Arsenic from Groundwater to Paddy Fieldsin Bangladesh: Solid–Liquid Partition, Sorptionand Mobility

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Arsenic from groundwater to paddy fields in Bangladesh: solid-liquid partition, sorption and mobility.

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ABSTRACT

The arsenic contamination of Bangladesh groundwater involves heavy arsenic inputs to irrigated rice fields. Beside adsorption on soil colloids, iron-arsenic co-precipitation phenomena can affect arsenic retention in soils. In paddy fields of Satkhira District, Bangladesh, the study of the arsenic and iron forms in the irrigation waters and in soils at different times and distances from the irrigation well, evidenced that a higher Fe/As ratio in the well water was related to a faster oxidation of Fe(II) and As(III) in water and to a close Fe-As association in soils, together with a greater accumulation of arsenic and poorly ordered iron oxides. The concentration of arsenic and of labile iron forms decreased with the distance from the well and with the depth, as well as the reversibility of arsenic binding. The fate of the arsenic added to the soils by irrigation hence resulted strongly influenced by iron-arsenic co-precipitation, depending on the Fe/As ratio in water. Irrigation systems favouring the sedimentation of the Fe-As flocks could help in protecting the rice from the adverse effects of dissolved arsenic.

KEY WORDS: Arsenic, iron, soil, water, Bangladesh.

1 INTRODUCTION

In Bangladesh the need to increase the rice production has been met, during the last years, by the cultivation of high yielding varieties ("Boro" rice) during the dry season. The high water requirement of the Boro rice cultivation has been satisfied by irrigation from the shallow aquifer that may contain high concentrations of arsenic (Nickson et al., 1998; BGS-DPHE, 2001). Ali et al. (2003) estimated an annual arsenic input to paddy fields up to 9.7 kg/ha in the most severely affected zones. The arsenic added to the soil by irrigation can accumulate in the topsoil, it can be released to the deep or surface water bodies, or taken up by biota, including crops, thus entering the food chain. The pathways of the arsenic added by the irrigation water are still poorly understood, although a health risk in the consumption of rice and other crops grown in arsenic affected zones has been reported (Meharg, 2004). The arsenic remaining in solution in the irrigation waters is directly available to plants, while the bioavailability of the arsenic fraction associated with soil solid phases depends on the retention by the solid phases. The main processes involved in arsenic retention by soils are adsorption and (co-)precipitation reactions, their relative importance depending on several parameters, such as chemical composition, pH, Eh, ionic strength of the solution, and microbial activity (Smith et al., 1998; Bissen and Frimmel, 2003). In Bangladesh, the arsenic affected groundwater is characterized by neutral to sub-alkaline pH, low redox potential, high concentrations of bicarbonate, phosphate, divalent iron, calcium, barium, manganese, and other metals (BGS-DPHE, 2001). After the withdrawal from the aquifer and the exposal to atmospheric oxygen, Fe(II) in solution is oxidized and form colloidal flocks of iron (hydr)oxides, which may scavenge arsenic and other elements from the solution. This naturally occurring phenomenon is used for water treatment in some simple Fe-As removal plants, whose effectiveness increases with the water Fe/As ratio (Ahmed, 2001), and its occurrence in paddy fields irrigated with As-contaminated water has been documented (Roberts et al., 2007). The accumulation of As-Fe co-precipitates can contribute to the increase of As concentration in soils, particularly in

proximity of the irrigation tubewell (Dittmar et al., 2007; Saha and Ali, 2007). The co-precipitation of arsenic with iron flocks and the stability of these compounds in field could represent a fundamental factor in regulating arsenic partitioning between the solid and liquid phases and the mobility of arsenic reaching agricultural soils.

However, the kinetics of Fe and As oxidation, persistence of each As form in solution and stability of As-Fe co-precipitation products in soil can be affected by many factors, such as the physico-chemical characteristic of arsenic affected groundwater and its Fe/As ratio, the physico-chemical characteristics of the irrigated soil, the cropping practices, the irrigation system used, often linked to local traditions. In typical rice fields, the area served by a single irrigation tubewell is subdivided in sub-units, and shallow irrigation channels supply the water to each sub-unit (Ali et al., 2003). In some other cases, groups of 2-3 adjacent sub-units can receive the water in sequence and not directly from the channel, with a longer and slower path of the water to the farthest plots.

In the present work the concentration of iron and inorganic arsenic species in solution in the irrigation water of paddy fields, their persistence in solution at increasing distance from the water source were evaluated in sites characterized by a different Fe/As ratio. The study of the forms of arsenic and iron in the soils at different depths and distances from the water source in the two sites is aimed to bring new light on the possible role of co-precipitation products, as affected by chemical characteristics of the incoming water, on the stability and potential availability of the arsenic added with the irrigation groundwater to the soils.

2 MATERIALS AND METHODS

2.1 Sampling area

The studied paddy fields were situated in South-Western Bangladesh, Satkhira district, close to the villages of Koila (22°50'56.0'' N; 89°04'09.1'' E) and Mahmoodpur (22°40'39.4'' N; 88°59'08.9'' E). The geographic coordinates were registered at the location of the irrigation tubewells. The soils develop on recent deltaic deposits of the Gangetic floodplain (BGS-DPHE, 2001). The climate of

the area is monsoonal, with rainfall concentrated from June to October; the crops grown during the summer season are thus mainly rain-fed, while during the dry season they completely depend on groundwater irrigation from tubewells.

In both sampling sites, the tubewells were nearly 60 m deep and they have been used during the last 8 years for the irrigation of a total surface of nearly 2.5 ha. The paddy fields were subdivided in plots of nearly 18x36 m, separated by small soil embankments that were manually interrupted in one point to let the water flow to the next plot. In Koila the water was contemporary supplied to three consecutive plots on the right side of the channel, while in Mahmoodpur three plots on the right and two on the left side of the channel were irrigated at the same time (Fig. 1).

2.2 Water sampling and analysis

Water samples were collected directly from the tubewell after at least 1 hour pumping and from each plot during the irrigation, 1 hour after the interruption of the water supply and again after 6 hours. The water samples (200 mL) were collected in 250 mL polyethylene bottles containing 2 ml of 6M hydrochloric acid or 5 g of anionic resins (DOWEX 1-Dow Chemical Company, Midland, Michigan) for the selective retention of arsenate, allowing the speciation of the dissolved inorganic arsenic. The resin-treated samples were shaken by hands for 10 minutes and then transferred to other bottles containing 2 mL of 6M HCl. Arsenate is selectively retained by strong anionic exchange resins with respect with arsenite, since arsenate is present in anionic form at most environmental pH conditions ($pK_{a1} = 2.3$; $pK_{a2} = 6.8$; $pK_{a3} = 11.3$), while arsenite is mostly indissociated ($pK_{a1} = 9.2$; $pK_{a2} = 12.7$) (Lide, 2007). The selective retention of arsenate by most anionic resins is well known (Ficklin, 1983; Dambies, 2004), and was here further checked before use by preliminary experiments to determine the minimum contact time required to ensure arsenate adsorption. All the water samples were then colorimetrically analyzed for Fe(II) (1,10-phenanthroline method, Loeppert and Inskeep, 1996) and for As (Frisbee et al., 2005) within two hours after collection. The standard deviation was within 10% for Fe and 15% for As replicates.

2.3 Soil sampling and analysis

Samples from the top 0-5 cm were collected in April 2006 from each one of the 3 consecutive plots and samples at the depths of 0-2, 2-8, and 8-20 cm were collected in the first and third plot (Fig. 1). All the analyses were carried out on the fine-earth fraction.

Soil pH in water (1:2.5 w/v) was determined potentiometrically; the particle size was determined by the pipette method after dispersion with Na-hexametaphosphate, carbonates were determined volumetrically and the total organic carbon and nitrogen were obtained with a CN analyzer (NA2100 Protein, 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 *aqua regia* extractable As. The amounts of Fe extractable in dithionite-citrate-bicarbonate (DCB) (Mehra and Jackson, 1958), Fe and As extractable in ammonium oxalate at pH 3 (Schwertmann, 1964), Fe and As extractable in 0.2M citrate at pH 6 (weakly bound Fe forms, partly linked to organic matter) and 0.2 M citrate-0.05 M ascorbate (selective extraction of poorly crystalline Fe oxides in the presence of magnetite) (Reyes and Torrent, 1997), were also determined. The desorbability of As was evaluated in presence of anion exchanging resins (Sibbesen, 1988). For resin extraction, 1.00 g of soil was shaken for 48 hours in presence of 2.5 g of resin and 100 mL of deionized water on a reciprocating shaker. The anions adsorbed on the resins were then exchanged with 0.5 M HCl. 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 was determined with flame-AAS. The standard deviations for all these analysis were within 5%; except resin extractions (7%).

The statistical analysis of the data was performed using the SPSS 12 for Windows (SPSS Inc, Chicago, IL).

3 RESULTS AND DISCUSSION

3.1 Dynamics of As in the flooding waters

The tubewell water from Mahmoodpur contained 0.60 mg L^{-1} of arsenic and 4.8 mg L^{-1} of Fe(II) (Fig. 2a), with a Fe/As mass ratio of 8.0, corresponding to a molar ratio of 10.7. In Mahmoodpur rice field, As and Fe concentrations in water did not decrease passing from the tubewell to the first irrigated plot during active water pumping. After 1 h from the interruption of the water supply As concentration decreased to 85% of the total incoming content and, after 6 h, to 14%. The passage from the first plot (M I) to the third plot (MIII) involved the decrease of the As concentration to 0.05 mg L^{-1}, and this concentration did not substantially vary within six hours after the irrigation had been stopped. The decrease in Fe(II) concentration with time was more pronounced compared with As, becoming nearly 50% of the tubewell concentration after 1 h and, after 6 h, Fe(II) was no longer detectable (Fig. 2a).

The tubewell water in Koila contained 0.31 mg L^{-1} of As and 6.1 mg L^{-1} of Fe(II), with a Fe/As mass ratio of 19.8, corresponding to a molar ratio of 26.5 (Fig. 2b). In this case, during water pumping, the concentrations of As and Fe(II) were lower in the water sampled from the first plot (K I) compared with the tubewell, indicating that some precipitation of dissolved As and Fe(II) probably occurred in the irrigation channel (Roberts et al., 2007). The proportional decrease in As and Fe(II) concentrations with time in the first plot was more marked compared with Mahmoodpur (Fig. 2b): after 1 h the As concentration was reduced to 38% of the initial tubewell concentration and Fe(II) to 44%. The concentration of As in the water reaching the third plot (K III) during irrigation was comparable to that in Mahmoodpur, although here a further decrease with time was observed, and the decrease in Fe(II) concentration from the first plot (M I) to the third plot (M III) was more marked.

The speciation of the arsenic obtained with anionic resins showed a predominance of As(III) in the tubewell water of both sites (Fig. 3a and 3b). In Mahmoodpur As(III) was the dominant specie in all the water samples and, in the plot M III, the As(III) was nearly 80% even after 6 h (Fig. 3a). In Koila, by contrast, the As(III) fraction decreased with time and, in the plot K III, after 6 h it was

approximately 50% (Fig. 3b).

A very important mechanism for arsenic removal from the water could be represented by the adsorption/coprecipitation on iron (hydr)oxides forming after the oxidation of the dissolved Fe(II) in the tubewell water (Hussam et al 2003; Roberts et al., 2007). The co-precipitation of As along with the formation and flocculation of iron (hydr)oxides is a well known process, commonly utilized for As removal by passive sedimentation of the naturally occurring Fe, or after the addition of Fe salts (Singh, 2007). The efficiency of As removal by co-precipitation with Fe increases with the initial Fe/As ratio in water (Ahmed, 2001), thus a better removal could be expected in Koila compared to Mahmoodpur. The proportional decrease of the As concentration in the first plot within one hour was in fact greater in Koila, possibly for a faster coagulation and sedimentation of the Fe flocks. The absolute amount of As removed, however, was greater in Mahmoodpur water: after 6 h from the interruption of the water supply, 0.52 mg L^{-1} of arsenic were removed from the solution in the first plot in Mahmoodpur and 0.26 mg L^{-1} were removed in Koila. Beside the co-precipitation of Fe-As colloids, other mechanisms including adsorption on soil minerals, uptake by biota, or volatilization, could play an important role in arsenic sequestration in Mahmoodpur site. The presence of a greater amount of Fe(II) in Koila water could also contribute to justify the decrease of the As(III)/As(V) ratio in this site, since the presence of Fe(II) can enhance the oxidation of As(III) by the oxygen from the air, by the enhancement of Fenton reaction involving the formation of ·OH radicals (Hug and Leupin, 2003).

In both sites, the decrease in arsenic concentration was related to temporal and spatial factors, as described by Roberts et al. (2007). In the present study the spatial distance from the irrigation tubewell seemed to play a major role, since in both sites, whatever the initial As concentration and the Fe/As ratio, the arsenic concentration in the water reaching the third plot during the water pumping was comparable or lower than the concentration in the first plot after six hours from the interruption of the water supply. In the studied area, the rice fields were subdivided in plots which did not all receive the water directly from the irrigation channel, as in the paddy field studied by

Roberts et al. (2007) and Dittmar et al. (2007); instead, the water flowed from one plot to the following one for a maximum of three contiguous plots. This irrigation method favoured a slower, longer and more tortuous water path. The water needed nearly one hour to completely flood the third plot after the beginning of the irrigation; the great decrease of As concentration in the water of this plot was hence not justified by time only, but probably also the slow tortuous flow from one plot to the following one favoured the sorption of As on the forming Fe colloids and their successive sedimentation. Also other mechanisms that could contribute to As removal from water, such as sorption on soil minerals and interactions with the biota, are favoured by a very slow water flow with a long pathway. Consequently, the rice cultivated in the plots not directly supplied by the water channel is less exposed to As uptake from the water.

3.2 Dynamics of As in soils

The soils from both sampling sites were slightly calcareous, and showed an organic C content ranging between 15 and 22 g kg^{-1}, with higher carbon contents detected at increasing distance from the irrigation channel, as well as the C/N ratio (Table 1). The amounts of iron extracted with DCB (Fe$_d$) and ammonium oxalate (Fe$_o$) (Table 1), as well as with the other extractants (Fig. 4), were always higher in Koila, (where the average Fe$_d$ and Fe$_o$ contents of the surface samples were 10 ± 1 and 4.5 ± 1 g kg^{-1}, respectively) compared with Mahmoodpur (average Fe$_d$ and Fe$_o$ content of 7 ± 1 and 3.9 ± 1 g kg^{-1} respectively). The amounts of iron extracted with DCB did not follow a specific trend with the distance in both sites (Table 1). In Mahmoodpur, the amounts of Fe extractable with oxalate (Fe$_o$), citrate-ascorbate (Fe$_{ca}$) and citrate at pH 6 (Fe$_c$) were generally higher in the farthest plots from the irrigation channel (except Fe$_c$ in plots M IA and M IIA) (fig. 4a); differently in Koila the amounts of Fe$_o$ and Fe$_c$ showed a clear decreasing trend with the distance from the tubewell (Fig. 4b). The deposition of co-precipitation products from the irrigation water was expected mainly to affect the non-crystalline or scarcely crystalline iron forms, such as the oxalate-extractable iron pool, related to poorly ordered oxides (Schwertmann, 1964), or the pool weakly bound to organic

matter and extractable with a mild complexing agent, such as citrate at pH 6 (Reyes and Torrent, 1997). The latter fraction was very high in these soils, representing more than 50% of the oxalate-extractable iron in both sites (against an average 20% calculated on the values of 75 soils reported by Reyes and Torrent, 1997). This pool of Fe, which poorly ordered structure might be stabilized by the presence of organic matter, could represent an important sink for arsenic reaching the soils with groundwater.

The decreasing trend of Fe_o and Fe_c fractions with the distance from the tubewell observed in Koila site suggested a relationship with the deposition of Fe colloids from the irrigation water. While in Koila a rapid oxidation of Fe(II) to Fe(III) occurred (Fig 2b), and Fe (hydr)oxides precipitated within a short distance, in Mahmoodpur Fe oxidation, and thus the sedimentation of co-precipitation products, appeared to be slower (Fig 2a). Thus, the forming Fe colloids tended to be carried farther by water, as could be suggested by amounts of extractable Fe generally greater in the farthest plot from the irrigation channel compared to the closest one. Differently, Dittmar et al. (2007, supporting information) did not found a spatial variation in the amount of oxalate extractable Fe with the distance from the water source: this could be partly explained by the different irrigation system, where each plot of the paddy field received the water directly from the irrigation channel.

Even if an important presence of magnetite was found in the soils samples analyzed by Ghosh et al. (2006) in nearby arsenic affected zones of West Bengal, in the soils of the present study the possible formation of crystalline magnetite did not appear to be significant. The amounts of oxalate extractable Fe were in fact generally smaller than those of Fe extractable with citrate/ascorbate (Fig 4), although the latter method is reported to be more selective for the extraction of scarcely ordered Fe oxides in the presence of crystalline magnetite (Reyes and Torrent, 1997). The amounts of arsenic extracted with the two procedures, differently from iron, were not comparable, the oxalate-extractable As being generally more than twice the amount extracted with citrate/ascorbate (Fig. 5). This suggests that the pools extracted with these two methods might not be the same, possibly due to the different extraction mechanisms.

As observed for iron, the total arsenic and the arsenic pools extracted with all the procedures were higher in Koila compared with Mahmoodpur (Fig. 5a and 5b). The extractable arsenic was always decreasing with the distance from the tubewell in both sites, as expected if the irrigation water was the main arsenic source in the studied soils (Dittmar et al., 2007; Saha and Ali, 2007); however, the decreasing trend was more marked in Koila compared with Mahmoodpur.

The much larger amount of As extracted from Koila soils compared with Mahmoodpur was unexpected, considering the lower concentration in the irrigation water (Fig. 2), and suggested that the added As was less effectively retained by soil colloids in Mahmoodpur. This was possibly related to the lower amount of dissolved Fe in the irrigation water that could co-precipitate with arsenic, and to a scarcer availability of surfaces involved in As specific adsorption in soil, in particular Fe (hydr)oxides (Table 1 and Fig. 4). Especially in Koila, these iron minerals could at least partly derive from deposition of precipitation products from the irrigation water. The more marked decrease in Koila with the distance from the channel of extractable As and Fe, could further support these hypotheses.

Since the most important adsorbing sites for As in soils are represented by Fe oxides, positive correlations could be expected between As and the forms of Fe more involved in As sorption. Moreover, in case of a relevant role in As sequestration played by the formation of Fe-As co-precipitation products in the irrigation water, the expected positive correlations between As and Fe would involve mainly the extractions targeting the poorly ordered oxides and the weakly bounded Fe forms extractable with citrate at pH 6. In Koila site, where the Fe/As ratio in the irrigation water was higher, significant positive correlations were actually found between the amounts of As and those of Fe extracted with oxalate ($r = 0.716$; $p < 0.05$) and with citrate at pH 6 ($r = 0.967$; $p < 0.01$), but not in Mahmoodpur site, suggesting a different distribution of As forms in the two soils and a significant sequestration of As in co-precipitated forms in the site where the amount of dissolved Fe was large enough.

The fraction of arsenic extractable with anion exchange resin, representing the pool of desorbable

arsenic, was the only one showing a decreasing trend with the distance from the channel more marked in Mahmoodpur than in Koila (Fig. 5). In Mahmoodpur site, the percentage of *aqua regia* extractable As that could be desorbed with resins was 22% in the plot M I and 3% in the plot M III while, in Koila, these percentages were 20% and 12% in the plots K I and K III respectively. The decrease in As desorbability with the distance could be partly explained with a smaller proportion of freshly co-precipitated Fe-As compounds, since the reversibility of As adsorption is inversely related to the ageing time of the As-mineral bonding (Pigna et al., 2006). The differences in As desorbability in the two sites and in the different plots of each site could also be related to their mineral association (Martin et al., 2007), which could result in correlations between the As desorbed by resins and the amounts of As and Fe in the different pools. In Mahmoodpur, the arsenic extracted with resins was correlated only with As extracted in *aqua regia* and oxalate, and with Fe extracted in citrate-ascorbate and citrate at pH 6 (Table 2).

In Koila site, highly significant correlations ($p < 0.01$) were found between resin extractable As and all the other pools of As, except As extracted in *aqua regia* (Table 2) suggesting that most As pools could be involved in As desorption. The desorbable As was also significantly correlated with the pools of Fe extractable with oxalate ($p < 0.05$) and with citrate-ascorbate and citrate at pH 6 ($p < 0.01$). In Koila, hence, the arsenic associated with most Fe pools could contribute to the desorbable fraction. Some reversibility of the binding between freshly formed As-Fe complexes, with relatively short ageing time was expected (Pigna et al., 2006) and the found correlations could further suggest that the poorly ordered oxides may represent, in this site, a major sink of As.

The vertical decrease at increasing depth in the first plot in both Mahmoodpur and Koila of the amounts of arsenic extractable with *aqua regia*, oxalate and resins, as well as of the oxalate extractable iron, (Fig 6), confirmed a combined addition to the soil of As with poorly ordered Fe minerals, mainly in Koila, but also in Mahmoodpur. In both sampling sites, however, the decreasing trend of As and Fe concentrations at increasing depth was not observed in the third plot of the rice fields. In the soil plots close to the water source, the continuative accumulation of co-precipitation

products from groundwater on the soil surface probably maintained a clearer vertical trend in the distribution of As and Fe (Dittmar et al., 2007), while in the farthest plots, the smaller residual amounts of As and Fe carried by the irrigation water were not great enough to determine vertical concentration trends.

4 CONCLUSIONS

The arsenic and iron dissolved in the groundwater decreased with the distance and with time in both the studied sites and only a small proportion of the initial content in the water source reached the farthest irrigated plots. Consequently, the concentration of As and poorly ordered Fe minerals in the topsoil decreased with the distance from the water source. This trend, as well as the gradient in As and Fe vertical distribution, was more marked in Koila, where the irrigation water had a higher Fe/As ratio and As was retained in soil in greater amounts. Conversely, in Mahmoodpur, in spite of a nearly double initial As concentration in water, the As concentration in soil was lower, and the association between As and poorly ordered Fe minerals was not evident. The fate of As added to rice fields with the irrigation water, thus, depended not only on soil characteristics, but it was also strongly influenced by the chemical composition of water, mainly by the initial As/Fe ratio. In irrigation systems like the examined one, the rice growing in the farthest plots from the irrigation channel would be exposed to lower As concentration in water and to a smaller and less desorbable amount of As accumulated in soils compared with the rice growing in the plots directly supplied by the channel. The construction of longer and more tortuous water paths prior the cultivated plots, although land-consuming, would help in partly protecting the rice from the adverse effects of the arsenic inputs by irrigation water. A better effect would be achieved with waters with a high Fe/As ratio.

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FIGURE CAPTIONS

Figure 1. Schematic representation of the sampling sites of Mahmoodpur and Koila. The arrows indicate the water flow through the plots of each paddy field. The square labels indicate the sampling points of the topsoil samples (0-5 cm), while the circles indicate the points where the samples were collected at different depths (0-2; 2-8; 8-20 cm). The roman numbers indicate the plots of the rice fields successively reached by the water.

Figure 2. Total arsenic and bivalent iron concentrations in the water in (a) Mahmoodpur and (b) Koila rice fields at the withdrawal from the tubewell, in the first and third plots during the water pumping (0 h) and one hour or six hours after the end of the water supply.

Figure 3. Percentage distribution of arsenate [As(V)] and arsenite [As(III)] in the water of (a) Mahmoodpur and (b) Koila rice fields at the withdrawal from the tubewell, and in the first and third plots six hours after the end of the water supply.

Figure 4. Iron extracted with ammonium oxalate at pH 3, citrate-ascorbate at pH 6, and sodium citrate at pH 6 from (a) Mahmoodpur, and (b) Koila topsoil samples (0-5 cm).

Figure 5. Arsenic extracted with *aqua regia*, dithionite-citrate-bicarbonate, ammonium oxalate at pH 3, citrate-ascorbate at pH 6, sodium citrate at pH 6, and anion exchange resins from (a) Mahmoodpur, and (b) Koila topsoil samples (0-5 cm).

Figure 6. Vertical distribution in the first and third plot in Mahmoodpur and Koila rice fields of Fe extracted with ammonium oxalate at pH 3, and of As extracted with *aqua regia,* ammonium oxalate at pH 3, and anion exchange resin.

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Table 1. Selected characteristics of the topsoil (0-5 cm) of the rice fields in Mahmoodpur and Koila sites. Fe_t is *aqua regia* extractable Fe; Fe_d is

dithionite-citrate-bicarbonate extractable Fe, and Fe_o is oxalate extractable Fe.

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	pH	CaCO$_3$ (g kg^{-1})	C $_{organic}$ (g kg^{-1})	N (g kg^{-1})	C/N	Fe$_d$ (g kg^{-1})	Fe$_o$ (g kg^{-1})	Fe$_o$/Fe$_d$	Sand (%)	Silt (%)	Clay (%)
					Mahmoodpur						
M 1 A	8.1	19	17	1.6	11	8.2	4.7	0.57	12	55	33
M 2 A	8.0	20	22	2.2	10	7.5	4.6	0.60	20	52	28
M 1	8.2	19	17	1.6	10	6.0	3.2	0.53	23	58	19
M 2	8.3	22	18	1.7	11	5.9	3.3	0.56	18	60	22
M 3	7.9	13	20	1.8	11	7.6	3.8	0.50	16	56	28
					Koila						
K 1	8.1	19	15	1.6	9	11.7	5.7	0.49	21	52	27
K 2a	8.2	19	16	1.6	10	9.4	4.5	0.48	17	52	31
K 2b	8.1	19	17	1.7	10	8.7	4.3	0.50	28	41	31
K 3	8.2	22	18	1.7	11	9.3	3.4	0.36	18	43	39

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2 Table 2. Correlation coefficients (r) between As extracted with resins and different forms of As and

3 Fe in soil samples from Mahmoodpur and Koila paddy fields.

Element	Extraction procedure	Koila	Mahmoodpur
		As resin	
		r	
As	*Aqua regia*	0.500	0.667*
	Oxalate	0.878**	0.779*
	Citrate-ascorbate	0.949**	0.486
	Citrate pH 6	0.954**	0.186
Fe	Oxalate	0.766*	0.061
	Citrate-ascorbate	0.808**	0.916**
	Citrate pH 6	0.989**	0.663*

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5 * $p < 0.05$

6 ** $p < 0.01$

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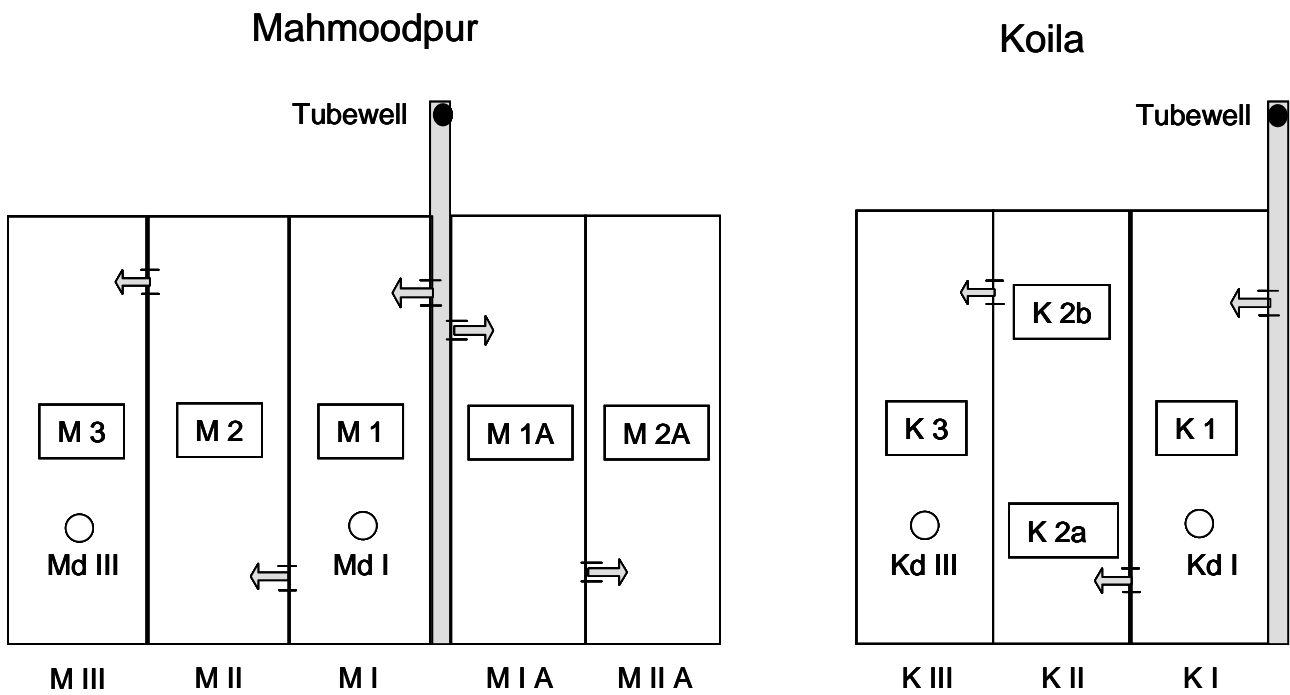
Mahmoodpur

Koila

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Figure 1. Schematic representation of the sampling sites of Mahmoodpur and Koila. The arrows

indicate the water flow through the plots of each paddy field. The square labels indicate the

sampling points of the topsoil samples (0-5 cm), while the circles indicate the points where the

samples were collected at different depths (0-2; 2-8; 8-20 cm). The roman numbers indicate the
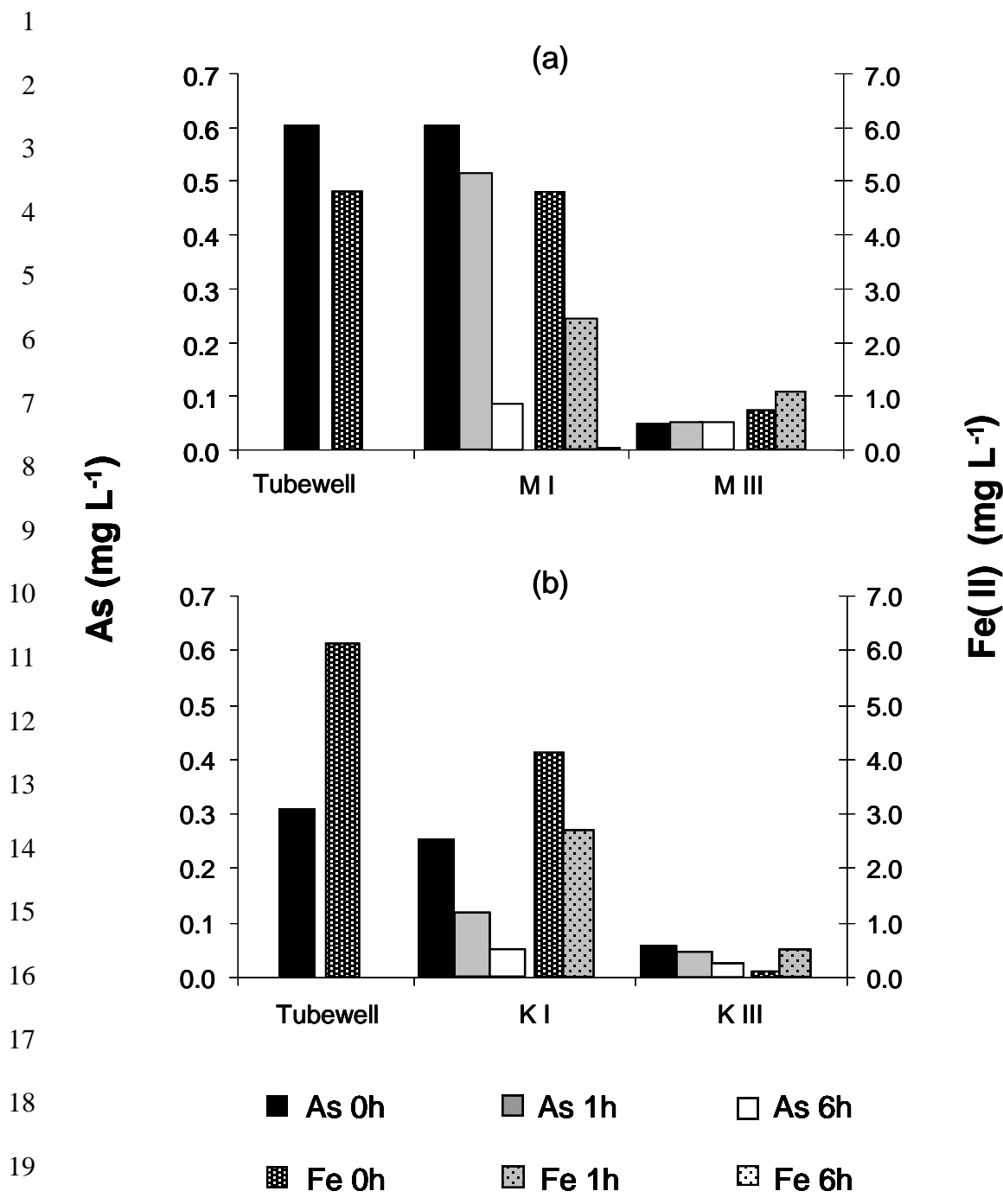
plots of the rice fields successively reached by the water.

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Figure 2. Total arsenic and bivalent iron concentrations in the water in (a) Mahmoodpur and (b) Koila rice fields at the withdrawal from the tubewell, in the first and third plots during the water pumping (0 h) and one hour or six hours after the end of the water supply.

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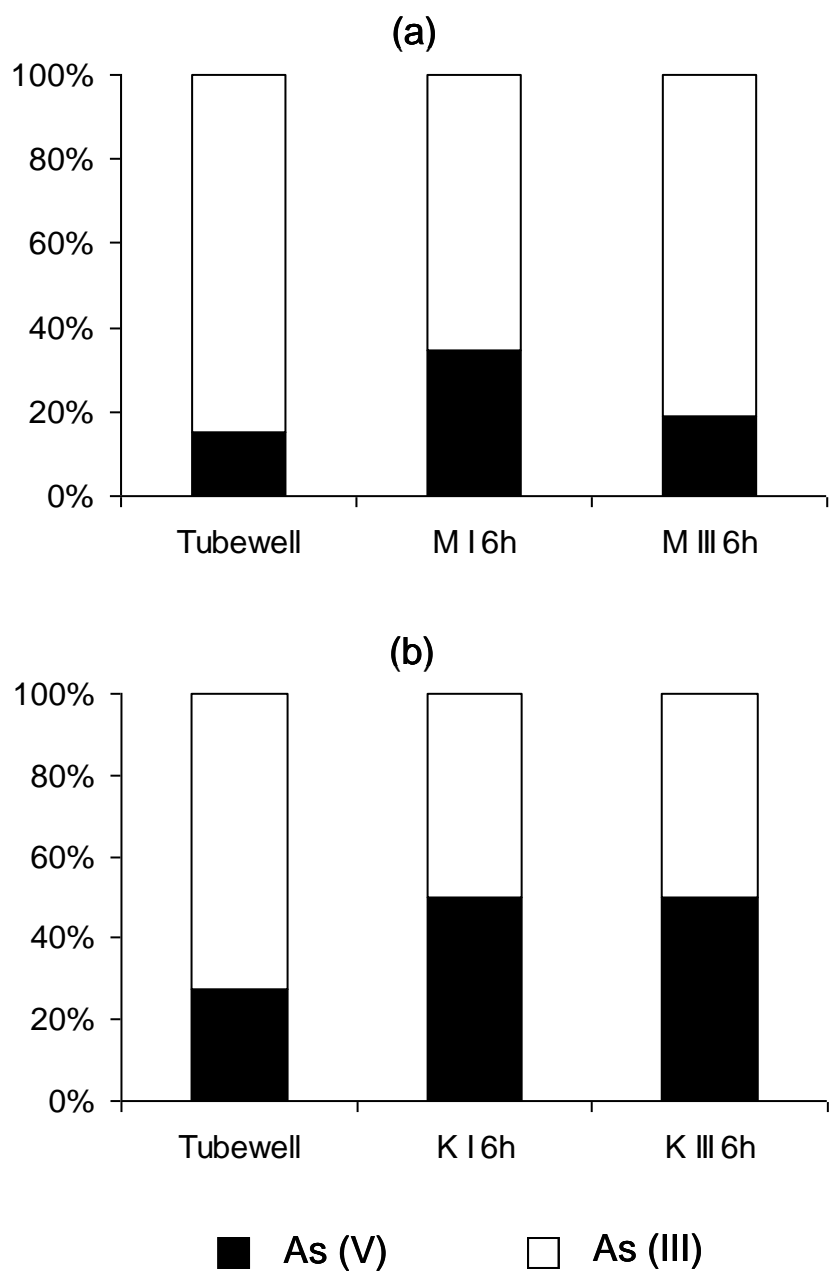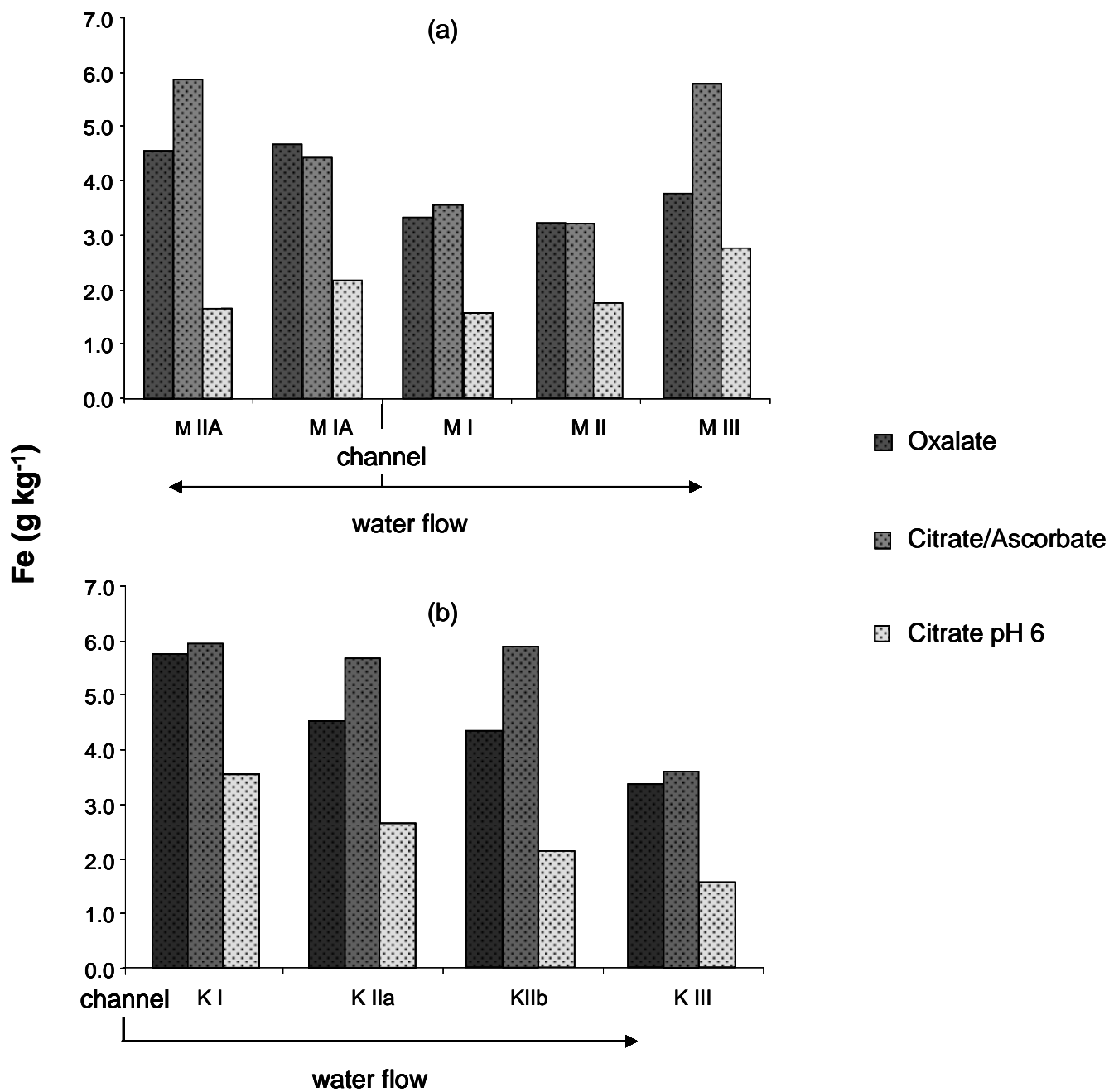21

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Figure 3. Percentage distribution of arsenate [As(V)] and arsenite [As(III)] in the water of (a)

Mahmoodpur and (b) Koila rice fields at the withdrawal from the tubewell, and in the first and third

plots six hours after the end of the water supply.

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10 **Fe (g kg^{-1})**

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22 Figure 4. Iron extracted with ammonium oxalate at pH 3, citrate-ascorbate at pH 6, and sodium

23 citrate at pH 6 from (a) Mahmoodpur, and (b) Koila topsoil samples (0-5 cm).

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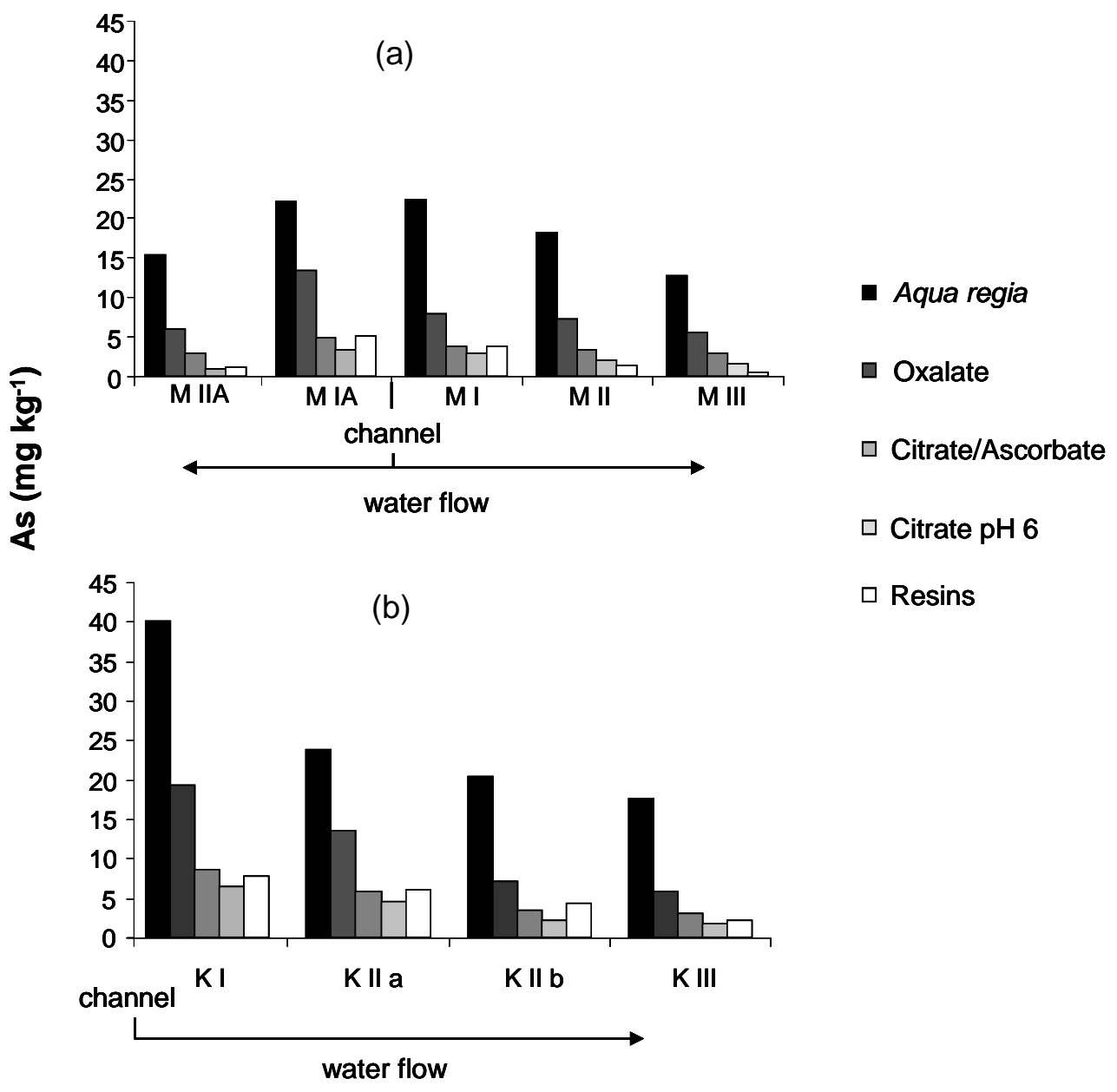16

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21 Figure 5. Arsenic extracted with *aqua regia*, dithionite-citrate-bicarbonate, ammonium oxalate at

22 pH 3, citrate-ascorbate at pH 6, sodium citrate at pH 6, and anion exchange resins from (a)

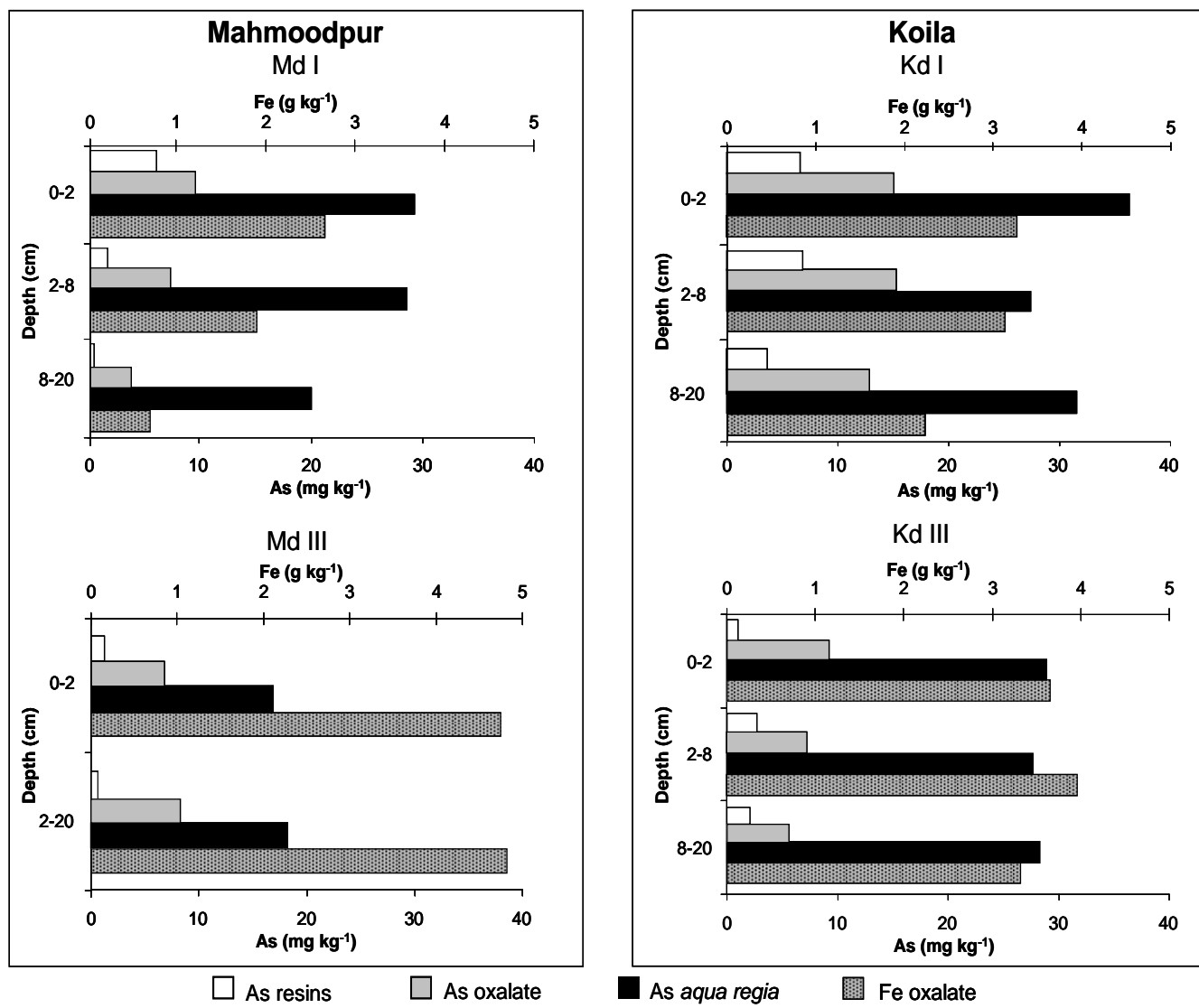23 Mahmoodpur, and (b) Koila topsoil samples (0-5 cm).

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Figure 6. Vertical distribution in the first and third plot in Mahmoodpur and Koila rice fields of Fe extracted with ammonium oxalate at pH 3, and of As extracted with *aqua regia,* ammonium oxalate at pH 3, and anion exchange resin.