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TITLE:

Arsenic fixation and mobilization in the soils of the Ganges and Meghna Floodplains. Impact of pedoenvironmental properties

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Abstract

Arsenic contamination of groundwaters in the floodplain of the Ganges-Meghna river system can represent a serious threat to human health and to the sustainability of irrigated rice cultivation. The extent of As accumulation in the soils irrigated with As-containing groundwater seems to vary among different study areas and the relationships between the pedoenvironmental conditions and As fixation/mobilization are not yet completely elucidated. This work was aimed to assess how soil and environmental properties interact in affecting the fixation/mobilization of As in the soils of the Ganges and Meghna agricultural zones. For this purpose, soil samples from different districts in the Ganges and Meghna floodplains have been characterized, different pools of As, Fe, Mn and P have been quantified and the results have been related to the main soil and environmental characteristics of the two areas. The As content in groundwater and the baseline As concentration in the parent material in the two zones would point to a higher As accumulation in the Meghna floodplain soils, however the Ganges floodplain soils had higher contents of As in all fractions, proving the key role of the factors controlling the release/fixation of As. The soils of the two floodplains, in fact, differed for most physicochemical properties. The ones from the Ganges floodplain were calcareous, with finer texture and generally richer in Fe but oxalate extractable Fe was higher in the Meghna floodplain soils, suggesting a higher degree of waterlogging. This is in agreement with the averagely longer duration and higher depth of submersion of the soils of this area, that enhanced Fe dynamics and favored the release of the less tightly bonded As forms. The competing effect of P was probably similar in the two areas, since P concentrations did not differ significantly among the two soil series. However, more P was Olsen extractable in the Meghna floodplain soils, in contrast with As, that was more easily extracted from the Ganges floodplain soils. The concentration and potential mobility of the retained As was hence greater in the soils of the Ganges floodplain.

1. Introduction

Arsenic (As) contamination of soils and waters is a widespread problem posing a great risk to human health and environmental safety. The contamination of groundwater with As in the Ganges-Brahmaputra-Meghna plain is one of the widest cases of As poisoning in the world (BGS, DPHE 2001; Brammer and Ravenscroft 2009; Chakraborti et al., 2004 and 2010). In many areas of the Bengal basin, agriculture depends mainly on groundwater for irrigation, and in 40% of the net cultivable area in Bangladesh As contaminated groundwater represents the main water source for irrigation (Huq et al., 2003 and 2006). A huge amount of As is thus transferred every year from the contaminated aquifer to the surface water-soil-plant system (Ali et al., 2003a). The As reaching the soil by irrigation could accumulate in the soil solid phase, could be released to the deep or surface waterbodies, could be metabolized and possibly volatilized by microorganisms, and could be taken up by crops from the soil-water system.

Among different crops, rice is particularly subjected to As accumulation because of the required great amounts of irrigation water, potentially As-polluted in this country, and the submerged cropping conditions that enhance the release of the As accumulated in soils to the porewater , which can reach concentrations higher than those of the irrigation water itself (Garnier et al., 2010). In Bangladesh rice cultivation can hence represent one of the main As inputs from groundwater to the soil-crop system (Brammer and Ravenscroft, 2009); moreoverm, beside rice, also different crops and vegetables grown in As affected areas, often in rotation with rice, can accumulate high As concentrations (e.g., *arum*), contributing to As dietary intake (Huq et al., 2006; Smith et al., 2006).

The accumulation of As from irrigation water seems to differ largely in Bangladesh agricultural soils (Ali et al., 2003b). In fact, As accumulation could be at least partly counteracted by soil submersion during the monsoon season (Dittmar et al., 2007; Roberts et al., 2010; Saha and Ali, 2007), but the fraction of the As removed differs among the considered locations (Saha and Ali, 2007) and in several situations a progressive build-up of As content in soils along the years can be foreseen (Dittmar et al., 2010a and 2010b; Khan et al., 2009; Saha and Ali, 2007; van Geen et al., 2006). In other cases, As content in soils does not seem to build up over time, undergoing only seasonal variations around a baseline (Lu et al., 2009). Differences in the pedoenvironment , i.e. soils, climate and other site characteristics including land use, of the studied sites could contribute in explaining these contrasting results, since the overall mobility of the added As depends on the physico-chemical properties of the soils, on As forms, and on the climatic conditions (Begum and Huq, 2007; Huq et al., 2008). In the soil, the quantity and nature of adsorbing phases, mainly iron (Fe) and aluminum (Al) oxides, pH, redox potential, and presence of competing ligands play the most important role (Violante et al., 2011).

Most agricultural soils of Bangladesh develop on the alluvial deposits of the delta formed by the fluvial systems of Brahmaputra, Ganges and Meghna rivers and about 78% are represented by alluvial or flooded soils (FAO, 1988). The soils of the Ganges floodplain, in the South-West of the Country, and of the Meghna floodplain, in the South-East are those subjected to the highest addition of As with groundwater irrigation (Ali et al., 2003a) and differ widely in texture and pH (BARC, www.barc.gov.bd/data_stat.php). Several studies considered potential accumulation and mobility of As in soils in these physiographic units (Hossain et al., 2008; Islam et al., 2004; Rhaman et al., 2010; van Geen et al., 2006), but most of the available studies describe As accumulation and/or mobility in one or few sites. Even when soils from different physiographic units are sampled (Saha and Ali, 2007) or very large sample sets are considered (Meharg and Rahman, 2003) the physico-chemical characteristics of the soils are seldom directly related to the differences in the adsorbing phases and to the forms in which As is retained. Thus, the differences in As accumulation in soils are not yet completely explained and a prediction of As fate in the most contaminated sites is still difficult.

The aim of this work was thus to assess how soil and environmental properties interact to affect the amounts of As in the soils of the Ganges and Meghna agricultural areas and to evaluate, through the extraction of As forms, possible differences in the capacity to retain/release As between the soils of the two areas. This would contribute to correctly evaluate the risks linked to the use of As contaminated groundwaters.

2. Materials and Methods

2.1. Study areas

The Ganges (GF) and the Meghna (MF) Floodplains differ in climatic conditions and soil types. Annual rainfall in GF ranges from 1400 to 2000 mm, but is much higher in MF (2600-2900 mm), and in both cases wide seasonal variations are present (Shahid, 2010). On the average, more than 75% rainfall occurs in the monsoon season, from June to October. The higher amounts of annual rainfall that contribute to flooding and soil submersion (Shahid, 2010), together with local geomorphology induce some variability in land types between the two floodplains. According to the depth of inundation, Bangladesh surface is classified in different inundation land types, from Highlands that normally not inundated, to Very Lowlands that are inundated above 300 cm depth. The Highlands and Medium Highlands appear to be the most frequent inundation land types in GF, while Medium Lowlands, Lowlands and Very Lowlands are more frequently found in the MF (BARC, www.barc.gov.bd/data_stat.php).

The Bengal Basin is dominated by Holocene alluvial deposits. In the Gangetic plain soils are mostly calcareous and clay-loamy, while in the Meghna floodplain non calcareous, silty loam to silty clay soils prevail (BARC, www.barc.gov.bd/data_stat.php). The sediment mineralogy is dominated by quartz and feldspars; the clay fraction is composed by illite and kaolinite in nearly equal proportions, whereas chlorite and montmorillonite are in lesser amounts. The sediments of the Ganges system have a higher amount of smectite and a lower amount of kaolinite in comparison to the Meghna one. In general, the heavy minerals include amphibole, pyrope, and epidote. Some pyrite is also found in the basin sediments (Datta and Subramanian, 1997).

The studied areas are located on recent alluvial and deltaic sediments, and belong to the districts of Meherpur, Gopalgaj, Jessore and Sathkhira (GF), Brahmanbaria, Comilla and Chandpur (MF). In agreement with the expected distribution of land inundation types in the two floodplains, in the sampled upazila (i.e. administrative unit within districts, see supplementary table), Medium lowlands, Lowlands and Very Lowlands accounted for 69% of the surface in MF and 22% GF (BARC, www.barc.gov.bd/data_stat.php). According to the British Geological Survey (BGS, DPHE, 2001), the highest average As concentration in groundwater (366 µg L^{-1}) is reported in Chandpur district. The average reported As concentrations for the other districts of the Meghna Floodplain studied in this work are 142 µg L^{-1} for Comilla and 101 µg L^{-1} for Brahmanbaria district. The average As concentrations for the studied districts of the Ganges Floodplain are 187 µg L^{-1} for Gopalganj, 133 µg L^{-1} for Satkhira, 116 µg L^{-1} for Meherpur and 70 µg L^{-1} for Jessore district. The contamination level of the groundwater in the abovementioned districts, also considering the percentage of contaminated wells, is confirmed by more recent works (Chakraborti et al., 2010).

2.2. Soil sampling, analysis and data treatment

Samples from the topsoil (0-10 cm) were collected in the period June-July 2008 from irrigated paddy fields. Twenty-nine samples were taken in the districts of the Ganges Floodplain physiographic unit and 30 in the Meghna Floodplain physiographic unit (Figure 1). Rice was generally in rotation with one or more different crops.

The soil samples were air-dried and all the analyses were carried out on the fine-earth fraction (< 2 mm). The pH was determined potentiometrically in a 1:2.5 soil/deionized water suspension. The particle size distribution was evaluated by the pipette method after dispersion of the sample with Na-hexametaphosphate; carbonates were determined volumetrically and the C and N contents were determined through dry combustion (NA2100 Protein elemental analyser, CE Instruments, Milan, Italy). Standard deviations for the above mentioned analysis were within 5% and, for CN determination, within 2%.

The soil samples were analyzed for As, Fe, Mn, P extractable with *aqua regia* (As_R, Fe_R, Mn_R and P_R), with a reducing solution composed by 0.2M ammonium oxalate-oxalic acid buffered with ascorbic acid (As_{OA}, FeO_{OA}, Mn_{OA} and P_{OA}) shaken at 96°C for 30 min (Shuman, 1982, as adapted by Wenzel et al., 2001), and with ammonium oxalate buffer in the dark (As_O, Fe_O, Mn_O and P_O Schwertmann, 1964). In this last case Al in the extract was also measured (Al_O). These extractions were aimed to bring in solution different fractions of Fe (Mn and Al) oxides together with the bound As and P, i.e., a pseudo-total fraction, a reducible fraction (mainly Fe and Mn oxides, including well-crystallized Fe oxides), and the poorly ordered fraction of Fe and Al (hydr)oxides. Single-step extractions were adopted instead of sequential extraction procedures in order to avoid some limitations of the sequential extractions, as suggested by Audry et al. (2006), and because of the greater simplicity and rapidity, that appears not to decrease the extraction efficiency (Baig et al., 2009). Bicarbonate extractable As and P (As_{Olsen} and P_{Olsen}, Olsen and Sommers, 1982) were determined as an estimate of the loosely bound pools.

Arsenic was determined by hydride generation (HG) coupled with AAS (Perkin-Elmer 4100 equipped with a FIAS 400 hydride generator; Perkin-Elmer Inc., Waltham, Massachusetts). Iron, Mn and Al were determined with flame-AAS (Perkin-Elmer 3030). Phosphorus was determined colorimetrically (Murphy and Riley, 1962). Standard deviations for all these analysis were within 5%.

The statistical analysis of the data was performed using the SPSS 17 package for Windows (SPSS Inc). The relationships between variables were evaluated using Pearson’s correlation coefficient (two-tailed), after a visual inspection of the data to verify that the relationship was linear. Linear regressions between the total As and the As forms were also calculated. Differences in soil properties between floodplains or districts were evaluate by one-way ANOVA. To reduce the number of variables and better evaluate the effect soil has on As forms, the extraction of Principal Components was performed. From the evaluation of communalities, all measured soil properties were included in the analysis; an eigenvalue > 1 was set as the threshold for component extraction and a Varimax rotation was applied to maximise the correlation between components and measured soil properties. The component scores were saved and correlated to As forms. The threshold used for significance in all statistical tests was set at 0.05.

3. Results

Selected physical and chemical characteristics of the soils sampled in the Ganges (GF) and Meghna Floodplain (MF) are reported in Table 1 and the whole set of data is shown in the electronic annex. The soils from the two physiographic zones differed for all examined characteristics (p always <0.05). Some variability at the district level was however present in texture in MF and in pH and carbonate contents in GF. The soils from the Ganges floodplain were mostly moderately calcareous, dominated by dark grey colors (e.g. 5Y 4/1, 2.5Y 4/2), with prevalent silt-loam to silt-clay and clay texture, while the Meghna Floodplain soils were noncalcareous, dark grey, with prevalent silt-loam texture. The organic C and N content were higher in the GF, however ranged from low to medium in all soils.

Selective extractions of Fe (Figure 2) demonstrated that the two units differed significantly also in all forms (p always <0.01). The *aqua regia* extractable Fe (Fe_R), as well as the Fe extracted with the oxalate-ascorbate reducing solution (Fe_{OA}), was higher in the GF series than in the MF series. Conversely, the amount of oxalate extractable Fe (Fe_O), mainly representing poorly ordered forms, was significantly greater in the MF soils and particularly in the Brahmanbaria and Comilla districts. As a consequence, poorly crystalline forms represented a much higher proportion of the total contents in MF (>20% on the average in Brahmanbaria). This was further evidenced by the ratio between poorly ordered Fe oxides (Fe_O) and total reducible Fe oxides (Fe_{OA}) passing from 0.35 in MF to 0.18 in GF soils, clearly distinguishing the two soil series ($p<0.01$). All Mn fractions and poorly ordered Al oxides (Table 2) were more represented in the GF soils, particularly in those from the Meherpur district. The highest Mn content detected in MF (Comilla district) was still lower than that of all GF districts.

In general, all As forms were significantly higher in the GF soils than in MF (p always <0.01). The average *aqua regia* extractable As (As_R) in the GF soils was more than double compared with that in the MF soils (Figure 3). The Jessore and Satkhira districts had significantly higher amounts of As than the other two districts of GF and As_R exceeded 20 mg kg^{-1} in 20% of the samples; 45% of the samples exceeded 10 mg kg^{-1}. In the MF all samples were below 20 mg kg^{-1} of As content and only 13% of the samples, coming from Comilla and Brahmanbaria districts, exceeded 10 mg kg^{-1}. The As extracted by the oxalate-ascorbate solution reducing the free Fe oxides (both crystalline and poorly ordered ones), was also significantly higher in the soils from GF (Figure 3) and represented the major part of the *aqua regia* extractable element confirming the expected major role of Fe (hydr)oxides in As retention. More than one-half of the *aqua regia* extractable As was brought in solution by ammonium oxalate, targeting mainly the scarcely ordered oxides (56% in GF and 61% in MF). Calculating the amount of As bound to crystalline Fe oxides as the difference between the amount extracted with the reducing solution and that extracted with oxalate, the average amount represents 32% in the GF soils and only 15% of the *aqua regia* extractable amount in MF ($p<0.001$). The As to Fe molar ratio was $2x10^{-4}$ in both units with *aqua regia* extraction, passing to $4.6x10^{-4}$ in GF and $2.6x10^{-4}$ in MF soils with the oxalate-ascorbate solution ($p<0.01$) and to $1.7x10^{-3}$ for GF and $5.9x10^{-4}$ for MF with oxalate ($p<0.001$). The differences in the molar ratio obtained with the oxalate-ascorbate solution were caused by the extracted poorly crystalline Fe forms, more As-loaded in GF, as the molar ratio calculated for the most crystalline oxides (Fe_{OA}-Fe_O) was not different between the two physiographic units ($p=0.138$). The amount of As that can be extracted with the Olsen method was greater in the GF soils than in the MF ones (Figure 3), representing, respectively, 6.2% and 3.7% of the *aqua regia* extractable As. The less tightly bound As pool was therefore greater in GF, and represented a larger part of the total content. Particularly in the Satkhira district, the average proportion was the highest, around 9%.

All the As forms were well correlated with *aqua regia* extractable As (Figure 4) without distinction between the two floodplains, except for As_{Olsen}, where the relationship was improved dividing the two soil series and linear trendlines with different slope were obtained (Figure 4c).

The two series did not differ significantly for *aqua regia* extractable P (Figure 5), probably because the variability among districts was very high: in GF P_R ranged from 353 to 1477 mg kg^{-1}, in MF from 135 to 1564. The fractions of P extracted with the reducing solution or with oxalate did not differ among the two units either, and represented respectively an average of 66% and 62% of the *aqua regia* extractable P. The Olsen P, on the contrary, was significantly different in the two units ($p<0.01$, Figure 5). In the GF soils the average was 18.6 mg kg^{-1} (range, 2.9-71.4 mg kg^{-1}, with the highest values observed in Satkhira district), while in the MF soils the average was 40.8 mg kg^{-1} (range 3.0-113.1 mg kg^{-1}, the soils from Comilla having much greater amounts than all the other districts).

Five significant components were identified that accounted for 89% of the total variance. As shown by the loadings reported in Table 3, the first component (C1) was significantly positively correlated to Al concentration, both as Al_O and Al_R, clay, Fe_R, Fe_{OA}, organic C, carbonates, pH and negatively correlated to silt contents; C2 was correlated to all P forms, C3 to all Mn forms, while C4 was positively correlated to Fe_O and negatively to pH and $CaCO_3$; C5 was negatively correlated with sand and positively with silt. The scores calculated for each sample were plotted in the space identified by the components; as visible in the first column of Figure 6 (a to d), a good discrimination between samples located in the two floodplains was obtained with C1 ($p<0.01$). The samples belonging to GF were in fact mainly located on the positive side of the C1 axis, showing therefore higher concentration of all variables positively correlated with this component, while those of MF were situated on the axis negative side. Due to their high P concentration, the samples belonging to the samples belonging to the Comilla district (MF floodplain) were all located on the positive side of the C2 axis, but this component showed little discrimination capacity between floodplains (Figure 6a and e to g), as well as C3 (Figure 6b, e, h and i) and C5 (Figure 6d, g, i and j). The distribution of the soil samples along the C4 axis (Figure 6c, f, h and j) indicated a more scattered distribution of the samples from GF, which showed both the highest and the lowest values of this component scores although the differences between floodplains were significant ($p<0.01$).

Arsenic forms were significantly correlated to C1, but the proportion of explained variance was rather low (up to a maximum of 33% in the case of As_{OA}, Table 4). When the dataset was split in the two floodplains the correlation results suggested different relationships between soil properties and As forms in the MF and GF samples (Table 4). In the case of GF the only significant correlation was between As_{Olsen} and C2, which described P forms ($r=0.398$, $p<0.05$, $n=29$), while in MF both C1 and C2 were significantly correlated to all As forms. The As concentrations thus increased with increasing Al, Fe, clay and organic C concentrations, as well as with pH and P contents.

4. Discussion

The general soil characteristics correspond to the most widespread types of soils of the Agro Ecological Zones (AEZ) included in the Ganges and Meghna Floodplains (BARC, www.barc.gov.bd/data_stat.php), and thus, as expected, differences in pH, carbonate contents and texture were found and were well depicted by the first extracted component (C1). Some variability at the district level was however present and linked mainly to soil texture, pH and content of Fe and Mn.

In addition, different amounts of As were present in the two soil series, with higher concentration of *aqua regia* extractable element in GF (Figure 3). This finding is in agreement with the data reported by Meharg and Rahman (2003) who found As concentrations between 3.1 and 21.6 mg kg^{-1} in some soils from Comilla and Chandpur districts (MF) while the concentration was up to 68 mg kg^{-1} in samples from Meherpur and Jessore (GF). The amount of As in the soils depends on the background concentration, on the inputs from irrigation water, on the presence of suitable sorbing phases, and on the equilibrium between retention and release phenomena.

According to Datta and Subramanian (1997), the average As content of the Ganges sediments is lower than that of the Meghna ones, with an average of 2.03 and 3.49 mg kg^{-1}, respectively. The differences in the average As concentration in water between the two units and the percentage of wells with As concentration above 50 μg L^{-1} also suggest higher As concentrations in MF (BGS, DPHE, 2001; Chakraborti et al., 2010), although an important variability was reported at local level. However, if suitable adsorbing phases are present and the equilibria of adsorption/desorption and precipitation/dissolution reactions are favorable, repeated irrigation with contaminated water may increase the contents of As in the soil of GF, as found by several authors (e.g., Dittmar et al., 2010a and 2010b; Rahman et al., 2010; van Geen et al., 2006).

Arsenic can be immobilized in soils after coprecipitation with Fe and Mn (hydr)oxides, adsorption on the solid phases, mainly Fe and Al oxides, and, to a lesser extent, clay minerals. The soil pH, the presence of competing ligands and redox fluctuations are expected to affect the equilibrium between retention and release on/from these solid phases. The quantitative effect of the adsorbing phases was resumed by component C1, including the high-affinity surfaces, i.e., organic C, clay, Fe and Al oxides (Table 3), and which was positively related with all the As forms (Table 4). This result suggests that no single phase can fully account for As retention in the complex soil system. While the positive relationships of As with clay and total oxides ($r=0.404$ and 0.570, respectively, $p<0.001$) were expected, organic matter ($r=0.317$, $p<0.05$) is reported to display different effects on As retention/release. The competition of organic molecules for surface adsorbing sites can enhance As release and, under submerged conditions, by favoring the microbial activity, may accelerate the reduction of As bearing solids and of As itself (Williams et al., 2011). On the other hand, similarly to the present study, Huq et al. (2008) found a positive relationship of As content with organic C along several Bangladesh soil profiles. A possible explanation is the formation of cation bridging and/or of As-bearing Fe-organic colloids with large reactive surface and a disordered structure stabilized by the organic molecules (Bauer et al., 2008).

Iron (hydr)oxides represent a preferential substrate for As retention in soils, following adsorption (De Brouwere et al., 2004; Livesey and Huang, 1981) and/or coprecipitation reactions, which can play an important role in these environments (Roberts et al., 2007; Martin et al., 2010).). Indeed, in Bangladesh paddy soils most of the As is linked to the different fractions of Fe oxides (Dittmar et al., 2007; Hossain et al., 2008; Martin et al., 2007 and 2010). A much higher Fe_R and Fe_{OA} content clearly distinguished the GF soils (Figure 2), and the greater As accumulation could be justified by a larger amount of adsorbing minerals. However, the adsorption capacity of a soil depends on the extent of the reactive surfaces rather than on the absolute amount of the adsorbing solids. Hence, poorly ordered oxides displaying a large active surface can adsorb much greater As amounts than crystalline ones (Dixit and Hering, 2003). The present data revealed that MF soils were characterized by a dominance of the scarcely ordered Fe forms (Figure 2). Fe_O was significantly greater than in the GF soils and represented a greater proportion of Fe_R. Furthermore, the ratio between the scarcely ordered Fe oxides (Fe_O) and total free Fe oxides (Fe_{OA}) was nearly double in the MF than the GF, with no differences at district level. As a consequence, when taking into account the available active surface for As adsorption, the differences between the two units could be substantially reduced, considering the greater adsorbing surface displayed by the poorly ordered Fe oxides dominating in MF compared to the more crystalline ones in GF. Delgado and Torrent (1999) calculated an index for the phosphate potential retention by soil, which has a sorption behavior similar to that of arsenate, considering the sorption capacity of crystalline Fe oxides nearly

1/5 of that displayed by poorly ordered ones. Their Phosphate Adsorption Capacity Index (PACI) is given by:

$$PACI = (Fe_O + Al_O) + \frac{Fe_D - Fe_O}{5}$$

where Fe_D is the amount of Fe in crystalline plus poorly ordered oxides. When applied to the soils of the present study, this calculation gives an average adsorption capacity index of 6.1 for MF soils and 7.0 for GF soils ($p=0.095$). The differences between the two units in terms of active adsorbing surfaces displayed by the oxides seem, thus, not to be much relevant.

Beside the high-affinity surfaces of the Fe oxides, the higher percentage of clays in the GF soils also involves a greater amount of phyllosilicate minerals that, in spite of a lower affinity, may play a certain role in As retention due to their large amount. However, since As adsorption occurs on surfaces with variable charge, the larger presence of kaolinite in MF than in GF clay fraction (Datta and Subramanian, 1997, Egashira et al., 2004) could contribute in leveling the differences in sorption sites caused by texture. As a consequence, the As derived from the irrigation water may be potentially comparably adsorbed in the two soil series and the lower amounts found in the MF soils might be related to a greater As release linked to an interaction between soil and environmental conditions.

The amount of total As present in the soils at the sampling time was, actually, the result of a series of input and output during the years. This may justify the variability in the correlations when the effects of soil properties on As forms were evaluated by splitting the two soil series. In MF, soil properties, synthesized by C1 and P forms (C2), deeply affected the amounts of all As forms, while in GF As forms were not significantly related with any component, except a weak relationship of As_{Olsen} with C2. The lack of correlation may be related to the possibility of As to accumulate in soils by repeated addition with irrigation even when water concentration is relatively low if an efficient mechanism of removal is not present. The two areas in fact differed in the extent and duration monsoon-induced reducing conditions (BARC, http://www.barc.gov.bd). In the presence of a wide number and amount of adsorbing sites and relatively low As saturation, if the submersion during the monsoon season is absent or moderate, such as in GF, soil would be a sink for As even under the fluctuating redox conditions accompanying rice cultivation, as observed by Ahmed et al. (2011), Khan et al. (2009 and 2010), Dittmar et al. (2010a and 2010b). By contrast, the prolonged period of submersion with rainwater in the monsoon season and the consequent strong and long lasting reducing conditions have been identified as the major cause of As depletion from Bangladesh soils (Dittmar et al., 2010b, Huq et al., 2008; Roberts et al., 2010; Saha et al., 2007). The effects of monsoon water on As (and Fe) mobility depend on the depth and duration of the submersion and, hence, the inundation land type can become an important factor (Huq et al., 2008).

In the MF more drastic and prolonged inundation periods have to be expected, since in this area there is a more extended presence of lowlands and medium lowlands than in GF (BARC, http://www.barc.gov.bd). Moreover, the average rainfall is much higher in the South-Eastern than in the South-Western part of the Country (Shahid, 2010). The different depth and length of flooded periods indicated by the Land Type classification most likely influences the proportion of Fe hydr(oxides) forms (Cornell and Schwertmann, 1996) in the two plains and the great difference in the Fe_O/Fe_{OA} ratio in the two series contributes to support the indication of a greater degree of waterlogging in the MF. During the submersion period, the poorly crystalline Fe oxides dominating in the MF soils (Figure 2) can more readily undergo reductive dissolution processes than the better ordered ones, with a consequent greater As release from these adsorbing phases. Thereafter, part of the dissolved Fe can be re-oxidized when aerobic conditions are re-established in soils, as reflected by the high proportion of poorly ordered minerals; As, mainly reduced to the labile trivalent form, would be only partly co-precipitated or re-adsorbed on the solid phase, with the migration of an important proportion together with the floodwater, as evidenced by Roberts et al. (2010) for paddy soils subjected to heavy seasonal flooding. The very scarce As content observed in soils from districts characterized by heavily polluted groundwater, such as Chandpur in the MF (Figure 3), suggest that factors governing release mechanisms (i.e., mainly the drastic and prolonged drop in the redox conditions during the monsoon season) are those controlling accumulation or depletion equilibria of As in MF soils (Roberts et al., 2010). The mobilized As could recycle to the aquifer, although, according to some studies, most of it would be horizontally transferred to the surface water bodies (Roberts et al., 2010) and/or flow trough field bunds (Neumann et al., 2011).

In both soil series the extraction of most As with the total free oxides (averagely 82%) and, in particular, with the scarcely ordered ones (averagely 58%) was expected and well supported by the literature (Khan et al., 2009 and 2010; Hossain et al, 2008; Martin et al., 2007 and 2010). In the most intensely flooded soils the long term retention of the As introduced during the irrigation season seemed however to be limited to the most tightly bound forms as evidenced by the different proportion between As_{Olsen} and As_R in the two floodplains. The slopes in Figure 4c in fact indicated that As was more easily extractable from GF. In the MF soils therefore, the long term fixed As would mainly include the Fe-As complexes that did not completely dissolve under reduction (as suggested by the positive correlation of the well crystallized Fe oxides with As forms in MF soils, r ranging from 0.388 to 0.494), or the pool reprecipitated or readsorbed within the transformation of the solid phases occurring during submersion (Kirk, 2004) (as indicated by the relation with Fe_O in MF, r from 0.438 to 0.590). By contrast, the soils less subjected to monsoon flooding, according to our results, seem to be more prone to As accumulation, as suggested by Ahmed et al., (2011), Khan et al., (2010), Roberts et al., (2010).

Beside the reductive dissolution, also the presence of competing ligands could limit As retention. Phosphorus competition with As for the sorbing sites on soil mineral surfaces is well known (Violante and Pigna, 2002). Here, positive relationships between As and P forms were found. The two elements however, for their chemical resemblance, share most adsorbing sites and mechanisms in soil and hence the positive correlation between As and P in all extracts simply indicates their coinciding dissolution, as can happen also under submerged conditions (Khan et al., 2009). However, even if the relationship between As and P is positive, a certain degree of competition cannot be ruled out and the different P forms have been hence examined.

Total P concentrations (P_R) are similar in the two physiographic units and the P forms associated to Fe (hydr)oxides (P_{OA} and P_O) in the two units are similar as well, while P_{Olsen} was much higher in MF than in GF soils (Figure 5), in contrast with As behavior. The differences between the two units found in the present work could be partly attributed to different agricultural managements, such as the presence of vegetables in the cropping pattern of the P-rich soils sampled in Comilla district, as well as to several other factors, including differences in the main P binding mechanisms (e.g. precipitation and/or adsorption) between the two units. The prevailing mechanism will in turn affect the ability of P to compete with As and the extractability of these elements.

In the GF soils, the average pH and availability of Ca^{2+} ions would result in a greater incidence of P fixation in Ca-precipitated form compared to the MF, where the lower pH mainly enhances P adsorption on the surfaces of Fe and Al minerals (Celi et al., 2001). The precipitation of calcium arsenates and the formation of As-substituted hydroxylapatite is also possible (Zhang et al., 2011); however, the activity of arsenate ions in soil solution is generally lower than that of phosphate ions and the solubility of Ca-arsenates is higher than that of the P homologous minerals (Zhang et al., 2011), explaining the greater extractability of As, but not of P, with the Olsen procedure in GF soils. In GF therefore competition between P and As is expected to be limited, further stressing the possibility of As accumulation in these soils. In noncalcareous soils, the binding to Fe and Al (hydr)oxides is the main factor regulating both As and P mobility. The maximum P adsorption on Fe and Al oxides is reached at acidic pH, as well as for arsenate, and the P competition toward As adsorption is reported to be stronger at pH below neutrality (Violante and Pigna, 2002) thus, in MF soils P competition could influence As adsorption/desorption equilibrium to a greater extent, particularly in the soils from Comilla district.

5. Conclusions

The fixation/mobilization of As in the soils of the Ganges and Meghna floodplains of Bangladesh is the result of a complex interaction between soil properties, climate and agricultural management. Although the concentrations in sediments and irrigation water would indicate possibly high As contents in the MF floodplain, the amounts in the soils are much higher in the samples taken from the Ganges floodplain, where in addition As is more potentially mobile. The higher incidence of the monsoon-induced waterlogging conditions of the Meghna floodplain might have stimulated a fast dynamics of Fe forms and favored the permanence of only the most tightly bound As forms. As a result the present As state is more critical for the soils located in the Ganges floodplain, both in terms of total concentration and extractability; on the other hand the long term environmental sustainability of the use of As-rich irrigation waters in the Meghna floodplain remains an open issue as As seems to be transferred from agricultural soils to other environmental compartments.

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7. References

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Table 1. Results of the analysis of variance and descriptive statistics of selected characteristics of the soils of the Ganges (GF) and Meghna (MF) Floodplains.

		N	Mean	Min	Max	P§		N	Mean	Min	Max	P§
	GANGES						**MEGHNA**					
pH	Gopalganj	6	7.14	5.62	8.05	b	Brahmanbaria	10	5.75	5.50	5.99	
	Jessore	8	8.01	7.28	8.18	a	Chandpur	10	6.01	4.91	7.22	
	Meherpur	9	7.89	7.54	8.21	a	Comilla	10	5.87	5.20	7.30	
	Satkhira	6	7.46	6.65	8.38	ab						
	GF	*29*	*7.68*	*5.62*	*8.38*		*MF*	*30*	*5.88*	*4.91*	*7.30*	**
CaCO$_3$ (g kg^{-1})	Gopalganj	6	0.0	0.0	0.0	b	Brahmanbaria	10	0.0	0.0	0.0	
	Jessore	8	25.7	9.9	65.3	a	Chandpur	10	0.0	0.0	0.0	
	Meherpur	9	8.6	2.0	17.8	b	Comilla	10	0.0	0.0	0.0	
	Satkhira	6	0.0	0.0	0.0	b						
	GF	*29*	*9.8*	*0.0*	*65.3*		*MF*	*30*	*0.0*	*0.0*	*0.0*	**
Corg (g kg^{-1})	Gopalganj	6	19.8	8.0	49.6		Brahmanbaria	10	11.1	7.5	17.4	
	Jessore	8	14.1	5.9	22.9		Chandpur	10	9.5	6.3	12.8	
	Meherpur	9	12.2	8.9	22.4		Comilla	10	9.1	5.1	12.9	
	Satkhira	6	12.4	7.1	17.7							
	GF	*29*	*14.3*	*5.9*	*49.6*		*MF*	*30*	*9.9*	*5.1*	*17.4*	**
N (g kg^{-1})	Gopalganj	6	1.8	0.9	4.4		Brahmanbaria	10	1.1	0.8	1.6	
	Jessore	8	1.4	0.5	2.1		Chandpur	10	0.9	0.7	1.2	
	Meherpur	9	1.3	0.8	2.3		Comilla	10	1.0	0.6	1.5	
	Satkhira	6	1.2	0.7	1.6							
	GF	*29*	*1.4*	*0.5*	*4.4*		*MF*	*30*	*1.0*	*0.6*	*1.6*	*
Clay (%)	Gopalganj	6	30.7	17.3	44.0		Brahmanbaria	10	8.0	3.4	13.7	b
	Jessore	8	31.0	8.4	45.2		Chandpur	10	6.4	4.6	8.4	b
	Meherpur	9	38.9	23.9	50.8		Comilla	10	13.2	6.3	21.0	a
	Satkhira	6	28.9	17.1	50.4							
	GF	*29*	*32.9*	*8.4*	*50.8*		*MF*	*30*	*9.2*	*3.4*	*21.0*	**
Silt (%)	Gopalganj	6	46.5	39.0	55.5		Brahmanbaria	10	60.6	37.8	75.0	b
	Jessore	8	48.9	39.8	56.8		Chandpur	10	75.2	55.6	87.5	a
	Meherpur	9	47.6	38.6	62.5		Comilla	10	52.6	32.8	77.2	b
	Satkhira	6	51.5	37.4	58.8							
	GF	*29*	*48.5*	*37.4*	*62.5*		*MF*	*30*	*62.8*	*32.8*	*87.5*	**
Sand (%)	Gopalganj	6	22.8	15.6	29.6	a	Brahmanbaria	10	31.3	18.4	54.1	a
	Jessore	8	20.1	13.4	39.4	ab	Chandpur	10	18.4	6.9	39.8	b
	Meherpur	9	13.5	5.4	24.7	b	Comilla	10	34.2	10.3	52.3	a
	Satkhira	6	19.6	12.2	31.6	ab						
	GF	*29*	*18.5*	*5.4*	*39.4*		*MF*	*30*	*28.0*	*6.9*	*54.1*	**

§ different letters indicate significant differences ($p<0.05$, Duncan’s Test) among districts; * and -** indicate significant differences between floodplains ($p<0.05$ and $p<0.01$, respectively); ns: non significant

Table 2. Results of the analysis of variance and descriptive statistics of Mn extractions and oxalate-extractable Al in the soils of the Ganges (GF) and Meghna (MF) Floodplains.

		N	Mean	min	max	$P^{\S}$		N	Mean	min	max	$P^{\S}$
	GANGES						**MEGHNA**					
Mn_R (g kg^{-1})	Gopalganj	6	0.38	0.27	0.58	b	Brahmanbaria	10	0.19	0.13	0.25	b
	Jessore	8	0.42	0.30	0.78	b	Chandpur	10	0.27	0.09	0.45	ab
	Meherpur	9	0.71	0.46	1.08	a	Comilla	10	0.36	0.20	0.67	a
	Satkhira	6	0.50	0.43	0.62	b						
	GF	*29*	*0.52*	*0.27*	*1.08*		*MF*	*30*	*0.27*	*0.09*	*0.67*	**
Mn_{OA} (g kg^{-1})	Gopalganj	6	0.16	0.10	0.28	c	Brahmanbaria	10	0.11	0.08	0.14	b
	Jessore	8	0.19	0.11	0.35	bc	Chandpur	10	0.15	0.07	0.22	ab
	Meherpur	9	0.30	0.16	0.50	a	Comilla	10	0.19	0.08	0.37	a
	Satkhira	6	0.24	0.17	0.30	ab						
	GF	*29*	*0.23*	*0.10*	*0.50*		*MF*	*30*	*0.15*	*0.07*	*0.37*	**
Mn_O (g kg^{-1})	Gopalganj	6	0.11	0.03	0.21	b	Brahmanbaria	10	0.07	0.04	0.11	
	Jessore	8	0.14	0.04	0.34	b	Chandpur	10	0.11	0.02	0.19	
	Meherpur	9	0.24	0.12	0.42	a	Comilla	10	0.16	0.04	0.32	
	Satkhira	6	0.17	0.09	0.25	ab						
	GF	*29*	*0.17*	*0.03*	*0.42*		*MF*	*30*	*0.12*	*0.02*	*0.32*	**
Al_O (g kg^{-1})	Gopalganj	6	1.02	0.65	1.40		Brahmanbaria	10	0.62	0.34	0.98	a
	Jessore	8	1.22	0.37	1.72		Chandpur	10	0.44	0.31	0.56	b
	Meherpur	9	1.40	0.76	1.92		Comilla	10	0.75	0.39	0.93	a
	Satkhira	6	1.12	0.55	1.52							
	GF	*29*	*1.21*	*0.37*	*1.92*		*MF*	*30*	*0.60*	*0.31*	*0.98*	**

§ different letters indicate significant differences ($p<0.05$, Duncan's Test) among districts; * and -** indicate significant differences between floodplains ($p<0.05$ and $p<0.01$, respectively); ns: non significant

Table 3. Variance explained by the extracted Principal Components and component loadings after Varimax rotation. Only loadings > 0.5 are shown

	Component				
	C1	C2	C3	C4	C5
Variance (%)	32.48	20.92	16.61	9.17	7.48
Clay	0.906				
Sand					-0.847
Silt	-0.632				0.747
pH	0.559			-0.587	
$CaCO_3$				-0.587	
Corg	0.644				
Al_R	0.928				
Al_O	0.880				
Fe_R	0.840				
Fe_{OA}	0.860				
Fe_O				0.831	
Mn_R			0.807		
Mn_{OA}			0.913		
Mn_O			0.847		
P_R		0.923			
P_{OA}		0.977			
P_O		0.955			
P_{Olsen}		0.901			

Table 4: Correlations between As forms and component scores

		C1	C2	C3	C4	C5
Whole dataset (n=59)	As_R	0.527^{**}	0.234	0.050	-0.041	0.084
	As_{OA}	0.575^{**}	0.189	-0.064	-0.050	0.053
	As_O	0.510^{**}	0.222	-0.079	0.050	0.079
	As_{Olsen}	0.415^{**}	0.198	-0.013	-0.053	0.059
GF (n=29)	As_R	0.255	0.272	-0.068	0.158	0.355
	As_{OA}	0.326	0.209	-0.267	0.141	0.279
	As_O	0.290	0.279	-0.205	0.211	0.270
	As_{Olsen}	0.160	0.398^{*}	-0.163	0.166	0.257
MF (n=30)	As_R	0.698^{**}	0.620^{**}	-0.162	0.292	-0.017
	As_{OA}	0.709^{**}	0.577^{**}	-0.113	0.347	-0.043
	As_O	0.723^{**}	0.498^{**}	-0.224	0.386^{*}	0.023
	As_{Olsen}	0.628^{**}	0.626^{**}	-0.151	0.196	-0.065

** $p<0.01$; * $p<0.05$

Figure captions

Figure 1. Map of Bangladesh evidencing the sampling areas within the districts

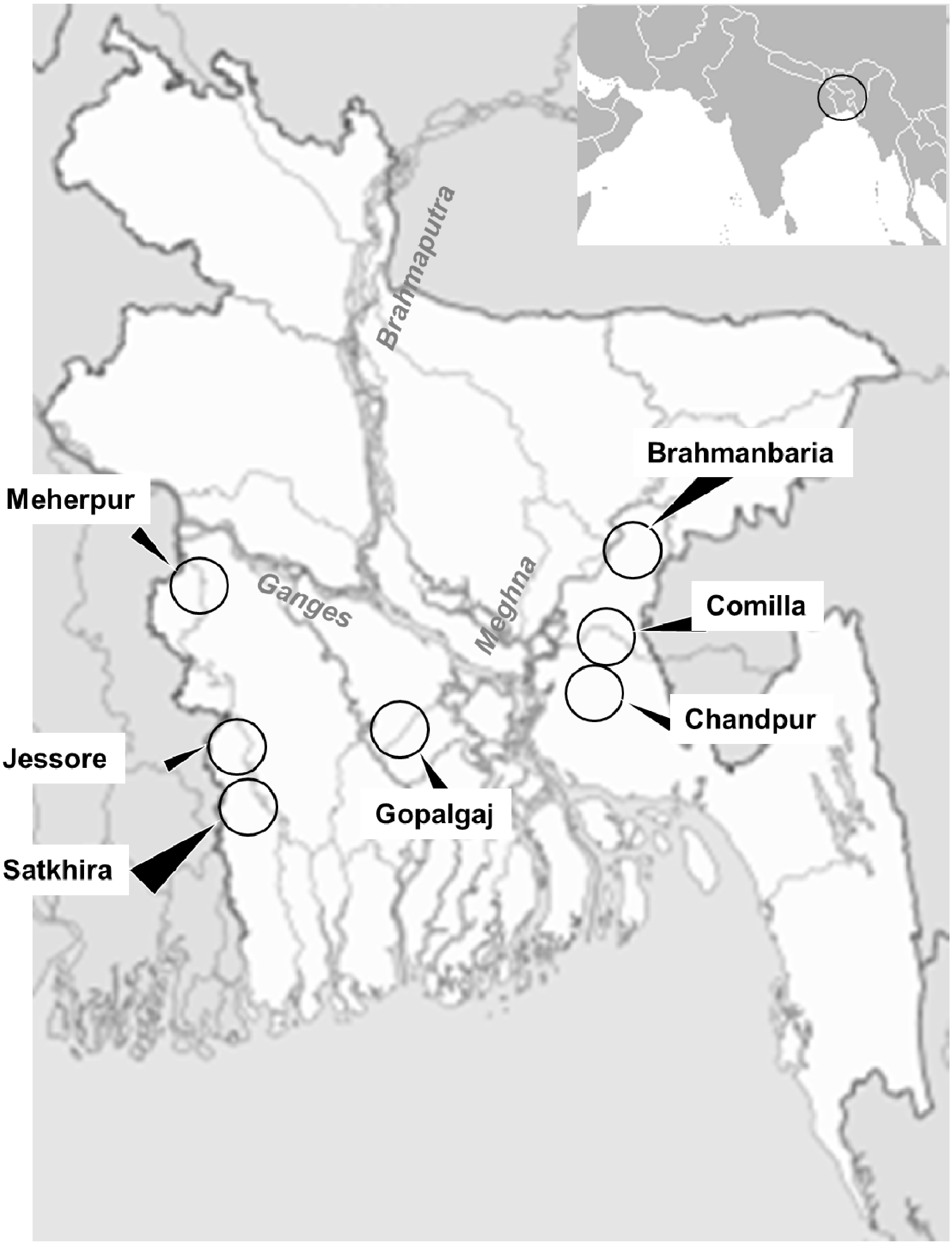
Figure 2. Fe forms extracted with *aqua regia* (Fe_R), oxalate-ascorbate (Fe_{OA}), oxalate (Fe_O), and the Fe_O/Fe_{OA} ratio in the soils of Ganges Floodplain (GF) and Meghna Floodplain (MF). The Fe_O/Fe_{OA} ratio is multiplied by 100. Error bars represent standard error. Different letters denote differences at district level within the same floodplain ($p<0.05$); asterisks denote differences in each Fe form between the two floodplains (* $p<0.05$; ** $p<0.01$)

Figure 3. As forms extracted with *aqua regia* (As_R), oxalate-ascorbate (As_{OA}), oxalate (As_O), and Olsen procedure (As_{Olsen}) in the soils of Ganges Floodplain (GF) and Meghna Floodplain (MF). The data of As_{Olsen} are multiplied by 10. Error bars represent standard error. Different letters denote differences at district level within the same floodplain ($p<0.05$); asterisks denote differences in each As form between the two floodplains (* $p<0.05$; ** $p<0.01$)

Figure 4. Relationships between As extracted with *aqua regia* (As_R) and (a) oxalate-ascorbate (As_{AO}); (b) oxalate (As_O); (c) Olsen procedure (As_{Olsen}) in the soils of Ganges Floodplain (GF) and Meghna Floodplain (MF)

Figure 5. P forms extracted with *aqua regia* (P_R), oxalate-ascorbate (P_{OA}), oxalate (P_O), and Olsen procedure (P_{Olsen}) in the soils of Ganges Floodplain (GF) and Meghna Floodplain (MF). The data of P_{Olsen} are multiplied by 10. Error bars represent standard error. Different letters denote differences at district level within the same floodplain ($p<0.05$); asterisks denote differences in each P form between the two floodplains (* $p<0.05$; ** $p<0.01$)

Figure 6. Scatter plots of component scores (from C1 to C5) for the samples of Ganges Floodplain (GF) and Meghna Floodplain (MF)



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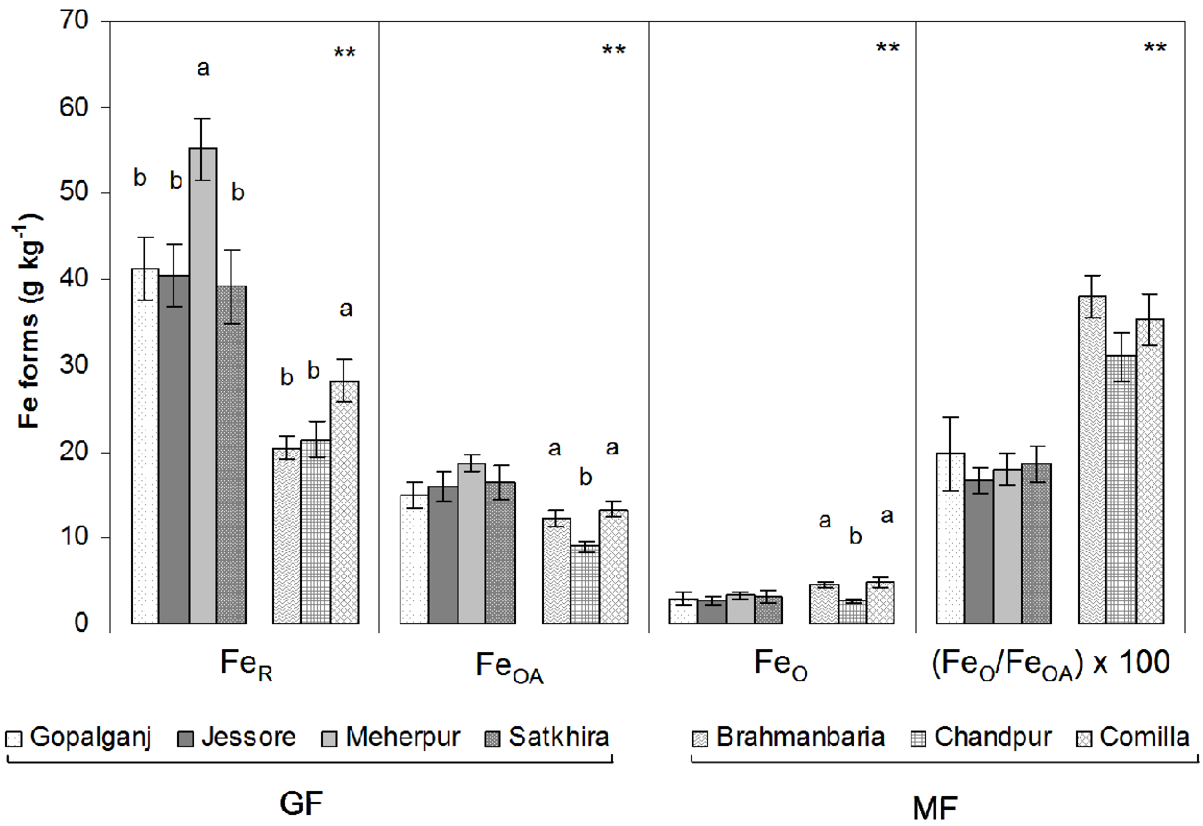

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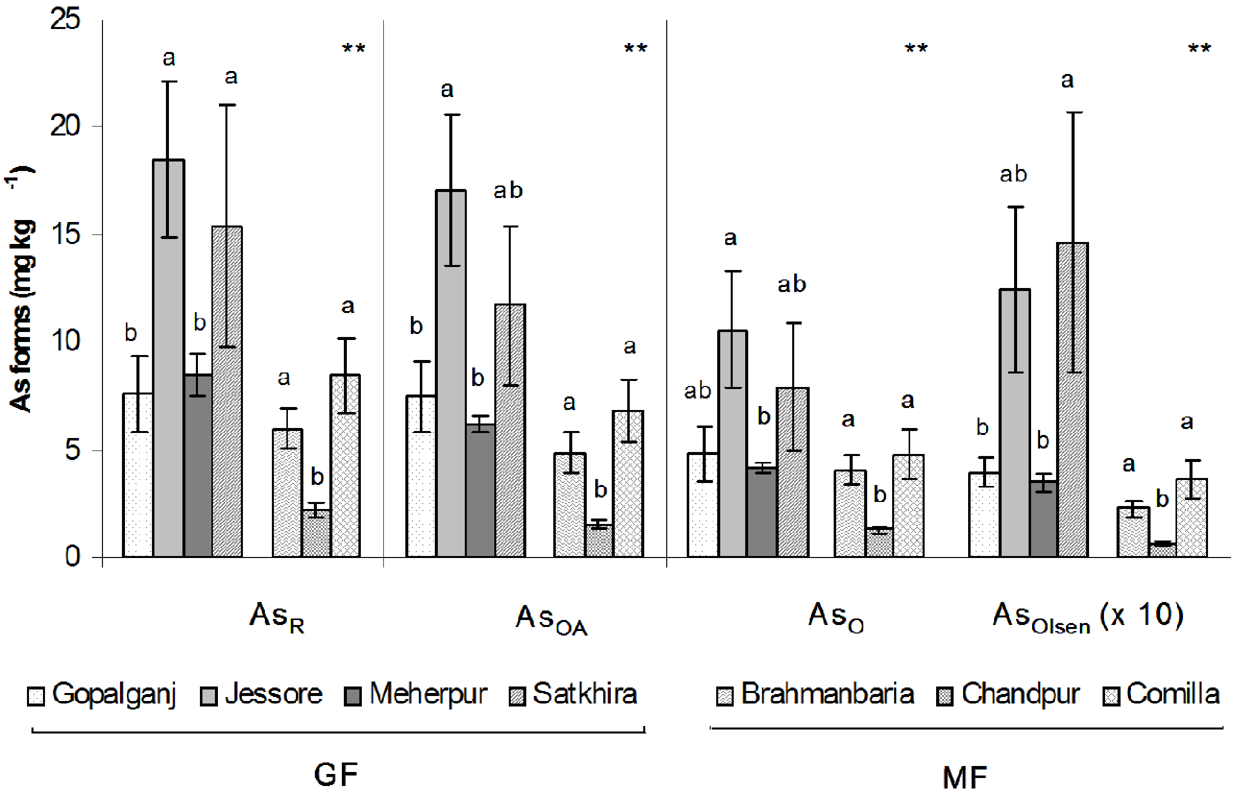

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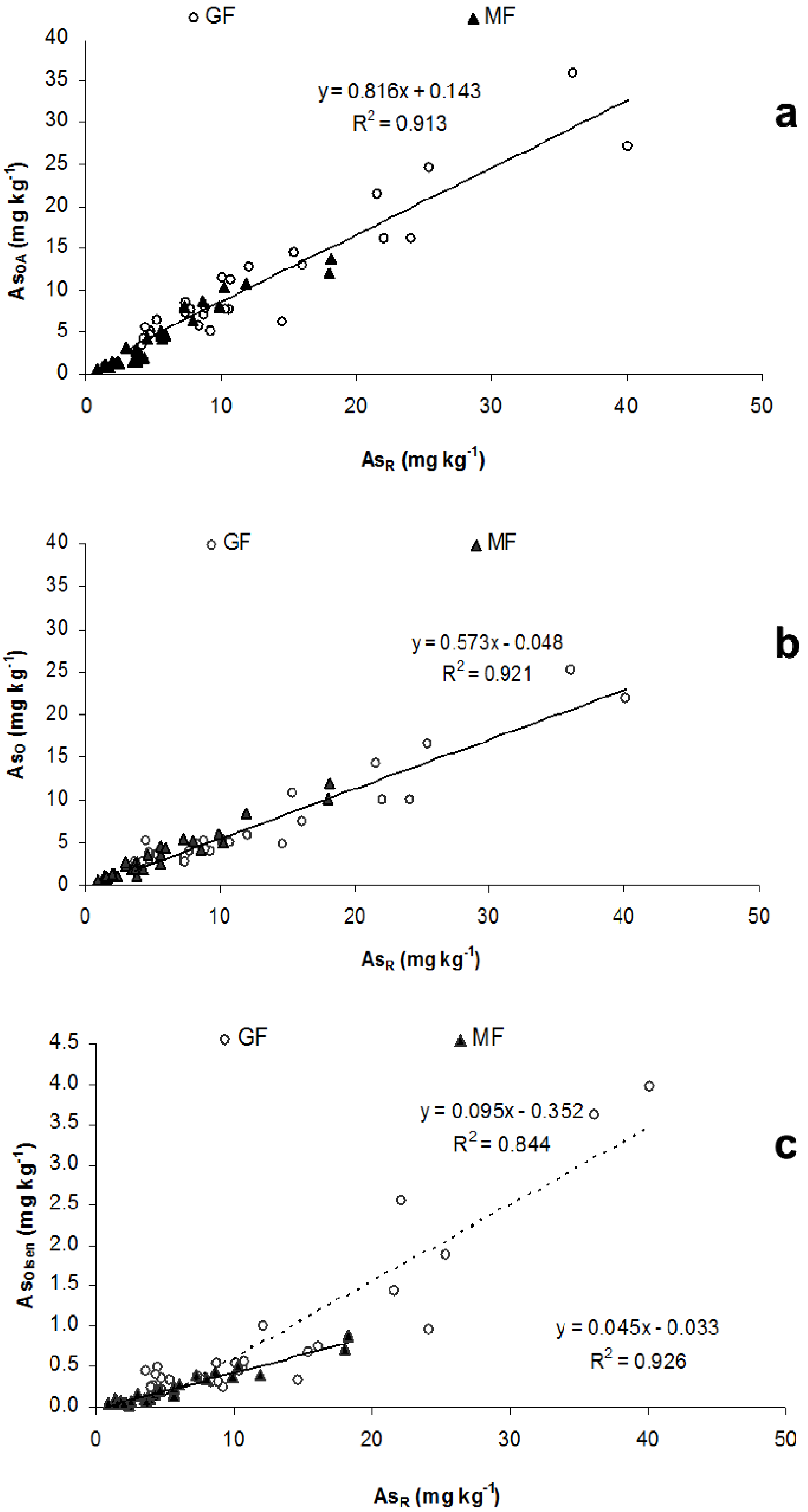

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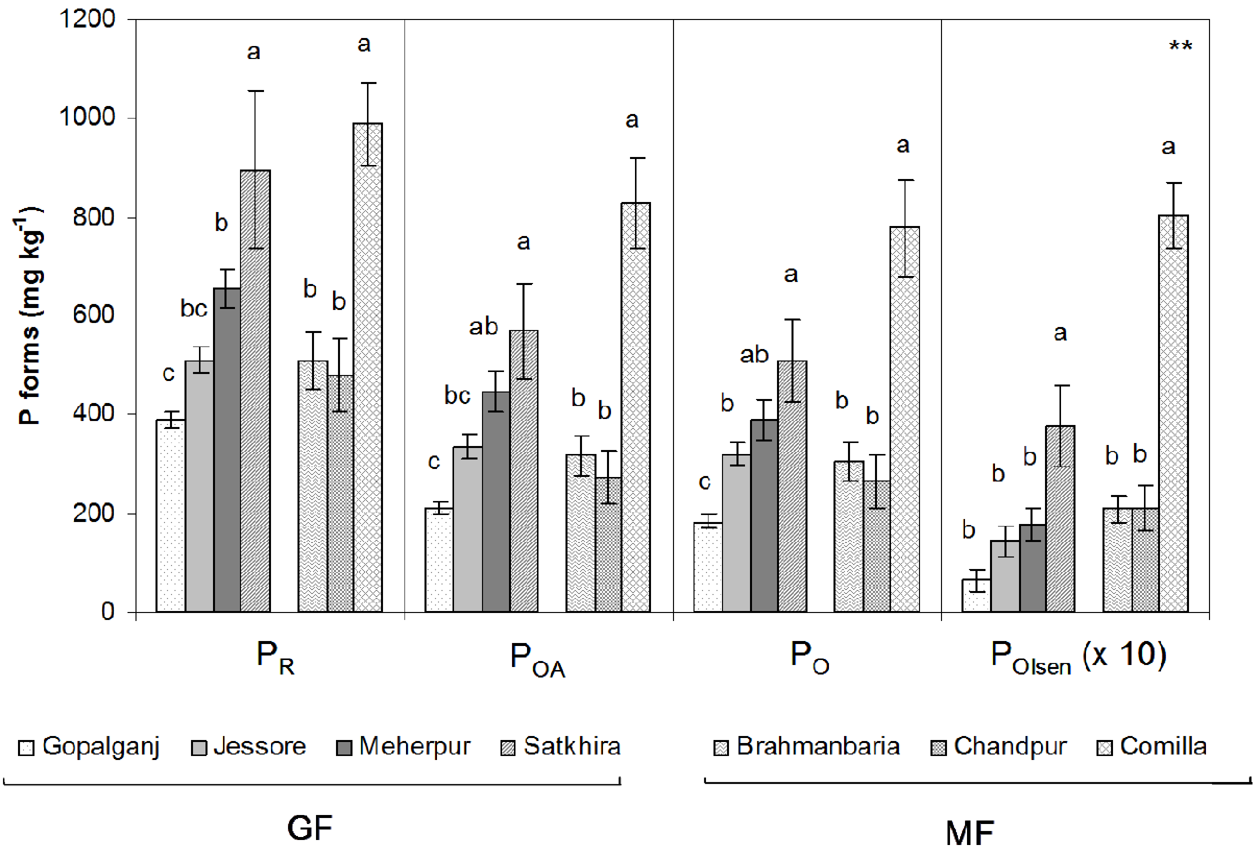

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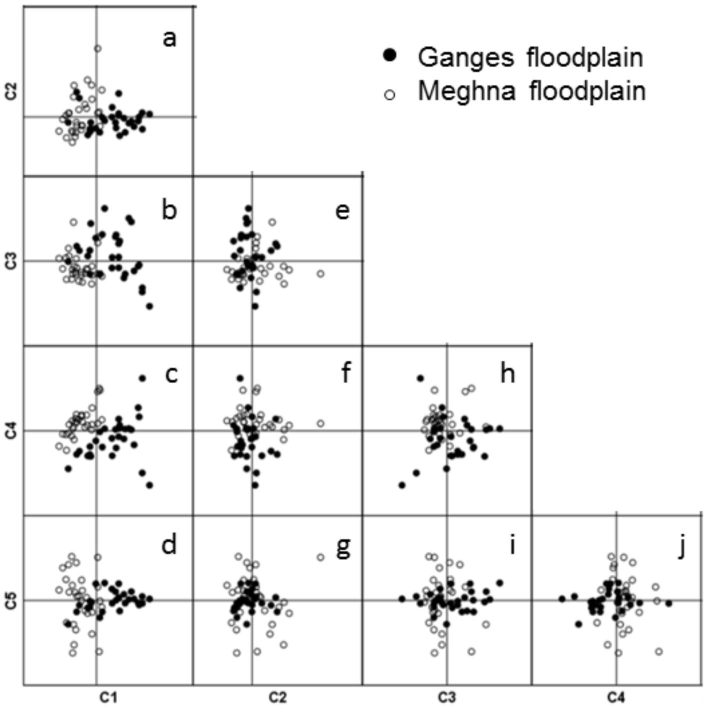

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