °C in January and 26.1 °C in August, based on weather data from the past 30 years. The annual average precipitation is 1287 mm, of which 64% occurs from June to September.

3. Method

For this study, we used six multilevel samplers (B1–B6) installed by Kim (2006) and 29 agricultural wells distributed in and around the point bar area (Fig. 1). An additional multilevel sampler (B7) was installed in November, 2007 as a part of this study at a site where the adjacent wells showed high As concentrations (>100 μg L^{-1}). All of the multilevel samplers were installed according to Kim (2003) using bundles of polyethylene tubes. Each sampler has 6–11 sampling ports placed at depths ranging from 3.9 to 30 m. The depths of all of the agricultural wells were less than 20 m except for one that was 60 m deep. These wells were generally screened over the entire depth range to maximize the groundwater yield. Wells with such a configuration may cause artificial mixing between groundwaters of different depths, so the sampled groundwaters may not appropriately represent the chemical compositions, especially in aquifers where the water chemistry is highly stratified. In contrast, the multilevel samplers of this study are almost free of this problem because each sampling port has a screen interval of only 5 cm.

Among the studied multilevel wells, wells B1–B6 were sampled twice in May and September 2007, while well B7 was sampled once in May 2008. All of the agricultural wells were sampled in December 2007. Groundwater samplings were performed using an overflow chamber to minimize the chemical disturbance caused by contact with air. Groundwaters were sampled after purging the wells sufficiently until the flowing water showed a stabilized temperature, pH, DO (dissolved oxygen), and Eh. All of the samples except for those for sulfur isotope ($\delta^{34}\mathrm{Sso}_4$) analysis were filtered through 0.42 μm membrane filters in the field. Water samples for the measurement of major cations (Na$^+$, Mg^{2+}, K$^+$, Ca^{2+}), trace elements (As, Fe), and PO$_4$ were collected in 100 mL bottles pre-cleaned with 10% HCl and treated with ultra-pure hydrochloric acid to pH < 2. Sample bottles for major anions (NO_3^-, SO_4^{2-}, Cl$^-$), NH$_4$, alkalinity, δ^{18}O, and δD were pre-cleaned with deionized water, and the samples were collected without any headspaces. Samples for $\delta^{34}\mathrm{Sso}_4$ were collected as BaSO$_4$ precipitates by dissolving a sufficient amount of BaCl$_2$ (Ba/SO$_4$ molar ratio > 3) in 1–20 L of the water sample after adjusting the pH to <4 with ultra-pure hydrochloric acid. All water samples were kept at 4 °C until analysis.

Alkalinity was immediately measured using the Gran titration technique upon arrival from the field site. Major cations (Na$^+$, Mg^{2+}, K$^+$, Ca^{2+}) and Fe were analyzed using flame atomic absorption spectroscopy (AAS). When the Fe levels were less than 0.5 mg L^{-1}, they were reanalyzed using a graphite furnace AAS. Arsenic was analyzed using a hydride generator connected to the flame AAS. Major anions (Cl$^-$, SO_4^{2-}, NO_3^-) were analyzed using an ion chromatograph. PO$_4$ concentrations were colorimetrically

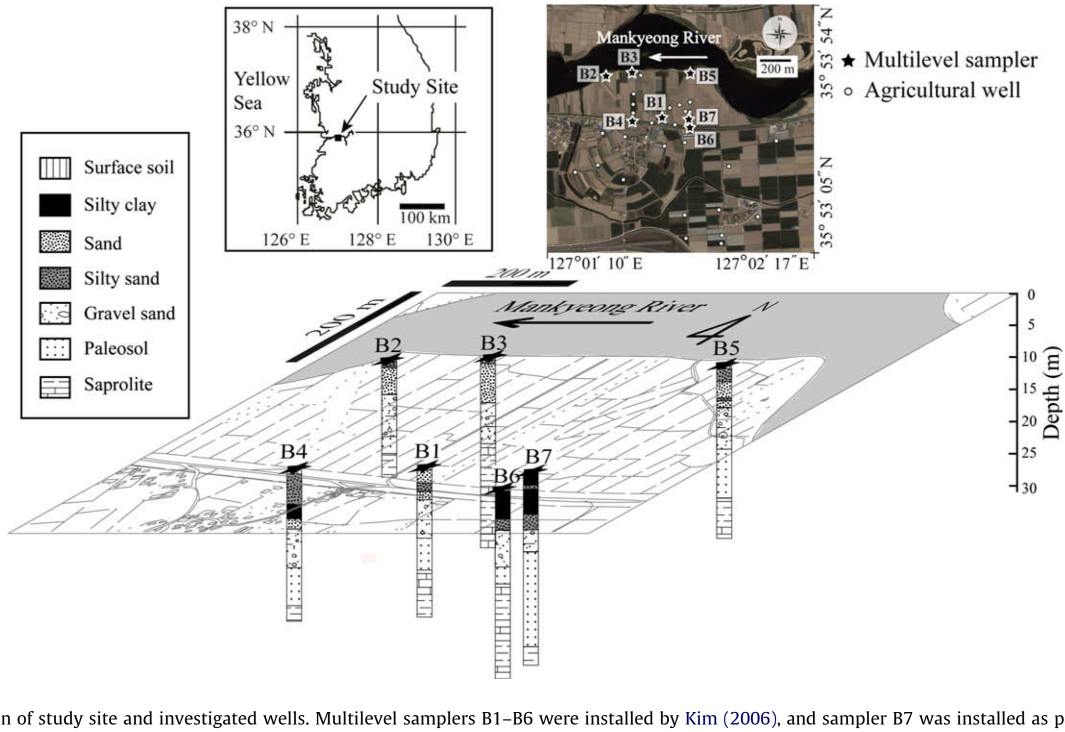

Fig. 1. Location of study site and investigated wells. Multilevel samplers B1–B6 were installed by Kim (2006), and sampler B7 was installed as part of this study.