

Relations of arsenic concentrations among groundwater, soil and paddy from an alluvial plain of Korea

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ABSTRACT: Serious groundwater arsenic (As) contaminations are frequently associated with alluvial plains, and which are mostly used for rice cultivation in Asian countries. Because rice cultivation requires large quantities of irrigation, the long-term use of As-contaminated groundwater for irrigation may cause As contamination in the soil with a consequent impact on rice grains. In this study, we investigated As concentrations in groundwater, soil and rice and the soil properties from an alluvial plain of the Mankyong River, Korea, to understand their relations from the viewpoint of As contamination in rice. Arsenic in the rice varied from 0.03 mg/kg to 0.22 mg/kg, with a mean of 0.13 mg/kg, which is much lower than the World Health Organization's maximum permissible limit of As in rice (1.0 mg/kg). Some groundwater samples showed As concentrations much higher than the drinking water standard (10 ug/L). Despite the rice As is independent of groundwater As it showed a good relation with soil As and Fe-oxide fractions. Because As is mainly occurred in Fe-oxide fractions and the soil is mostly silty, it is speculated that under flooding conditions arsenic can easily mobilize to the soil solution and potentially be available for plants. However, this availability can be controlled by As uptake mechanisms and/or incomplete reduction of Fe-oxides. It is observed that rice As is significantly correlated with soil exchangeable- PO_4 ($r = -0.41$, $p < 0.05$), indicating that PO_4 competition in the soil-rhizosphere may be one of the factors controlling rice As.

Key words: arsenic, paddy soil, groundwater, rice, soil properties, uptake mechanism

1. INTRODUCTION

Arsenic is a toxic metalloid that causes a variety of adverse human health effects, such as hyperkeratosis, cancer of the skin, lung, liver and kidney, and many other cardiovascular and neurological problems (Hopenhayn, 2006; Martinez et al., 2011). Until recently, it was thought that the drinking of As-contaminated groundwater was perhaps the most common exposure pathway of As (Smith et al., 2000; Ahmed et al., 2006). However, recent investigation has revealed that the intake of rice is another potential As exposure pathway that can harm human health, particularly for populations mainly dependent on a rice diet (Rahman et al.,

2008; William et al., 2005; Zavela and Duxbury, 2008). Moreover, rice is much more efficient at assimilating arsenic into grains compared with other cereal crops (Williams et al., 2007). Therefore, arsenic in rice is currently receiving much attention from researchers. Rice is the staple food for nearly one-half of the world's population (IRRI, 1993), including Chinese, Korean and other Asian countries. In the Korean population, the per capita average consumption of rice was 93.6 kg in 2000. Although consumption has decreased every year compared with 136.4 kg in 1970, rice still is a basic diet, contributing approximately 60% of the total cereal consumption in South Korea (Ministry of Agriculture and Forestry, 2003).

Arsenic in floodplain soil can be from various sources, including the use of pesticides and herbicides, atmospheric deposition, and irrigation with As-contaminated groundwater (Marin et al., 1992; Mandal and Suzuki, 2002). Irrigation with As-contaminated groundwater is the most significant cause of enhanced As levels in soil (Roberts et al., 2007; Hossain et al., 2008), with subsequent effects in rice grains (Williams et al., 2006; Rahman et al., 2007). Some studies (Meharg and Rahman, 2003; Dittmar et al., 2010) have shown positive relations among As contents in irrigated groundwater, soil and rice. However, other studies have shown poor or no identifiable relations between As contents in soil and rice, despite the soil As being enriched by irrigated groundwater (Islam et al., 2004; Patel et al., 2005; van Geen et al., 2006). Although the cause of this relation is poorly understood, many studies have revealed that As accumulation in rice is dependent on various environment and soil factors because they regulate the As availability and uptake by plants (Abedin et al., 2002; Bogdan and Schenk, 2009; Fu et al., 2011). Understanding these relations is essential for estimating As risk in rice and reducing As uptake by plants.

In the present study, As concentrations in groundwater, soil and rice samples were geochemically investigated from a floodplain of the Mankyong River, Korea, which is mainly used for paddy cultivation. This floodplain was reported to have high arsenic concentrations in the groundwater (Kim

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et al., 2009a). The aim of this work is to assess the arsenic risk in paddy rice coupled with its relationship with soil properties and the arsenic in groundwater and soil.

2. STUDY AREA

The present study was conducted in a point bar area formed by the meanders of the Mankyong river, Korea, which flows westward toward the Yellow Sea (Fig. 1). This floodplain is well known for its flat topography and widespread rice cultivation. According to the geologic logging undertaken by Kim (2006), the area contains 10–15 m of alluvial sediments, consisting of silty clay, silty sand, sand, and gravel sand layers that cover the paleosol and saprolite layers. A 5- to 6-m-thick gravel sand layer, which unconformably overlies the paleosol layer, acts as the main aquifer.

In the paddy field of the point bar area, groundwater is used as the major irrigation sources. Because of this reason, many small irrigation wells are available in the study area. However, Mankyong River water is used for irrigation near the riverside.

The study site has an average monthly temperature of 0.6 °C in January and 26.1 °C in August, according to weather data from the past 30 years. The site's average annual precipi-

tation is 1287 mm, of which 64% occurs during summer (June to September).

3. MATERIALS AND METHODS

For the present work, groundwater chemistry data from three multi-level wells (B3, B4 and B7) and 25 agricultural wells were utilized (Fig. 1). B3 and B4 were installed by Kim (2006), while B7 was installed by Kim et al. (2009a). All of the multi-level samplers were installed using bundles of polyethylene tubes according to Kim (2003), and the water samples were collected in 2009. Agricultural well data were taken from Kim et al. (2009a). Twenty-one rice grain samples were collected in 2010 from the alluvial plain (Fig. 1). For each point, approximately 5 plants were harvested and merged to a single sample. Twenty-one soil samples were collected from the root zone (<15 cm depth), corresponding to rice samples during the early harvest period, and were stored in plastic bags. A sediment core retrieved while installing B7 multi-level well was used to see the vertical variation of As concentrations in the sediment. Groundwater is the major irrigation source near B7 and the high As concentrations (>50 µg/L) are typically observed there (Kim et al., 2009a; Fig. 1).

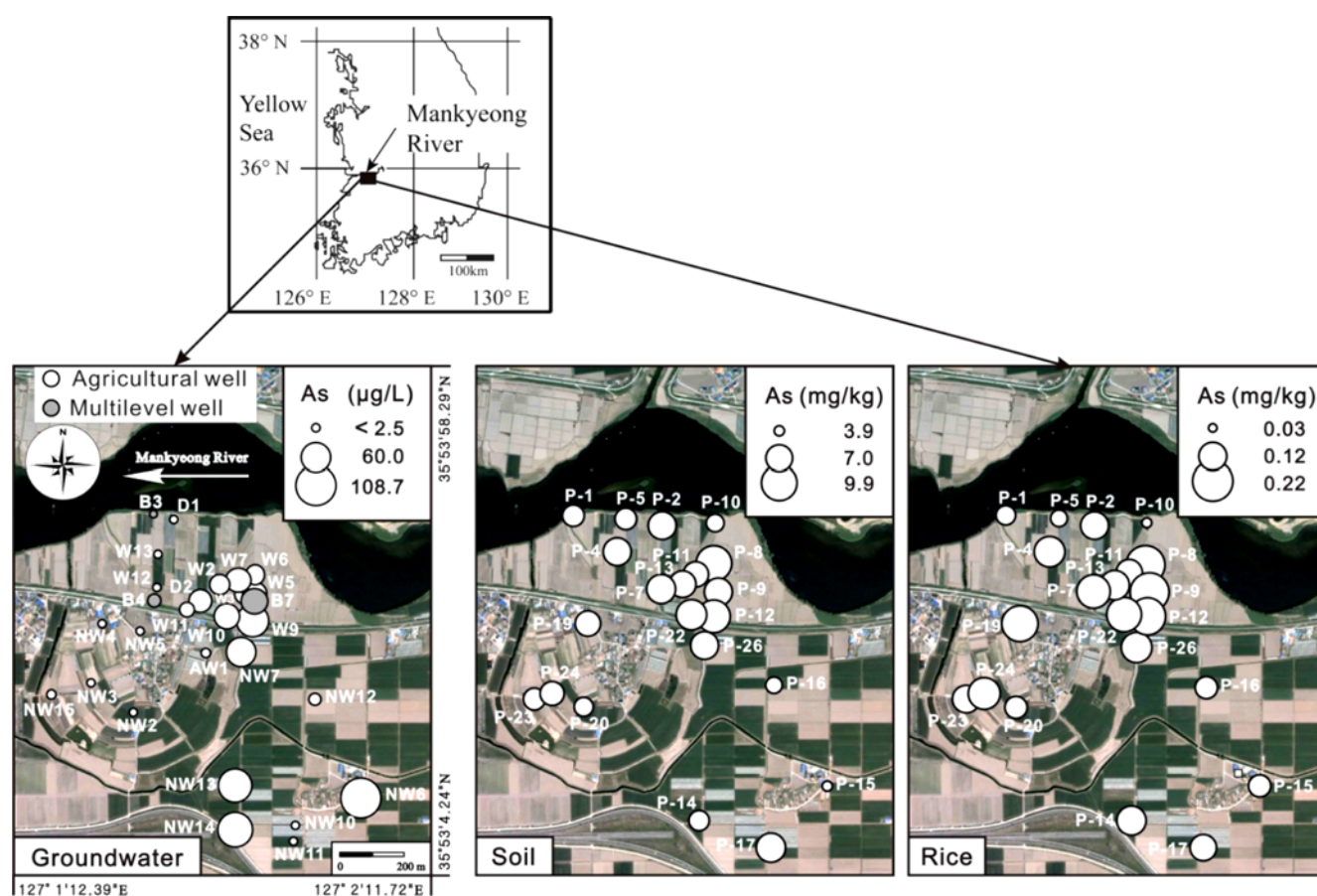


Fig. 1. Location of the study area and the distribution of arsenic in groundwater, soil and rice grains.

Water samples for chemical analysis were filtered immediately onsite through 0.45- μm -membrane syringe filters. Samples for major cation, $\text{PO}_4\text{-P}$, As, and Fe analysis were acidified with concentrated HNO_3 to $\text{pH} < 2$, while non-acidified samples were used for the measurement of anions (alkalinity, SO_4^{2-} , Cl^- and NO_3^-). The Eh and pH were measured onsite using a flow-through chamber. Prior to measurement, the Eh and pH probes were calibrated with Zobel and standard pH-buffer solutions, respectively. Alkalinity was measured using the Gran titration method upon arrival from the field site. $\text{PO}_4\text{-P}$ was measured colorimetrically using an ascorbic acid reduction method. Major cations (Ca, Mg, Na, and K) and total Fe were measured using flame atomic absorption spectroscopy (AAS), and total As was measured using AAS with a hydride generator. Anion analysis was performed using ion chromatography. The ion balance errors for the water analysis were within $\pm 10\%$.

For rice samples, the husks were removed from grains, oven-dried at 75°C and then milled to fine powder using an electric grinder made of stainless steel. The total As concentration in rice was determined following the method used by Jung et al. (2005). Two grams of the pulverized rice samples were taken in a large test tube, and 5 ml of concentrated HNO_3 (70% w/w) was added to wet the samples. An air condenser was attached to the tube, and 3×5 ml of fuming HNO_3 (95% w/w) was added to the samples, followed by mixing and frothing, which were maintained between each addition. The tube was then heated sequentially: 3 h at 50°C , 3 h at 100°C , 10 h at 150°C and 1 h at 160°C . Once cooled, the condenser was disconnected, and 3 ml of concentrated perchloric acid (60% w/w) was added to the tube and then heated for another 18 h at 150°C . The residue left behind was leached with 2 ml of 5 M HCl at 70°C for 1 h. After leaching, 8 ml of deionized water was added, shaken properly and filtered. The filtrate was measured for total As concentration using AAS with a hydride generator. To check the accuracy of the analysis, the standard materials of the National Analysis Center for Iron and Steel of China (ZC73008, rice) were analyzed for As. The accuracy of the measurements was 99%.

The soil samples were dried at normal atmospheric conditions in the laboratory and stored in plastic bags. Soil pH was measured in a 1:5 (w/v) soil:deionized water suspension after 1 hr of equilibrium. The silt content was determined by a sieve technique (the amount of soil passed through a 230-mesh sieve), while organic carbon (OC) was determined by a total organic carbon analyzer. Soil exchangeable PO_4 was extracted using 2 M NH_4Cl for 1 h and then measured colorimetrically. The total As concentration in the soil and sediment was determined using a HNO_3 digestion scheme. In this scheme, 0.5 g of the pulverized sample was treated using 25 ml of 10 N HNO_3 at 105°C for 2 h in an autoclave, and the concentration was measured using AAS with a hydride generator.

Sequential extraction analysis was performed according to the method described in Kim et al. (2009b): 0.1 g of pulverized samples was extracted using 1 M MgCl_2 (10 ml, $\text{pH} 7$, 25°C , 1 h shaking) for exchangeable As forms (Step 1), 1 M $\text{NaOAc} + \text{HOAc}$ (25 ml, $\text{pH} 5$, 25°C , 4 h shaking) + 1 M MgCl_2 (10 ml, $\text{pH} 7$, 25°C , 0.5 h shaking) for carbonate forms (Step 2), 0.2 M NH_4 -oxalate buffer (25 ml, $\text{pH} 3.35$, 4 h shaking in the dark) for amorphous Fe oxide forms (Step 3), 0.2 M NH_4 -oxalate buffer + 0.1 M ascorbic acid (25 ml, $\text{pH} 3.25$, 96°C , 0.5 h shaking) for crystalline Fe oxide forms (Step 4), and 10 N HNO_3 (2 ml, autoclave at 110°C 2 hr) for residual forms (Step 5). The percentages of error of the extraction sums were generally -6 to 28% of the bulk extraction results based on Step 5.

4. RESULTS AND DISCUSSION

4.1. Arsenic in Groundwater

The distribution of As in the groundwater is shown in Figure 1, which shows the As concentration ranging from <2 to $109 \mu\text{g/L}$. Fifteen out of the 25 agriculture wells were exceeded the WHO drinking water standard of $10 \mu\text{g/L}$. Most of the groundwater with an As concentration $>50 \mu\text{g/L}$ was found in the eastern part of the study area. In the multi-level wells, the As concentrations were always less than $10 \mu\text{g/L}$ at shallow depths (<7 m), but the concentrations increased up to $43.4 \mu\text{g/L}$ at greater depths (8–14 m).

As demonstrated by the overall groundwater chemistry, the higher arsenic concentrations in wells were associated with lower Eh, NO_3^- and SO_4^{2-} and higher alkalinity, Fe and $\text{PO}_4\text{-P}$ (Fig. 2), indicating that the reductive dissolution of Fe (hydr)oxides may be the major As release mechanism (Harvey et al., 2002; McArthur et al., 2001; Kim et al., 2009a).

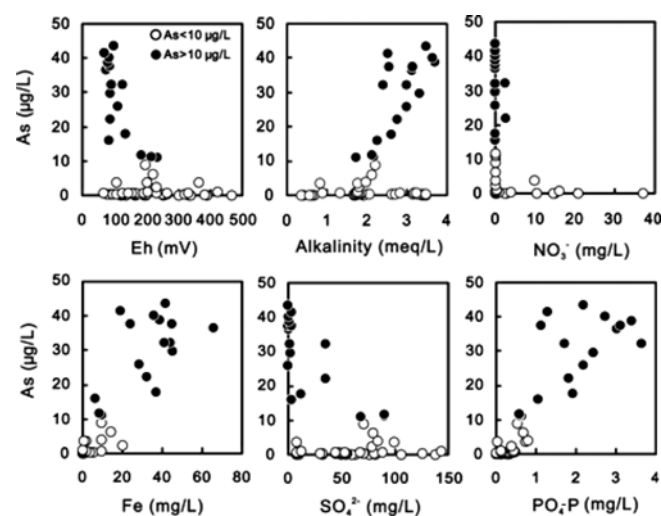


Fig. 2. Relations between As and various chemical parameters in multilevel wells.

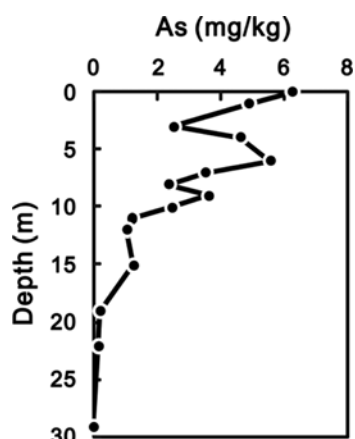


Fig. 3. Vertical distribution of As in sediment profile (B7).

4.2. As Levels in Soil

The total As content in the surface soils ranged from 3.9 to 9.9 mg/kg (Fig. 1). Arsenic occurs in all soils of the world, but its average normal concentration in soils is approx. 5 mg/kg (ATSDR 2000; Loska et al., 2003). Our results show that the soils are within the normal level of As. Numerous studies indicate that the irrigation with As-contaminated groundwater can increase the soil As levels (Hossain et al., 2008; Roberts et al., 2007). The As concentration profile of the sediment at B7, which shows the highest As levels at the surface (Fig. 3), may also reflect the groundwater irrigation effect. The sediment As concentrations varied with depth decreasing from 6.27 mg/kg in the uppermost soil layer to ~0 mg/kg at a 30 m depth. However, there is no clear relationship between As in groundwater and the surface soil (Fig. 1).

4.3. Chemical Properties of Soils

Selected chemical properties in the soil samples are shown in Table 1. Although the pH values of the soils varied from 4.9 to 7.3, the majority were within the range of 5.4 to 6.2, which is considered medium to slightly acidic. The silt con-

Table 2. Pearson correlation coefficient (r) between soil properties and total soil As (n = 21)

Variables	Total soil As (r)
Soil pH	-0.31
Silt fraction	0.28
Organic Carbon	-0.04
Exchangeable-PO ₄	-0.51 ^a
Amorphous Fe-As	0.87 ^b
Crystalline Fe-As	0.75 ^b

^aSignificant level at $p < 0.05$; ^bSignificant level at $p < 0.01$.

centration (<63 μm) ranged from 42 to 75%, and most of the samples were greater than 50% of the bulk weight, implying that samples are fine-grained soil according to the Unified Soil Classification System (ASTM D-2487-98). Most of the soil samples showed low levels of organic carbon (mean value of 1.53%). The concentration of exchangeable-PO₄ varied widely, from 2.4 to 18.8 mg/kg. The total As content in the soil was significantly correlated with the soil PO₄ ($r = -0.51$, $p < 0.05$), but not with pH, OC or silt content (Table 2). This result indicates that PO₄ in soil may enhance the downward movement of As because it competes with arsenic for sorption sites in soils (Smith et al., 2002), which may be one of the causes of the variation of the total As concentration among the studied soils.

4.4. Fractionation of Soil As

Arsenic in soils is present in various forms, from easily leachable to recalcitrant. Because the total arsenic concentration gives only a poor indication of the As bioavailability, many previous studies have used multi-step sequential extraction techniques to obtain better information on the bioavailability of soil As (Cai et al., 2002; Postma et al., 2007; Gonzaga et al., 2008; Kim et al., 2009b). Our sequential extraction results indicate that the majority of the As (for more than 70% of the total) exists in amorphous and crystalline Fe (hydr)oxide fractions (Table 1). The correlation results also indicate that these two fractions are significantly correlated

Table 1. Chemical parameters and As fractionation in soil samples (n = 21)

		Avg	Max	Min
Chemical Parameters	pH	5.69	7.29	4.91
	Silt (%)	59.09	74.78	42.21
	OC (%)	1.53	2.30	0.80
	Exchangeable-PO ₄ (mg/kg)	7.15	18.81	2.41
As Fractionation	Exchangeable (%)	1.10	2.10	0.60
	Carbonate (%)	6.10	9.50	4.20
	Amorphous Fe (%)	52.80	60.90	42.40
	Crystalline Fe (%)	39.90	52.40	33.40
	Residual (%)	0.20	1.20	0.00

Avg: Average; Max: Maximum; Min: Minimum.

(amorphous Fe-As: $r = 0.87$, $p < 0.01$; crystalline Fe-As: $r = 0.75$, $p < 0.01$) with total soil As. Arsenic associated with exchangeable, carbonate and residual fractions are minor, which shows that Fe oxide/hydroxide fractions are the most dominant solid phase controlling As concentrations in soil (Smith et al., 1998).

4.5. Arsenic in Rice

The arsenic in the rice grains in this study varied between 0.03 and 0.22 mg/kg (mean 0.13 mg/kg) and was comparable with values reported in other Korean provinces (mean 0.12 mg/kg) by Jung et al. (2005). However, our data were lower than those reported from a mining area (mean 0.41 mg/kg) by Lee et al. (2008). Compared with the data published in other countries (Fig. 4), the As level in our rice was lower than in most other countries. Further, our data are significantly lower than the permissible limit of As in rice according to the WHO's recommendation (Bhattacharya et al., 2009), indicating that the rice from the Mankyong floodplain is safe for consumption.

4.6. Relations between As in Groundwater and Rice

In this study area, groundwater is one of the major irrigation sources. Because some groundwaters of the Mankyong floodplain show high As concentrations, there is a possibility of As transfer from groundwater to rice grains. However, the spatial distribution of As in the rice and groundwater (Fig. 1) indicated no clear relationships between them. For example, the As concentrations in groundwater at W7, W9, W10, NW6, NW7, NW13, and NW 14 were significantly higher than the drinking water standard limit (10 $\mu\text{g/L}$), but the rice near these sites showed a similar range with the other rice samples, which were collected near the

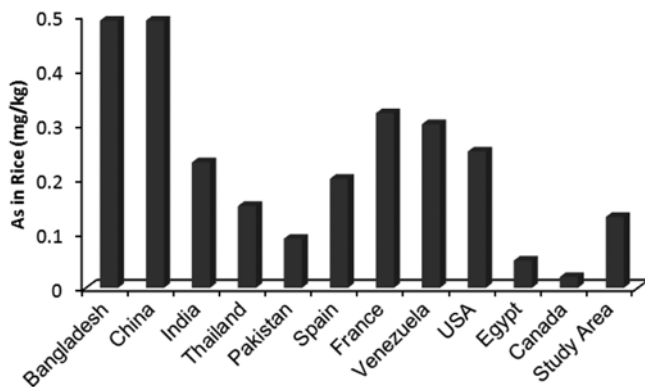


Fig. 4. Rice arsenic concentration in the study area compared with other published data. Bangladesh (Mehrag and Rehman, 2003), China (Xie and Huang 1998), India (Roychowdhury et al., 2003), Spain (Mehrag et al., 2009), France (Williams et al., 2007), Venezuela and USA (Mehrag et al., 2009), Egypt (Mehrag et al., 2007), Canada (Williams et al., 2005), and Thailand and Pakistan (Adamako et al., 2011).

sites where the groundwater As was much less than the drinking water limit. Norra et al. (2005) reported similar observations from Bangladesh, where no significant relationships were found in rice grown in elds irrigated with high and low concentrations of As, which indicates that various other factors may be controlling As uptake by plants. For example, Liu et al. (2004) reported that As uptake by rice plants is strongly controlled by Fe-plaque because it is coated at the root of the plant and adsorbs As on its surface.

4.7. Relations of Rice As with Soil Properties

Several soil factors could affect arsenic accumulation in plants (Lu et al., 2009; Bogdan and Schenk, 2009). In this study, we inspected the correlations of pH, OC, silt content, exchangeable PO_4 , and As fractionation with respect to rice As levels (Table 3).

4.7.1. Arsenic fractionation

Arsenic uptake by rice plants can be influenced by the As forms in soils (Fu et al., 2011). Generally, plants can take up the As fractions from soils when they dissolve into the soil water; thus, the exchangeable fractions are most preferred. Plants can also take up other fractions when they are slowly converted to a water-soluble fraction under different geochemical conditions. Our results show that the correlations of grain As with exchangeable and carbonate fractions were insignificant, probably as a result of their low concentrations. Among all the fractions, the amorphous ($r = 0.63$, $p < 0.01$) and crystalline Fe oxides ($r = 0.68$, $p < 0.01$) were correlated with grain As both significantly and positively (Table 3), indicating that these fractions are the important As source of the rice As. These two fractions were also the most abundant in the soil, accounting for more than 70% of the total. However, low As levels in rice may be due to incomplete reduction of Fe oxides due to oxidizing conditions in soils. Through changes in land use patterns due to flood conditions during rice cultivation, arsenic can mobi-

Table 3. Pearson correlation coefficient (r) between soil properties and grain As ($n = 21$)

Variables	Rice As (r)
Soil pH	-0.11
Silt fraction	0.37 ^a
Organic Carbon	0.14
Exchangeable- PO_4	-0.41 ^a
Total Soil As	0.75 ^b
Exchangeable-As (F1)	0.10
Carbonate-As (F2)	0.31
Amorphous Fe-As (F3)	0.63 ^b
Crystalline Fe-As (F4)	0.68 ^b
Residual-As (F5)	-0.10

^aSignificant level at $p < 0.05$; ^bSignificant level at $p < 0.01$.

lize from Fe oxides and potentially available for rice plants. Therefore, these two fractions in the soil could be considered as the predictors of arsenic concentrations in rice.

4.7.2. Soil chemical parameters

pH: Soil pH is one of the master parameters affecting As solubility and bioavailability (Fayiga et al., 2007). In general, arsenic mobility increases when soil becomes strongly acidic because the solubility of arsenic-binding species, such as Fe and Al oxyhydroxides, would be enhanced in very acidic pH conditions (Carbonell-Barrachina et al., 1999; Signes-Pastor et al., 2007). Furthermore, arsenic mobility can be increased at an alkaline pH (above 8.5) due to desorption from Fe-oxide surfaces (Dzombak and Morel, 1990). In our study, no significant relationships ($r = -0.11$) were found between rice As and soil pH, indicating that soil pH within a range of 4.9 to 7.4 has less impact on the accumulation of As in grains.

Organic Carbon: Organic carbon also affects As solubility in soils by interacting with mineral surfaces and/or with itself (Balasoieu et al., 2001). An increase in organic matter can enhance As release by competing with available adsorption sites and by changing the redox chemistry of site surfaces and As species (Wang and Mulligan, 2006). However, the presence of organic matter could also reduce As release by forming insoluble complexes (Pikaraya et al., 2005; Wang and Mulligan, 2006; Das et al., 2008). In our study, OC is found to have a low content in soils and does not play a significant role in controlling arsenic mobility in our soils, may be the reason for the lack of a good correlation ($r = 0.14$) between total organic carbon and rice grains.

Silt content: Arsenic bioavailability can be affected by soil texture (Sheppard, 1992; O'Neill 1995). Generally, silty and clayey soils contain more arsenic than sandy soils (O'Neill 1995), perhaps because of a high amount of Fe oxides. In flooding during rice cultivation, silty and clayey soils can appear to be favorable for reducing conditions, resulting in a greater availability of arsenic to plants. Although the soil type is not classified in this study, the silt contents, broadly classified as fine-grained soil, are significantly correlated ($r = 0.37$, $p < 0.05$) with rice As, indicating the silt content can influence As uptake in rice, although the relation is weak.

Soil exchangeable- PO_4 : Soil PO_4 is the most important parameter for rice paddies because it is a chemical analog of arsenate and both ions are taken up by plants through the same transport system (Zhao et al., 2009). It is more likely that PO_4 will compete with arsenate during uptake, resulting in a lower accumulation of arsenate. Several studies have shown the inhibition of arsenic uptake by PO_4 application (Abedin et al., 2002; Pigna et al., 2010; Fu et al., 2011). In our study, the exchangeable PO_4 showed a significant correlation with grain As ($r = -0.41$, $p < 0.05$) (Table 3), indicating that the competitive effect of PO_4 may be a crucial factor controlling As concentrations in rice in our study.

Overall, Fe-oxide fractions in soil are likely the most important source of As in rice. The silt fraction is also an important factor for rice As because it generally contains high amounts of iron oxides and is more favorable for a reducing condition under flooding during rice cultivation, making more As available to plants. Our results also indicated the significant relation between rice As and silt content. As indicated by the other soil parameters, soil PO_4 plays a significant role in controlling grain As, while pH and OC do not. The possible explanation for this result is that the soil pH belongs to a range that is unfavorable for As mobility and the OC in the soils showed a narrow and low range.

Several other soil factors, especially silica and sulfur content, could affect As uptake by rice, but these parameters were not measured in this study. Silicate generally competes with arsenate during plant uptake (Ma et al., 2008), while sulfur under reducing conditions forms insoluble As-sulfide minerals (Signes-Pastor et al., 2007) and reduces As content in rice due to the chelation of As with thiol (SH)-containing compounds in roots (Zhang et al., 2011). Genotypes and different environmental conditions are also important because they influence As uptake by rice.

5. CONCLUSIONS

Reductive dissolution of Fe-oxides is the major As release mechanism for the Mankyong floodplain. Despite the As concentrations in groundwater were high, the arsenic levels in the Mankyong floodplain soils were within the background levels, and the rice samples were lower than the most of other published data and the maximum permissible limits suggested by WHO. Even though, the As concentration profile in the sediment indicated the influence of groundwater irrigation, its effect is not serious for the surface soils in this floodplain. Neither groundwater As nor soil bulk As showed significant correlations with rice As. However, various other factors seem to control As transfer from groundwater and soil to rice in the study area. Rice As shows a significant relation with As-bound Fe-oxide fractions and soil PO_4 , indicating that these factors are mainly controlling As levels in rice. The low levels of As in rice may be due to the incomplete reduction of Fe oxides and/or PO_4 competition during As uptake by plants.

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