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Strong chemical evidence for high Fe(II)-colloids and low As-bearing colloids (200 nm–10 kDa) contents in groundwater and flooded paddy fields in Bangladesh: A size fractionation approach

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ABSTRACT

Arsenic speciation in groundwater and interstitial waters from soil irrigated with As-rich groundwater in Bangladesh was investigated through a size fractionation approach performed in the field and under conditions that allowed the preservation of natural anoxic conditions. Based on a simple chemical characterization, the presence of Fe(II) in the colloidal fraction (<200 nm–>10 kDa) in anoxic groundwaters and soil waters of flooded paddy fields was assessed. Arsenic was found to be present mainly as a "solute" oxy-anion as indicated by the small amount of As associated with the 200 nm–10 kDa colloidal fraction (most of the time, less than $10 \pm 5\%$ of total As). When As-colloids were observed, they were linked to high Fe concentration and the As-colloid percentage was relatively well correlated with the total Fe concentration in solution. This study underlined that under natural anoxic conditions, there was no impact of PO_4^{3-} , SiO_4^{4-} and Mn on the As-bearing colloids, which is not in agreement with results obtained under laboratory controlled conditions. Therefore, it is suspected that the impact of other naturally occurring ligands, such as organic matter, could modify Fe(II) speciation, and, in turn, As speciation. To assess the complexation of Fe(II) by organic matter, the WinHumicV model was used to calculate Fe(II) speciation. Using the standard parameters to describe organic matter reactivity, results showed that organically-bound Fe(II) ranges from 5% to 100% and 30% to 100%, for groundwater and soil water, respectively, depending on the pH and the Fe(II) and DOC contents. Evidence for independent speciation of Fe and As under natural anoxic conditions is of great importance for predictive modelling of the mobility, the availability and then the bioavailability of As in As-affected areas.

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1. Introduction

High As contents in shallow groundwater have long been a human health issue for millions of people in certain regions of southern Asia (Smedley and Kinniburgh, 2002). Moreover, As in soil inherited from increasing irrigation practices during the dry season with As-rich groundwater becomes of interest because of its potential transfer to plants such as rice (Meharg and Rahman, 2003). It is well recognized that high Fe and As concentrations observed in groundwater in Bangladesh result from reductive dissolution of Fe (oxyhydr)-oxides due to bacterially-induced anoxic conditions (van Geen et al., 2004; Mladenov et al., 2010). For paddy fields irrigated with As-enriched groundwater, it is worth noting that the As

content of the rice-submerging water and in soil water obviously depends on the As content of the irrigation water (Norra et al., 2005; van Geen et al., 2006; Roberts et al., 2010) but no direct relationship has been observed (Garnier et al., 2010). As far as As speciation and its availability in natural solution are concerned, they mainly depend on As and Fe redox status (As(III) or As(V), Fe(II) or Fe(III)) in solution but also on the impact of other component of natural systems such as PO_4 , silica, Mn or organic matter. Furthermore, more than dissolved species, it is now well accepted that natural colloids must be taken into account for accurate predictive modelling of the metal(loid)s speciation and then to determine their bioavailability. Arsenic mobility has been shown to be particularly controlled by interaction with Fe oxyhydroxide-colloids because of their strong ability to adsorb As at circum neutral pH (Dixit and Hering, 2003). However, interactions of As with Fe mineral phases may be indirectly and strongly modified by the presence of PO_4 , silica, Mn or organic matter that can act upon the Fe

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(oxyhydr)-oxides) formation and structure (Rose et al., 1996; Doelsch et al., 2003; Wolthoorn et al., 2004), and fixation of As on/in Fe minerals (Davis et al., 2001; Liu et al., 2001; Thoraj et al., 2005; Sahai et al., 2007; Ciardelli et al., 2008; Bauer and Blodau, 2009).

Aquifers and paddy fields in Asian deltaic areas have anoxic conditions. It has to be pointed out that Fe speciation in such an anoxic natural environment has received little attention, likely because anoxic conditions are difficult to preserve during and after sampling, for further investigations such as size fractionation (Hassellöv et al., 2007). In addition, very little is known about the presence of Fe(II) in colloidal fractions under anoxic conditions; as this has only been assessed in the two studies mentioned here. First, in the colloidal fraction of a stream in a catchment which includes some Fe-rich shale bands partly overlain with peat (Gaffney et al., 2008). Second, in suboxic groundwater from a sandy coastal aquifer where 4% of the Fe was associated with the colloidal fraction, but the authors did not indicate whether this small fraction was composed of Fe(II) or Fe(III) (Hassellöv et al., 2007).

Whether and how colloids influence As mobility and speciation under natural anoxic conditions is of great scientific interest due to the impact on the water and food supply of the local population. Indeed, in the case of rice, As complexation by colloidal particles may significantly reduce its bioavailability for the plant by competitive effects between colloidal reactive sites and As-specific sites (or Fe plaque) on the cell membrane of roots (Liu et al., 2004; Guo et al., 2005). Therefore, in the present paper, the leading role of such colloids was investigated through the occurrence of colloidal species and the impact of components such as Fe, Mn, PO_4^{3-} and SiO_4^{4-} on colloid formation. For this purpose, a size fractionation procedure was carried out (under controlled anoxic conditions) with decreasing pore size cut-offs in order to allow colloid isolation from the so-called “solute” dissolved forms. Moreover, the identification of processes controlling As mobility and As speciation in soil water being a key point when considering As uptake by rice plants in flooded paddy fields from As-affected areas, the investigations were performed on Bangladesh groundwaters and soil waters from paddy fields irrigated with As-rich groundwaters.

2. Material and methods

2.1. Water sampling

Twelve groundwaters used for irrigation during the dry season were sampled in the Arahazar sub-district (Bangladesh) between 2006 and 2008 from tube wells equipped with electrical pumps. Groundwater sampling points were selected according to their Fe and As concentrations in order to cover a large As/Fe ratio (see results below), with two samples W-F1 et W-F2 (see below nomenclature) collected at the same site 11 days apart. Nine interstitial water samples coming from three flooded paddy fields (irrigated with water pumped from three of the above selected tube wells) were sampled at different periods of time of irrigation during the dry season. Sampling at different places and periods of the rice growth also allowed covering different As/Fe ratios in relation to the great difference in observed geochemical conditions such as redox potential (Garnier et al., 2010). One sample corresponding to the water layer submerging the rice field was also collected. Soil water was extracted by squeezing soil cores (Top 6 cm of the soil) giving between 40 and 60 mL of water for each soil sample. Concerning irrigation groundwater, a 2 L bottle was filled by overflow until the O_2 concentration was stabilized to the lowest recorded value (generally a few%). It has to be noted that, due to the volume needed for dissolved organic C (DOC) analysis in soil solution, a

second core was sampled for this purpose in addition to the one used for the other analyses.

2.2. Size fractionation procedure

In both cases (aquifers and flooded paddy fields), the water was under reducing conditions before sampling and the challenge was to maintain these conditions during the sampling and the size fractionation procedure. This was realised by performing the different filtrations on site, a few minutes after sampling and under a N_2 atmosphere using a glove bag. Size fractionation was performed at the nominal cut-off of 200 nm, 25 nm and 10 kDa for the groundwater samples and only at the nominal cut-off of 200 nm and 10 kDa (due to the small amount of water available) for the soil water samples. The size fractioning was carried out using a cascade filtration procedure. The 200 nm filtration was performed using a syringe holder filter for the soil water samples and with a filtration set holder under N_2 pressure using 200 nm Nuclepore® membranes (0.47 mm diameter) in the case of groundwater. The 25 nm and 10 kDa filtrations were carried out under N_2 pressure with acetate membranes and polyethersulfone Millipore® membranes, respectively, using a 47 mm filter holder. According to the available water volume, the size fractioning took between 1 and 5 min for the 200 nm filtrations and between 5 and 15 min for the 10 kDa filtrations, for soil waters and groundwaters, respectively. Even if membrane clogging cannot be ignored, Nuclepore® and Millipore® membranes are known to be little affected by this process (Buffle et al., 1992) and no reddish colour was observed on the membranes after filtration. More details on the water sampling and the size fraction procedure of groundwaters and soil waters are given in Supporting information.

2.3. Sample nomenclature

Samples coming from wells (groundwater) or soils (soil water from flooded paddy fields) were named by “W” and “SW”, respectively, followed by letters and/or numbers identifying the location and by a final letter (A–C) corresponding to the fraction passing through 200 nm, 25 nm and 10 kDa membranes, respectively. The sample labelled SS corresponds to the water layer on a flooded paddy field.

In the present study, any element encountered in the fraction lower than 10 kDa will be considered as “solute” using the nomenclature proposed by Buffle et al. (1992). Even if a 25 nm filtration was performed in the case of groundwaters, only one colloidal fraction was considered in this paper, corresponding to the size fraction isolated between 200 nm and 10 kDa membranes. The percentage (with respect to the total) of an element in this operationally-defined colloidal fraction was calculated by subtracting the concentration in the 10 kDa fraction to the concentration passing through the 200 nm filter. It has to be noted that some negative values can be observed when calculating the colloidal fraction because of closed concentrations in fractions A and C falling within the range of analytical error.

2.4. Fe speciation in solution

Only filtered solutions were used for determination of Fe speciation in solution. Therefore, Fe potentially adsorbed on macro organic matter components was not taken into account in this study. Because of a probable rapid change of Fe speciation in the case of modification of the initial reducing conditions of the samples, Fe^{3+} and Fe^{2+} concentrations in filtered samples were determined in the field, immediately after sampling. This was carried out by colorimetric measurements on a 12 V spectrophotometer (Dr. Lange/Hach) using registered analytical kits (LCK 320) based

first, on Fe(II) complexation with phenanthroline and in a second step, after reduction of Fe(III) to Fe(II). Therefore, Fe(III) concentration in the filtered solution was calculated by difference between total Fe measured after reduction and Fe(II) concentration. The total Fe in the filtered solution (Fe(Tot)) refers to Fe measured in the laboratory or to the sum of Fe(III)+Fe(II) measured in the field. It should be noted that any change in the Fe(Tot)/Fe(II) ratio between two successive filtrations indicates an oxidation process during the filtration procedure. Therefore, determination of the Fe speciation in the field also allowed checking if the water samples had maintained their initial anoxic conditions during the different size fractionation procedures.

2.5. Water analysis

Filtered water samples were acidified with 1% supra pure HCl in the field. Arsenic and Al concentrations were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP MS – Elan DRC II – Perkin Elmer Sciex), and Fe, P, Mn, Si and K were measured by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP AES Optima 2000 DV Perkin Elmer). The analytical conditions used for both techniques are described in Supporting information (Table SI-1). The analytical error for both techniques was below 5% and the results are given in $\mu\text{mol L}^{-1}$, with the relative standard deviation (%RSD) obtained on five replicates.

2.6. Fe(II) speciation modelling

Various models have been developed to describe the interactions of natural organic matter (NOM) with proton or metals, using discrete or continuous distribution of binding sites (e.g. Tipping, 1998; Kinniburgh et al., 1999; Dudal and Gérard, 2004; Lenoble et al., 2008). In this study, to calculate Fe(II) speciation, and particularly its interactions with the dissolved organic matter, the Win-HumicV (Gustafsson, 1999) model has been used. It is based on the Humic Ion-Binding Model V, assuming a discrete distribution of binding sites which form mono- or bi-dentate complexes with proton and metal, as described in detail elsewhere (Tipping, 1998). To depict the metal-humic binding, the following parameters have to be defined: organic matter content (in g L^{-1}), percentage of reactive humic substances and percentage as fulvic acid. It is generally assumed that the organic matter is composed of 50% C. Default values for the other two parameters are both 100%, which has been used by several authors in comparable studies (e.g. Christensen et al., 1999; Jansen et al., 2003; Ge et al., 2005), even if some authors have tested other conditions, for instance 50% of reactive humic substances (HS) with 100% or 90% of fulvic acid (FA) (Unsworth et al., 2006). In this study, as it was not possible to speculate on these parameters, it was decided to test the following organic matter models: 50% or 100% of reactive HS with a proportion of 50% or 100% of FA. Considering the available data, Fe(II) speciation calculation was performed separately for groundwater and soil water samples, studying three different cases: (I – unfavourable) minimal pH and DOC values with maximum Fe(II) content; (II – favourable) maximum pH and DOC with minimum Fe(II); and (III – average) average values of pH, DOC and Fe(II).

3. Results

The groundwater and the soil water pH, respectively, varied from 6.3 to 7.4 and 6.5 to 7.5. Only seven values of dissolved organic C are available for the A fraction (fraction below 200 nm) (three groundwaters and four soil waters) and the values ranged between 2.8 and 4.2 mg L^{-1} for groundwaters and between 14.2 and 62.4 mg L^{-1} for soil solutions. Arsenic, Fe, Mn, SiO_4^{4-} and PO_4^{3-}

(when available) concentrations in A, B and C size fractions for all the studied samples are given in Tables 1a and 1b and as stacked histograms for easier comparison of the data in Figures SI-1a and SI-1b for groundwater and SI-1c for soil waters in Supporting information.

Determination of Fe speciation in the field was not possible for all samples (Tables 2a and 2b) because of the small volume available for the isolated fractions of some soil solutions. For high Fe concentrations, the total Fe (i.e. 200 nm-filtered Fe) concentrations measured in the field (when available) in all the different isolated fractions were in good agreement with the concentrations measured in laboratory (Fig. 1 and Tables 1a and 1b). However, for low Fe concentrations, the ratio between the concentration measured in the field and in the laboratory can deviate by up to 50%. It is worth noting that (for all the size fractions) Fe was mainly in the Fe(II) form as shown by the Fe(II) percentages as a function of total Fe concentration in groundwater and soil water samples measured in the field (Tables 2a and 2b and Fig. 1).

Arsenic concentrations in groundwater A fractions varied by an order of magnitude between samples (from 0.40 to 4.20 $\mu\text{mol L}^{-1}$). Compared to groundwaters, higher As concentrations were found in soil waters (0.40–8.9 $\mu\text{mol L}^{-1}$). The Fe concentrations in groundwater A fractions also varied by an order of magnitude between samples (from 30 to 290 $\mu\text{mol L}^{-1}$) but, contrary to what was observed for As, Fe concentrations decreased sharply in the B and C fractions. Very little variation was observed for Mn and SiO_4^{4-} concentrations between groundwater or soil water different size fractions. Yet, for Mn, higher concentrations were measured in soil waters (a maximum of 10 $\mu\text{mol L}^{-1}$ for groundwaters, and 170 $\mu\text{mol L}^{-1}$ for soil waters). Conversely, SiO_4^{4-} exhibited much higher concentration in groundwaters (around 700 $\mu\text{mol L}^{-1}$ against 380 $\mu\text{mol L}^{-1}$ maximum in soil waters). Concerning PO_4^{3-} , as for Fe, concentrations exhibited decreasing values from A to C size fraction for both groundwaters and soil waters.

4. Discussion

Arsenic speciation (arsenite As(III) and/or arsenate As(V)) in the different size fractions was not determined in the present study but previous studies on the same groundwaters and soil water from the same flooded paddy fields have shown that of the As in the <200 nm fraction was between 95% and 98% As(III) (Garnier et al., 2010; van Geen et al., 2006). It is then assumed that As speciation in the present samples is similar to that observed in the previous studies, even if this assumption could be less justifiable for soil water for which redox conditions are changing (Takahashi et al., 2004).

Lower concentrations of a given element observed between two different size fractions indicate the presence of a colloidal form of this element. This finding, as well as the variation of the ratio between some elements in the different size fractions can be used to determine the impact of the different components on As, Si, Mn and Fe-colloid formation, if any.

The total Fe (i.e. 200 nm-filtered Fe) concentrations observed in both groundwater and soil water are very high and obviously such high concentrations are found only because of the presence of Fe(II) species and not because of the presence of Fe(III). Therefore, for soil waters, even when the Fe(Tot)/Fe(II) ratio (Tables 2a and 2b) was not available and because of the similar environmental conditions for all the sample sites (paddy fields flooded with groundwater), it is reasonable to assume hereafter that Fe concentration mainly corresponds to Fe(II) species. In addition, and more surprisingly, it was observed that the Fe(II) concentration decreased with decreasing size of the isolated fractions (Tables 1a and 1b). Indeed, the

Table 1a
Concentrations ($\mu\text{mole L}^{-1}$) measured in the different size fractions of groundwater.

	As	%RSD	Fe	%RSD	Mn	%RSD	Si	%RSD	P	%RSD
W-K1-A	4.20	0.2	206.8	0.3	1.4	0.6	553	0.7	33.5	0.6
W-K1-B	3.96	0.3	162.9	0.2	1.4	0.5	544	0.8	22.0	0.7
W-K1-C	3.88	0.2	91.7	0.2	1.3	0.6	517	0.9	3.7	0.8
W-K2-A	2.49	0.5	156.1	0.6	4.4	0.4	586	0.6	29.5	0.2
W-K2-B	2.39	0.6	114.1	0.2	4.4	0.3	602	0.7	14.5	0.3
W-K2-C	1.88	0.5	33.0	0.4	4.1	0.2	568	0.8	2.9	0.7
W-C1-A	1.65	0.4	55.9	0.5	3.3	0.1	616	0.3	24.2	0.2
W-C1-B	1.62	0.5	48.9	0.4	3.2	0.2	611	0.6	21.4	0.2
W-C1-C	1.45	0.3	16.5	0.5	3.1	0.1	607	0.4	8.9	0.4
W-C2-A	1.48	0.7	59.5	0.4	2.9	0.4	470	0.4	21.5	0.4
W-C2-B	1.47	0.6	52.7	0.6	2.9	0.4	478	0.8	18.6	0.6
W-C2-C	1.38	0.4	23.7	0.4	2.8	0.6	472	0.6	4.8	0.7
W-G1-A	0.24	0.6	11.4	0.7	1.8	0.7	449	0.7	7.3	0.6
W-G1-B	0.26	0.7	8.0	0.9	1.8	0.7	451	0.9	6.0	0.6
W-G1-C	0.24	0.6	2.9	0.7	1.8	0.6	445	0.8	2.8	0.8
W-C3-A	1.79	0.6	57.0	0.23	3.1	0.51	569	0.65		
W-C3-B	1.73	0.7	45.0	0.59	3.1	0.72	577	0.88		
W-C3-C	1.55	0.7	11.3	0.03	2.9	0.8	544	2.53		
W-D1-A	2.52	0.4	32.3	0.1	2.7	1.26	527	0.34		
W-D1-B	2.41	0.3	22.4	0.24	2.7	0.72	537	2.14		
W-D1-C	2.35	0.3	1.8	0.26	2.6	0.87	541	0.94		
W-H1-A	0.64	0.2	30.6	0.35	4.6	0.04	708	1.7		
W-H1-B	0.51	0.6	24.0	0.37	4.0	1.92	566	0.6		
W-H1-C	0.65	0.7	21.0	0.34	4.6	2.5	708	0.54		
W-M1-A	1.13	0.4	117.4	1.59	10.1	0.11	726	0.45		
W-M1-B	1.11	0.3	108.2	1.4	10.1	1.37	719	0.3		
W-M1-C	0.98	0.4	57.7	0.24	9.9	0.71	712	0.11		
W-F1-A	1.13	0.2	57.2	0.3	2.2	0.3				
W-F1-B	1.19	0.3	44.1	0.5	2.1	0.2				
W-F1-C	1.08	2	17.3	2.2	2.0	1.3				
W-F2-A	1.18	0.4	45.9	0.6	2.2	0.8				
W-F2-B	1.15	0.3	32.0	0.7	2.1	0.2				
W-F2-C	1.21	1	28.6	0.2	2.1	0.4				
W-S1-A	0.44	0.6	288.5	2.55	4.5	0.65	569	1.22		
W-S1-B	0.44	0.4	270.6	0.07	4.6	1.06	559	2.07		
W-S1-C	0.27	0.4	57.0	0.34	4.2	0.36	548	0.13		

Table 1b
Concentrations ($\mu\text{mole L}^{-1}$) measured in the different size fractions of soil water and surface water.

	As	%RSD	Fe	%RSD	Mn	%RSD	Si	%RSD	P	%RSD
SW-1-A	3.71	0.7	258.6	0.8	93.8	0.5	171	0.3	13.9	0.8
SW-1-C	1.82	0.9	6.3	1.1	80.0	0.3	153	0.3	6.1	0.9
SW-2-A	1.82	0.8	156.5	0.5	111.1	0.6	64	0.3	11.3	0.9
SW-2-C	1.67	0.9	138.0	0.5	100.7	0.7	63	0.5	10.0	0.9
SW-3-A	8.91	0.4	141.9	0.4	72.1	0.2	298	0.5	9.4	1.1
SW-3-C	5.45	0.6	12.6	0.7	62.4	0.2	249	0.4	4.9	1.2
SW-4-A	4.60	0.2	297.1	0.5	168.5	0.4	182	0.5	13.2	1.3
SW-4-C	2.46	1.7	7.7	0.8	131.5	0.3	142	0.6	11.3	1.2
SW-6-A	8.41	0.7	43.9	0.6	171.4	0.1	372	0.5	3.9	1.1
SW-6-C	7.33	1.1	33.9	0.6	164.3	0.3	362	0.5	3.2	1.2
SW-7-A	0.40	1.6	6.5	1.6	36.1	0.6			1.4	1.6
SW-7-C	0.34	0.5	4.3	0.4	36.0	0.4			1.2	2.1
SW-8-A	0.57	0.9	7.7	0.7	29.8	0.2			0.8	7.4
SW-8-C	0.53	1.1	2.8	0.5	28.1	0.2			0.8	1
SW-9-A	1.86	0.3	188.5	0.5	85.2	0.4	382	0.7	5.0	0.4
SW-9-C	1.64	0.2	132.9	0.4	77.7	0.5	366	0.6	2.8	0.4
SW-10-A	1.46	0.5	14.1	0.4	25.4	0.2			12.6	0.7
SW-10-B	1.51	0.3	5.6	0.3	25.1	0.1			5.9	0.4
SW-10-C	1.52	0.2	3.2	0.6	24.4	0.1			4.8	0.6
SS-A	5.65	0.4	27.9	0.5	129.1	0.2	656	0.6	8.5	0.4
SS-B	5.20	0.3	1.2	0.6	122.1	0.1	638	0.5	8.5	0.2
SS-C	5.32	0.4	0.5	0.3	119.3	0.2	634	0.4	6.2	0.4

colloidal fraction (200 nm–10kD) represents between 12% and 98% of the total Fe for soil waters and between 40% and 95% for groundwater with an average of 67.2% and 65.4% for soil water and groundwater, respectively. Therefore, the two above findings clearly indicate the presence of Fe(II)-colloids in the colloidal fraction (200 nm–10 kDa) in anoxic groundwater and soil water of flooded

paddy fields. Due to the initial redox conditions encountered in the sampling sites, Fe(III) species were unexpected. However, even if the formation of Fe(II) due to the Fe(III) photoreduction during Fe measurement in the field is conceivable, this can be ignored because the kinetics of such a reduction is slow (a few hours; Chen et al., 2003) compared to the filtration time scale of the study and

Table 2a

Percentage of Fe(II) compared to the total Fe measured in the field, ratio of the total Fe measured in the laboratory to that measured in the field and molar Fe/As, Mn/As, Si/As and P/As ratios in groundwater.

	% Fe(II)	Fe(Lab)/Fe(field)	Fe/As	Mn/As	Si/As	P/As
W-K1-A	97	0.96	49.3	3.4	131.7	8.0
W-K1-B	85	0.84	41.2	3.5	137.6	5.6
W-K1-C	87	0.84	23.7	3.5	133.4	0.9
W-K2-A	99	1.02	62.8	17.6	235.9	11.9
W-K2-B	99	0.95	47.7	18.3	251.8	6.1
W-K2-C	96	0.47	17.5	21.5	301.2	1.5
W-C1-A	96	0.50	33.9	19.9	373.9	14.7
W-C1-B	97	0.47	30.2	19.7	377.5	13.2
W-C1-C	93	0.97	11.4	21.6	418.1	6.1
W-C2-A	99	1.03	40.2	19.6	317.7	14.5
W-C2-B	99	1.03	35.8	19.9	324.6	12.6
W-C2-C	99	0.70	17.2	20.1	341.8	3.5
W-G1-A	95	0.83	46.8	74.0	1841.7	29.8
W-G1-B	83	0.83	31.1	68.6	1749.8	23.3
W-G1-C	86	0.86	12.0	72.2	1820.7	11.4
W-C3-A	96	1.10	31.9	17.4	318.8	
W-C3-B	79	1.05	26.0	18.1	332.7	
W-C3-C	94	0.90	7.3	18.6	351.0	
W-D1-A	99	1.00	12.8	10.7	209.1	
W-D1-B	98	0.96	9.3	11.3	223.1	
W-D1-C	95	0.49	0.7	10.9	229.9	
W-H1-A	99	1.06	47.7	0.0	0.0	
W-H1-B	99	0.91	47.5	80.0	1119.1	
W-H1-C	89	1.16	32.4	70.9	1094.1	
W-M1-A	98	0.97	103.8	89.6	642.1	
W-M1-B	98	1.00	97.8	91.0	649.5	
W-M1-C	99	1.03	58.9	100.9	726.1	
W-F1-A	1.35	0.76	50.4	19.0		
W-F1-B	1.01	0.76	36.9	17.6		
W-F1-C	0.76	0.76	16.0	18.3		
W-F2-A	98	0.88	39.0	18.3		
W-F2-B	82	0.79	27.7	18.6		
W-F2-C	97	1.34	23.6	17.1		
W-S1-A	99	1.05	658.1	103.0	1298.7	
W-S1-B	100	0.75	617.4	103.9	1274.7	
W-S1-C	88	1.22	215.0	157.4	2067.9	

Table 2b

Percentage of Fe(II) compared to the total Fe measured in the field, ratio of the total Fe measured in the laboratory to that measured in the field and molar Fe/As, Mn/As, Si/As and P/As ratios in soil water and surface water.

	% Fe(II)	Fe(Lab)/Fe(field)	Fe/As	Mn/As	Si/As	P/As
SW-1-A	90	0.93	69.7	25.3	46.1	3.7
SW-1-C			3.4	43.9	84.1	3.4
SW-2-A	90	1.06	86.1	61.2	35.5	6.2
SW-2-C			82.6	60.3	37.7	6.0
SW-3-A	93	0.77	15.9	8.1	33.4	1.1
SW-3-C	99	0.78	2.3	11.4	45.7	0.9
SW-4-A	85	1.01	64.6	36.6	39.6	2.9
SW-4-C	71	0.61	3.1	53.6	58.0	4.6
SW-6-A	90	0.84	5.2	20.4	44.2	0.5
SW-6-C	91	0.82	4.6	22.4	49.3	0.4
SW-7-A			16.1	89.4		1.0
SW-7-C			12.4	104.6		3.6
SW-8-A			13.5	52.1		1.4
SW-8-C			5.3	53.2		1.7
SW-9-A			101.2	45.7	204.9	2.7
SW-9-C			81.2	47.5	223.5	1.7
SW-10-A			9.6	17.4		8.6
SW-10-B			3.7	16.6		3.9
SW-10-C			2.1	16.0		3.1
SS-A	0.96		4.9	22.8	116.0	1.5
SS-B	0.44		0.2	23.5	122.7	1.6
SS-C			0.1	22.4	119.3	1.2

no significant artefact was observed in the presence of high concentration of NOM (Viollier et al., 2000). As mentioned in the introduction, to the best of the authors' knowledge, this study is the first

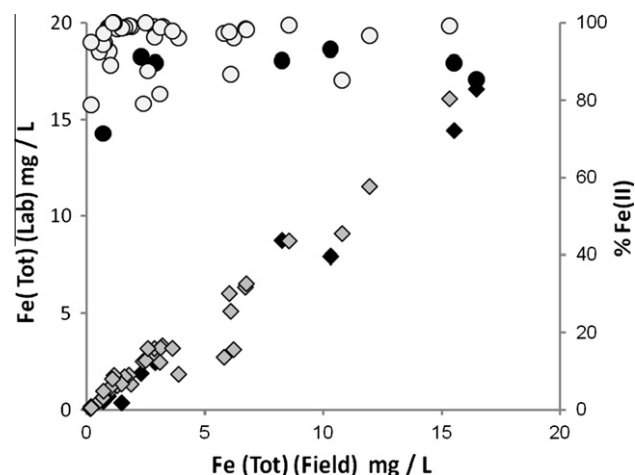


Fig. 1. Relationship between the total Fe concentration (i.e. 200 nm-filtered Fe) measured in field (Fe(Tot)Field) and in the laboratory (Fe(Tot) lab) in groundwaters (grey diamonds), and for soil waters (black diamonds) and the relationship between the percentage of Fe(II) (in all the different size fractions) and the total Fe concentration measured in field (Fe(Tot) field) in groundwater and soil water samples (grey and black circles symbols, respectively).

where results clearly showed the presence of a high proportion of Fe(II) in the colloidal fraction in the case of groundwater and soil water under anoxic conditions. Concerning the formation and the nature of Fe(II)-colloids, physical-chemical conditions of the waters, as well as Fe concentrations do not favour the precipitation of Fe(OH)₂ hydroxides (under saturation). However, in the organic matter-rich natural systems, the analogy with results obtained for Fe(III) in the presence of simple organic compound can be proposed. In addition, knowing that NOM is able to abiotically reduce Fe(III) (Chen et al., 2003), the occurrence of Fe(II) associated with NOM is enhanced. If so, it is postulated that Fe(II) may be linked (whether adsorbed or complexed) with organic matter and can exist as monomeric or small oligomeric polycations (2–20 Fe atoms). Indeed, in the case of Fe(III), it has been shown that for the 20–300 kDa colloidal fraction, Fe(III) was complexed by carboxylic groups leading to a strong hindrance of Fe polymerization-precipitation since Fe has been found to form dimers or trimers (Rose et al., 1998). It is difficult to determine the structure of the Fe(II) oligomers complexed by carboxylic ligands but it is supposed that the octahedral Fe(II) shares edge forming small clusters of the Fe(OH)₂ structure. It has been shown in the case of Fe(II) polymerisation under anoxic conditions that such structures exist (Doelsch et al., 2002).

Results of Fe(II) speciation calculation performed using the WinHumicV model for the different studied cases (depending on pH, and Fe(II) and DOC concentrations) are summarized in the Table 3. These results show that Fe(II) could be strongly bound by organic matter, especially for soil water samples due to higher DOC contents. For groundwater samples, the proportion of organic Fe(II) is predominant only in the case of low Fe(II) total concentrations (i.e. case II – favourable), almost independently of the parameters (i.e. percentage of reactive HS and FA proportion) used to describe the organic matter reactivity. This modelling confirms the hypothesis that Fe(II) speciation could predominantly be dominated by organic complexes of colloidal size, as experimentally observed by size fractionation.

In contrast to what was observed for Fe, the variation of As concentrations, between different size fractions for any given sample, most of the time were weak for both groundwater and soil water (Tables 1a and 1b). Most of the time, less than 10% ±5 of the total As was associated with the 200 nm–10 kDa fraction (Fig. 2).

Table 3
Results of Fe(II) speciation calculation using the WinHumicV model for the different studied cases (in bold – results with the default values of parameters used to describe the organic matter reactivity, see text for explanations).

Sample	Groundwater											
	I – unfavourable				II – favourable				III – favourable			
Reactive HS (%)	50		100		50		100		50		100	
FA proportion (%)	50	100	50	100	50	100	50	100	50	100	50	100
Calculated organic Fe(II) (%)	2.4	2.6	4.7	5.1	92.0	97.6	100.0	100.0	5.9	6.3	11.7	12.6
	Soil water											
Reactive HS (%)	50		50		50		50		50		50	
FA proportion (%)	50	100	50	100	50	100	50	100	50	100	50	100
Calculated organic Fe(II) (%)	13.8	14.9	27.5	29.7	100.0	100.0	100.0	100.0	63.0	67.7	100.0	100.0

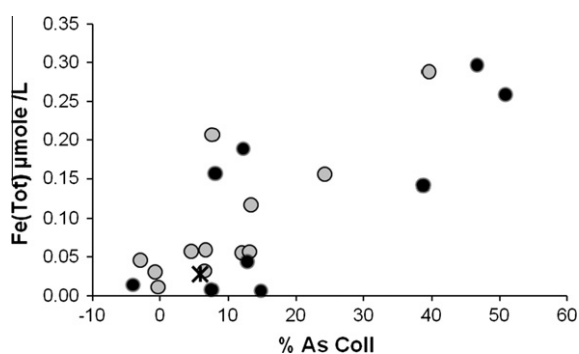


Fig. 2. Relationship between the total Fe (i.e. 200 nm-filtered Fe) concentration (Fe(Tot)) and the percentage of As-bearing colloids (% As coll) in soil waters (black circles), groundwaters (grey circles) and flooded surface water (cross).

Therefore, the relatively constant As concentration in the different fractions suggests that As is mainly present in the solute fraction. However, when As-colloids are observed (% As-coll values above 10–15% on Fig. 2), it must be noted that the percentage of As-colloids is relatively well correlated with the total Fe concentration in solution. Therefore, combining As and Fe results allowed the conclusion that, where present, As-colloids could be in the form of As(III)-bearing Fe(II)-colloids. In addition, where interaction between As and Fe is concerned, the decrease of the Fe/As ratio (Tables 2a and 2b) with size fraction in the case where As concentrations remain relatively constant (Tables 1a and 1b) implies relatively independent behaviour of these two elements. The low As bearing Fe-colloids as the colloid size decreased is not in agreement with the results of Mayo et al. (2007) who, for synthetic systems, showed that as the particle size of magnetite (Fe₃O₄) decreased from 300 to 12 nm, the adsorption capacities for both As(III) and As(V) increased nearly 200 times. Similarly, the present results are not in good agreement with the results of Thoraj et al. (2005) that detailed the strong affinity between As(III)–Fe(II) colloids for synthetic systems during the oxidation of Fe(II)–As(III) solutions. So, the very low affinity between Fe(II)-colloids and As(III) that was observed for natural systems may arise from the effect of other(s) component(s) that could act as competitors for sorption of As to (or coprecipitation on) Fe (oxyhydr)-oxides. In fact, Gaffney et al. (2008), have clearly demonstrated that Fe(II) even if weakly bound to colloidal organic matter is subject to modification of its behaviour. In addition, dissolved organic matter in Bangladesh aquifers has been found to act as a labile substrate for Fe- and humic-reducing bacteria (Mladenov et al., 2010).

Some of the components present in natural ecosystem are known to affect colloid formation, it is then of interest to compare the field results to those obtained in the laboratory, most of the time under controlled conditions. The presence of co-occurring

oxyanions such as PO₄³⁻ and SiO₄⁴⁻ that are effective competitors for As adsorption on Fe (oxyhydr)-oxides may significantly influence As mobility, according to its speciation (Dixit and Hering, 2003; Sahai et al., 2007; Ciardelli et al., 2008). However, most of the literature concerning the affinity between oxyanions and Fe (oxyhydr)-oxides has dealt with Fe(III). Because the majority of Fe was in the Fe(II) form in the samples, a direct comparison with previous studies was not possible. However, comparing PO₄³⁻, As and Fe variations in the different size fractions allowed drawing some specific conclusions regarding As behaviour in the systems. Phosphorus and Fe concentrations were found to decrease (Tables 1a and 1b) in the B and C size fractions. To assess whether P is associated with the Fe colloids, the % of colloidal P was compared to the initial Fe/P ratio, i.e. the Fe/P ratio in the 200 nm fraction. For the groundwater samples (W), the fraction of colloidal P linearly increased with increasing Fe/P ratios (Fig. 3), but not in the case of soil water (SW) a weak control of P on Fe-colloid formation is suggested. Similarly, the comparison between P/As ratio and the % of colloidal As did not show any relationship neither for groundwater nor for soil water (see Fig. SI-2 in Supporting information).

The absence of a clear correlation between Fe and P and the absence of correlation between P and As tends to confirm the impact of other competitors (knowing that the chemistry of P and As is similar) that inhibited As (and to a lesser extent for P) association with Fe-colloids.

As mentioned above, Si concentrations in the soil water were drastically lower than in groundwater used for irrigation (Tables 1a and 1b) of the paddy fields. The lower Si concentration in soil water likely reflected Si uptake by rice plants (Guo et al. 2005).

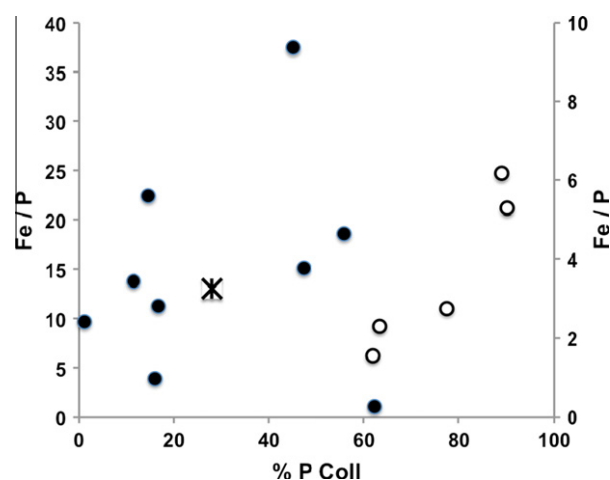


Fig. 3. Relationship between the Fe/P ratio and the percentage of P-bearing colloids (% P coll) in soil waters (black circles), groundwaters (grey circles) and flooded surface water (Cross). The secondary Y axis is the Fe/P ratio for groundwaters and flooded surface water.

Such a decrease for P (also needed for the growing of rice) between groundwater and soil water was not observed because of P addition as fertilizer by farmers. Here again, the constant Si concentration in the different size fractions (Tables 1a and 1b) confirms the absence of colloidal Si phase in the 200 nm–10 kDa fraction. Therefore, a direct impact of As-bearing Si-colloid formation on As mobility cannot be invoked in the Si-rich natural waters. An indirect impact of silica on As mobility could be due to its impact on Fe (oxyhydr)-oxides formation. However, in the case of Fe(II) (oxyhydr)-oxide formation, Doelsch et al. (2002) have demonstrated, in controlled systems, that the role of silica during the formation of Fe(OH)₂ is weak, leading to a limited hindrance of the formation of hydroxides. Therefore, in the present study, taking into account the absence of Si-colloids, the similar Si/As ratio in the different fractions (Tables 2a and 2b) and the limited observations of the presence of As-bearing Fe-colloids, it can be concluded that Si affected neither As sorption on, nor complexation with, Fe(II)-colloids.

As for Fe, the high Mn concentrations in groundwater and soil waters under flooded paddy fields resulted from the reductive dissolution of Mn oxides or Mn associated with Fe (oxyhydr)-oxides. For groundwaters, and for any given sample, the absence of variation of Mn concentrations between the different size fractions (Tables 1a and 1b) indicated the absence of Mn-colloids (Mn (oxyhydr)-oxides) in the 200 nm–10 kDa fraction. For soil waters, the higher Mn concentrations in the A fraction than in the C fraction implies Mn-colloid formation. The correlation ($R^2 = 0.76$; Fig. SI-3 in Supporting information) between the amount of Fe in solution and the fraction of Mn-colloids tends to suggest Mn coprecipitation with Fe-colloids. Yet, the Mn/As ratio is significantly higher in the C fraction than in the A fraction (Tables 2a and 2b) thus suggesting that As is not associated with Mn-colloids, which is in agreement with the net negative charge of Mn-oxides at circumneutral pH, not favourable for As sorption (Sadiq, 1997).

The results observed here under anoxic conditions are quite different from those obtained for synthetic systems under oxic conditions with As, dissolved organic matter and Fe(III) where relationships between these components (depending on Fe/C ratios) and the amount of As-bearing colloids have been demonstrated (Bauer and Blodau, 2009). This is likely due to the fact that, under oxic conditions, Fe is mostly insoluble and, therefore, has more potential to control the As speciation. Further investigations are needed to check if there is any link between organic matter and the occurrence of Fe(II)-colloids under the field anoxic conditions. In fact, the results presented were obtained in the field, therefore, the size-fractionation protocol was obviously not as efficient for the metal(loid) fractionation as for Carbon isolation (not the same type of filters, pore cut-offs, etc.). Future studies dedicated to As speciation under anoxic conditions should take into account Carbon isolation to better define the presence of Fe(II) colloids and to determine why some of the Fe(II) and As became effectively “insoluble” in some of the samples.

Because As-colloids might contribute to limit availability and bioavailability of this toxic element in waters, the evidence that a large amount of As(III) is not linked to Fe(II)-colloids but is present in dissolved “solute” form is of relevance when studying As mobility and transfer in soil/water/plant systems under anoxic conditions such as in flooded paddy fields (Liu et al., 2004; Chen et al., 2005; Bravin et al., 2008; Garnier et al., 2010).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apgeochem.2011.04.023.

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