

ARSENIC IN GROUNDWATER OF THE RED RIVER FLOODPLAIN, VIETNAM: SOME RESULTS OF THE VIETAS PROJECT

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ARSEN I GRUNDVAND OG DRIKKEVAND

HELNAN, MARSELIS HOTEL

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RESUMÉ

The mobilization of arsenic (As) to the groundwater was studied in a shallow Holocene aquifer on the Red River flood plain near Hanoi, Vietnam. Results show an anoxic aquifer featuring organic carbon decomposition with redox zonation dominated by the reduction of Fe-oxides and methanogenesis. The concentration of As increases over depth to a concentration of up to 550 µg/L. Most As is present as As(III) but some As(V) is always found. Arsenic correlates well with NH₄, relating its release to organic matter decomposition and the source of As appears to be the Fe-oxides being reduced.

INTRODUCTION

Groundwater contaminated with arsenic with a concentration exceeding the WHO drinking water limit of 10 µg/L As is a threat to the health of some 57 million people in Bangladesh and West Bengal /1/. Recently it has become clear that a similar problem exists in the Red River floodplain aquifers, Vietnam, where about 11 million people may be exposed to enhanced arsenic concentrations /2/. To remediate the problem of high arsenic concentration in groundwater used for drinking water it is imperative that the processes leading to the mobilization of arsenic into groundwater are properly understood. In Bangladesh the processes controlling the release of arsenic to the groundwater have been studied intensively but they remain subject of intense disputes among researchers /3/. One of the problems encountered in Bangladesh is the extreme variability in the groundwater arsenic content between boreholes only 100 m apart /4/. Apparently, this reflects the highly complex hydraulics in floodplain sediments with paddy rice fields, dug ponds, irrigation channels and intensified groundwater pumping for irrigation /5/.

The objective of the present work is to elucidate the processes controlling the arsenic release to groundwater in a Red River floodplain aquifer under more pristine conditions, avoiding the hydraulic complexities mentioned before.

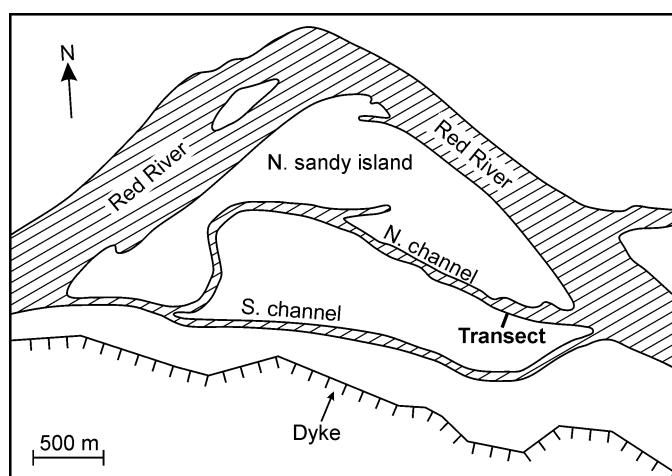


Figure 1. The location of the Dan Phuong field site on the banks of the Red River, approximately 30 km upstream of Hanoi. Note the position of the transect between the river and the dyke.

FIELD SITE AND HYDROGEOLOGY

A field site was established along the Red River about 30 km upstream from Hanoi, near the village Dan Phuong. The field site (Figure 1) is situated between the river and the dyke. The agricultural activities here consist of growing crops like corn and sweet potatoes and there are no paddy rice fields or irrigation channels. Geologically the field locality consists of a sand bar formed by the Red River. Because the sand bar becomes inundated during flooding, a clay layer of up to 7 m thick has formed on the top. Comparison with older maps and aerial photographs indicates rapid migration of the sand bars in the Red River and the sand bar at our field site is probably less than hundred years old.

Along one of the smaller channels a transect of boreholes was established parallel to the regional groundwater flow direction and almost perpendicular to the channel. Figure 2 shows the transect with the clay layer on top and a sandy Holocene aquifer below. The groundwater table varies from elevation 6 m in the dry season to 8.5 m in the wet season. One hundred boreholes were drilled, up to 22 m deep, each equipped with a short, 30 cm screen. The position of the screens is indicated in Figure 2.

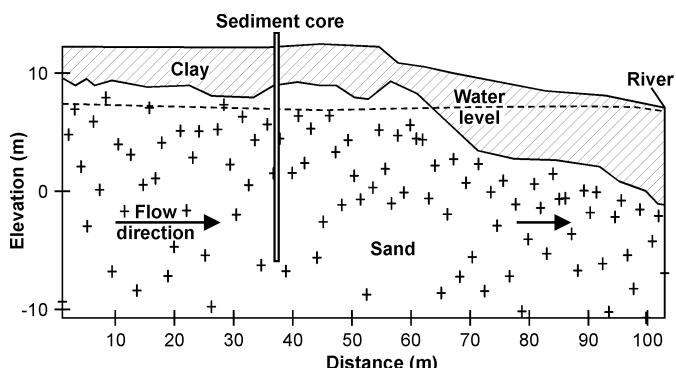


Figure 2 .The transect is orientated approximately SW-NE on the south bank of a side channel to the Red River (Fig. 1). The transect contains 100 boreholes penetrating the clay cover and screened at different depth in the underlying sandy Holocene aquifer. The screen length is 30 cm and their positions are indicated as crosses in the graph.

REDOX CONDITIONS IN THE AQUIFER

Figure 3 shows the distribution of some redox sensitive components in the aquifer. The upper 2 m of the saturated zone contains some O₂ but the concentration is significant lower than the concentration of 0.26 mM (27 °C) expected for equilibrium with the atmosphere. Nitrate is only found in superficial groundwater at a concentration of up to 0.5 mM and is particularly abundant in the distance range 50-65 m (Fig. 3), where the clay layer is thin. Below elevation 5 m, the aquifer is anoxic. Towards greater depth Fe²⁺ enters the water and the concentration gradually increases over depth to about 0.3 mM (17 mg/L). Up to 0.7 mM of sulfate is found in the uppermost groundwater and its concentration decreases sharply over depth while dissolved sulfide always remains below the detection limit of 0.5 µM. The sulfate distribution indicates that while some originates from the surface, most appears derived from seepage through the river bottom. The anoxic part of the saturated zone also contains methane (CH₄) but in contrast to Fe²⁺, the highest concentration of around 1 mM (16 mg/L) are here found within a horizontal band between elevation 0 and -5 m. Ammonia (NH₄) shows a distribution

in the groundwater that is very similar to that of methane and reaches at elevation -2 m a maximum of 0.4 mM (7 mg/L NH₄).

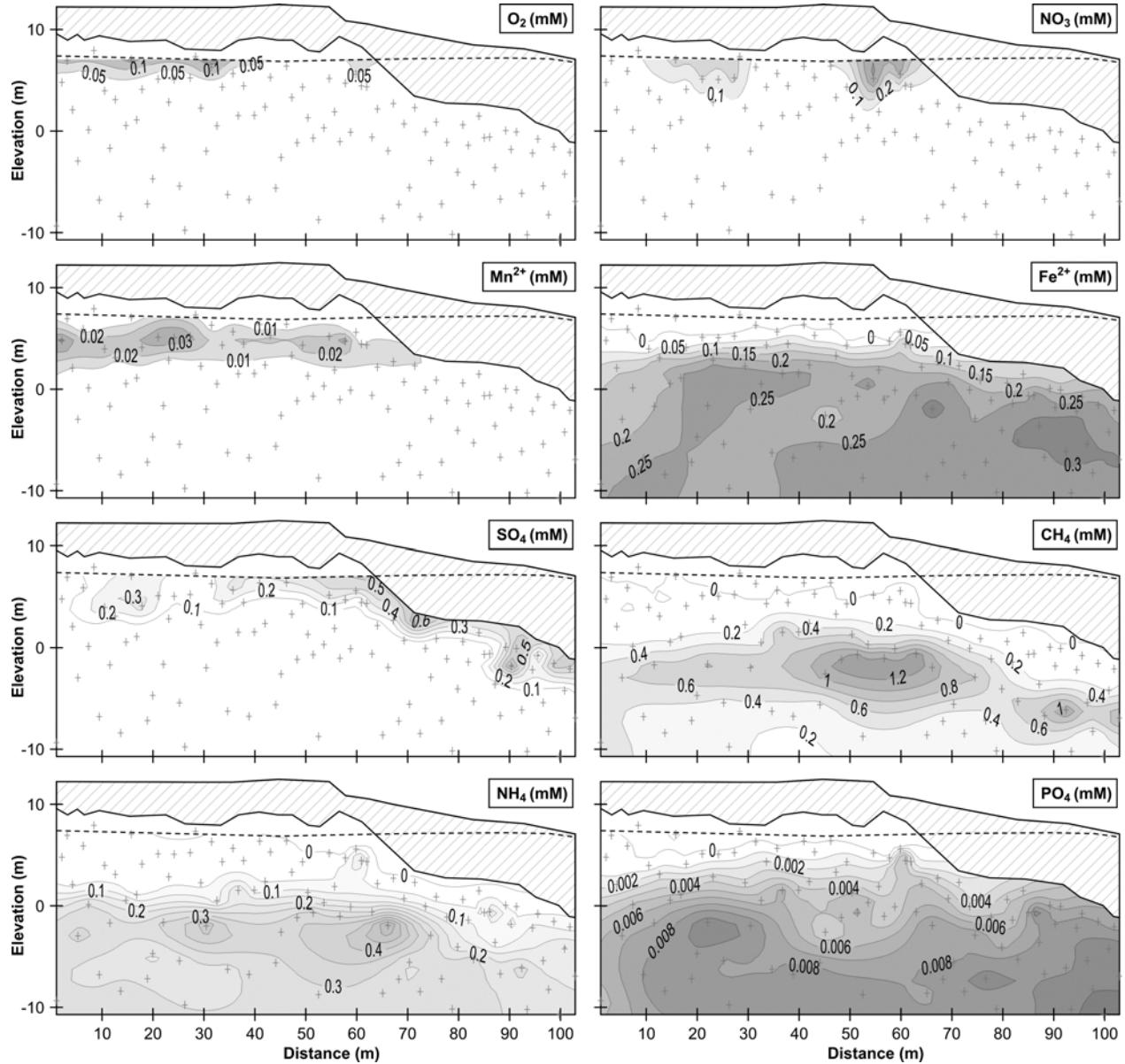


Figure 3. Redox components in the groundwater of the Dan Phuong transect. Crosses indicate sampling points and contouring is based on a measurement at each sampling point. Contours marked as zero refer to the detection limits (NH₄ < 0.0056 mM, Fe²⁺ < 0.0018 mM, CH₄ < 0.01 mM, PO₄ 0.0011 mM).

ARSENIC

The distribution of arsenic (As) in the groundwater is shown in Figure 4. The uppermost part of the saturated zone, roughly corresponding to the oxic zone (Figure 3) contains no arsenic. However, with depth the arsenic concentration increases, reaching values as high as 400 µg/L. Dissolved arsenic may be present in two oxidation states; as reduced As(3) and oxidized

As(5). Figure 4 shows that most arsenic is present in the reduced As(3) form but a small percentage of As(5) seems always to be present. Particularly in the deepest layers the relative percentage of As(5) seems to increase.

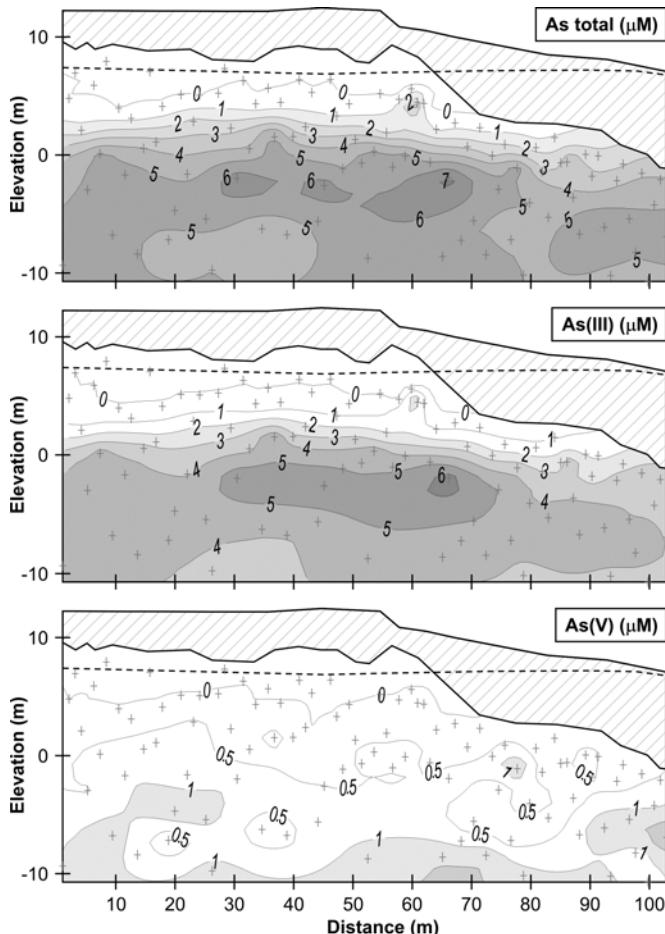


Figure 4. The distribution of arsenic in the groundwater of the Dan Phuong transect. Crosses indicate sampling points. Concentrations are given in $\mu\text{mol/L}$ ($1 \mu\text{mol/L} = 75 \mu\text{g/L}$). As(3) and As(5) indicate arsenic in oxidation states three and five.

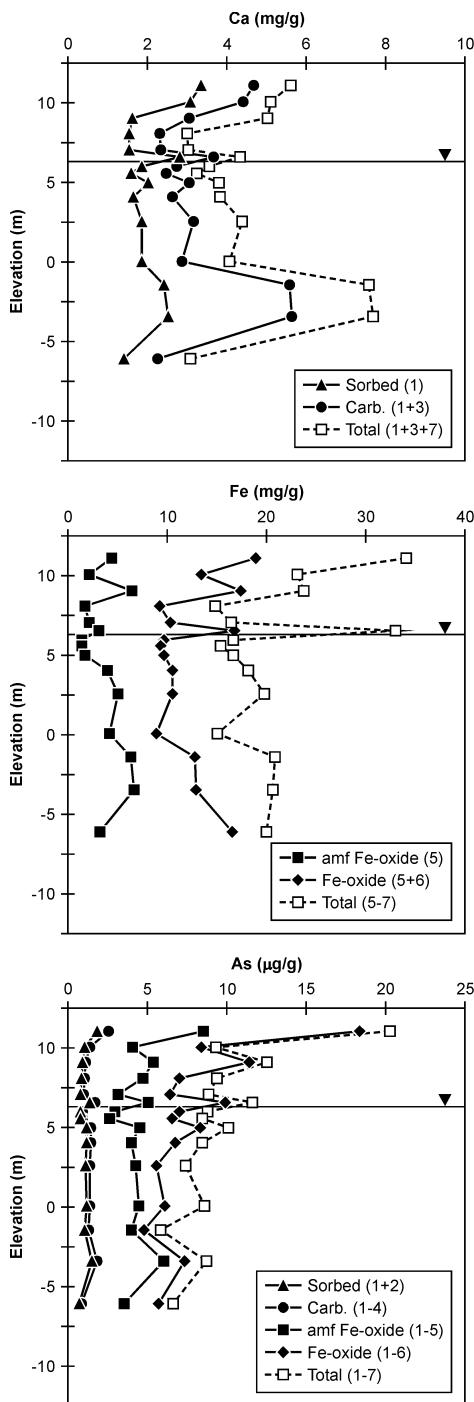
ARSENIC, IRON, CALCIUM AND CARBON SPECIATION IN SEDIMENTS

Sequential extractions were carried out to delineate the speciation of As, Fe and Ca in the sediment, using cores from a borehole at distance 37 m in the transect (Fig. 2). We used the sequential extraction scheme of Wenzel et al. /6/ extended with steps targeting carbonate dissolution (Table 1).

Table 1. Sequential extraction scheme for sediments, modified from Wenzel et al. /6/.
SSR indicates Solid-Solution Ratio

Step	Target phase	Extractant	Extraction conditions	SSR [g]:[m L]	Wash step
1	Non-specifically bound As	0.05M $(\text{NH}_4)_2\text{SO}_4$	4h shaking, 20°C	1:25	-
2	Specifically bound As	0.05M $(\text{NH}_4)\text{H}_2\text{PO}_4$	16h shaking, 20°C	1:25	0.05M $(\text{NH}_4)\text{H}_2\text{PO}_4$; SSR 1:12.5; 4h shaking
3	Carbonate bound As	1M NaOAc + HOAc, pH 5	6h shaking, 20°C	1:25	1M NaOAc + HOAc, pH 5; SSR 1:25; 4h shaking
4	Resorbed As, released from carbonates	0.05M $(\text{NH}_4)\text{H}_2\text{PO}_4$	4h shaking, 20°C	1:25	-
5	Amorphous hydrous oxide-bound As	0.2M NH ₄ -oxalate buffer, pH 3.25	4h shaking 20°C in the dark	1:25	0.2M NH ₄ -oxalate, pH 3.25; SSR 1:12.5; 10 min shaking in the dark
6	Crystalline hydrous oxide bound As	0.2M NH ₄ -oxalate buffer + 0.1M ascorbic acid, pH 3.25	30min, water basin at 96 ± 3°C daylight	1:25	0.2M NH ₄ -oxalate, pH 3.25; SSR 1:12.5;
7	As in sulfide minerals	16N HNO ₃ (65%)	Autoclave method 105min 110°C	1:25	10 min shaking in the dark -

The results (Fig. 5) show that "Sorbed Ca" resulting from step 1 with $(\text{NH}_4)_2\text{SO}_4$ extraction (Table 1) constitutes the largest Ca fraction. It includes Ca adsorbed on exchanger positions and probably some from dissolving carbonate minerals as well. The second step with $(\text{NH}_4)\text{H}_2\text{PO}_4$ extraction is likely to precipitate any extracted Ca. However, step 3 ("Carb." in Fig. 5) with Na-acetate/acetic acid should dissolve both carbonate minerals and any precipitate resulting from step 2. The "Carb" (step 3) fraction particularly extracts a pool of Ca between elevation 0 and -5 m. Finally "Total" reflects the additional amount of Ca extracted by HNO₃ (Table 1) which will dissolve any remaining carbonate and extract some Ca from silicate minerals as well. For Fe (Fig. 5) the amorphous hydrous oxide (step 5) and the crystalline Fe-oxide (step 6) fractions (Table 1) extract about equal amounts of Fe although the former tends to increase somewhat over depth. Finally, the total Fe (step 7) fraction will extract Fe from pyrite and silicates. The peaks in the Fe distribution at elevations +6 and +11 m correspond to the presence of clay layers.



The distribution of As (Fig. 5) shows that "Sorbed" As (steps 1+2 in Table 1) only constitutes a small part of the extracted As. The fraction of As specifically derived from carbonates ("Carb." in Fig. 8) is negligible and the zone between elevation 0 and -5 m where the Ca distribution indicates that most carbonate dissolution takes place is not at all reflected in the As distribution. Accordingly there is no evidence to support the association of As with CaCO_3 phases in the sediment. By far most of the As is extracted in the two steps (5 and 6) targeting Fe-oxides. As for iron, the As distribution shows peaks where there are clay layers in the sediment. There is also a trend showing the highest As values above the water table, and then somewhat decreasing with depth below the water table. Some additional As is extracted by HNO_3 ("Total" in Fig 5) which could be derived from pyrite and silicate minerals. However, the general conclusion is that most As must be associated

Figure 5. Results of sequential leaching of sediments. The sampling position is shown in Fig. 2. The data is plotted cumulatively. In the legend, the numbers in parenthesis refer to the extraction steps listed in Table 1.

Discussion

Generally the groundwater chemistry indicates that the degradation of organic matter is an important process in this aquifer. The first electron acceptor for organic matter degradation is dissolved oxygen and its consumption leads to complete oxygen depletion already a few meters below the water table. The next quantitatively important electron acceptor is iron oxide, present in the sediment, and its reduction leads to the gradually increasing Fe^{2+} concentration over depth. The sulfate concentration is low throughout the aquifer ($< 0.2 \text{ mM}$) and decreases over depth but dissolved sulfide was always below the detection limit. The final process in the redox sequence is fermentation of organic material, leading to the release of methane to the

groundwater. Organic matter always contains some nitrogen compounds and during degradation this results in the release of ammonia to the groundwater. In that sense, the ammonia concentration is a good indicator for the intensity of organic matter degradation and this is also confirmed by the correlation between the methane and ammonia concentrations (Figure 6). At low concentration Fe^{2+} also correlates with ammonia (Figure 6). However, towards higher concentration the correlation breaks down apparently because part of the Fe^{2+}

precipitates, probably as siderite (FeCO_3) because the water gets strongly supersaturated for this mineral.

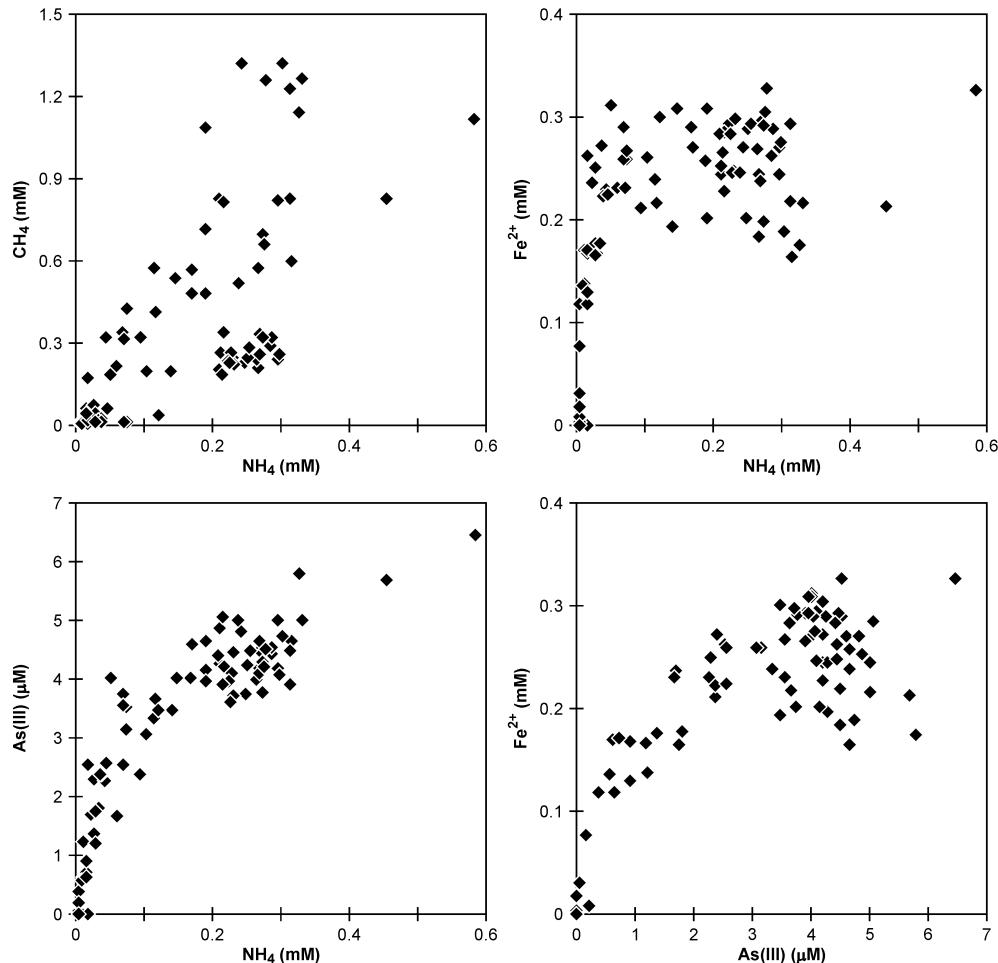


Figure 6. Correlation between ammonia, as indicator for organic matter degradation and other parameters in the groundwater of the Dan Phuong transect (Fig. 2).

The distribution of arsenic seems closely related to the changing redox conditions in the aquifer. The uppermost least reduced layers are free of arsenic, while the arsenic concentration increases as the waters become more reducing (Figures 3 and 4). The groundwater As(3) concentration also has a very good correlation with the ammonia concentration (Figure 6), suggesting a coupling between arsenic mobilization and organic matter degradation. The groundwater As(3) concentration also shows a correlation with Fe^{2+} . In combination with the correlation of As(3) with NH_4 this suggest that organic matter oxidation coupled to the reduction of iron oxides generates the release of arsenic to the groundwater. Previous investigations in Bangladesh have also suggested that arsenic may enter the aquifer associated with iron oxide coatings on the sediment grains and when conditions become reduced, the arsenic is released to the groundwater together with Fe^{2+} [7, 8]. According to Figure 6 the correlation between Fe^{2+} and As(3) becomes distinctly poorer towards high concentration. Data not presented here indicates that the groundwater becomes strongly supersaturated with respect to

several Fe(2)-minerals which are likely to precipitate. Apparently such precipitates do not remove As in the same proportion as Fe^{2+} .

CONCLUSION

The results at Dan Phuong suggest a rapid mobilization of arsenic in Holocene aquifers on the Red River flood plain. Apparently the arsenic is released from the floodplain sediment in relation to organic matter degradation. The measured arsenic concentrations did exceed 400 $\mu\text{g/L}$ or 40 times the WHO limit! The uniform increase in arsenic in the groundwater suggest that the problem with high arsenic is widespread in shallow aquifers of the Red River flood plain and should be taken very serious. The Dan Phuong aquifer differs from most other aquifers on the Red River flood plain by its pristine flow conditions and the geochemical processes are therefore easier elucidated. Most aquifers used for drinking water abstraction are located on the other side of the river dykes where groundwater hydraulics are more complicated and a much larger variability in the distribution of arsenic in the groundwater can be expected.

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