Soil redox-pH stability of arsenic species and its influence on arsenic uptake by rice.

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Abstract

Arsenic absorption by rice (*Oryza sativa*, L.) in relation to As chemical form present in soil solution was examined. Rice plants were grown in soil suspensions equilibrated under selected conditions of redox and pH, affecting arsenic solubility and speciation. A decrease in pH led to higher dissolved arsenic concentrations. When the soil redox potential dropped below 0 mV, most of the arsenic was present as As(III). Under more oxidizing conditions both As(III) and As(V) are present. Chemical speciation of As in the watersoluble fraction affected its phytoavailability. Most indigenous arsenic taken up by the plants remained in the root. Plant arsenic availability increased with increasing arsenic concentration in solution (lower soil pH) and with increasing amounts of soluble As(III) (lower soil redox). We also studied the uptake of monomethyl arsenic acid (MMAA), a widely used defoliant and herbicide, as affected by soil redox-pH condition. Amended MMAA was approximately two times more phytoavailable than the indigenous inorganic As forms and increased with decreasing pH and redox.

Introduction

Arsenic (As) is not essential for plants and appears not to be involved in specific metabolic reactions when supplied at low concentrations (Liebig, 1966; Marin 1989). At higher concentrations, however, As has been reported to interfere with metabolic processes and to inhibit plant growth, sometimes leading to death (Baker et al., 1976; Marin et al., 1992; Reed and Sturgis, 1936; Schweizer, 1967).

Accumulation of As by plants depends on plant species (Liebig, 1966; Walsh and Keeney, 1975), the concentration of As present (National Academy of Sciences, 1977), and the presence of other ions (Khattak et al., 1991; Woolson et al., 1973). Interactions between arsenate and phosphate are frequently reported in the literature (Barrow, 1974; Jacobs and Keeney, 1970;

Wauchope, 1975). In general, increasing the amount of soil P reduces As accumulation by plants, and vice versa. In a recent paper (Marin et al., 1992) we reported As phytoavailability and phytotoxicity to rice to be also affected by As chemical form present. While application of arsenate [As(V)] and dimethyl arsenic acid [DMAA] did not affect plant growth, both arsenite [As(III)] and monomethyl arsenic acid [MMAA] were phytotoxic to rice. Availability of As to rice followed the trend: DMAA < As(V) < MMAA < As(III). These observations, however, were made during plant growing experiments in nutrient solutions amended with different As chemical forms.

In soils of the rice-producing areas elevated As concentrations are most commonly associated with monomethyl arsenic acid (MMAA), a herbicide widely used for postemergence weed con-

trol in cotton (Frans et al., 1985) as a direct spray. Monomethyl arsenic acid residues can cause severe damage to succeeding rotational crops, such as rice (Frans et al., 1985; Gilmour and Wells, 1980; Marin, 1989). In rice-producing areas of the southern United States, for example, As is considered the probable cause for straighthead, a physiological disease of flooded rice (Gilmour and Wells, 1980) that results in blank florets, and distorted palea and lemma (Johnston et al., 1959).

The present study was undertaken with the objective to investigate the effect of soil redox-pH condition on As speciation and plant As uptake. This was achieved by studying As uptake by rice plants growing in soil suspensions equilibrated under controlled redox-pH conditions. The effect of changing soil redox-pH conditions on the solubility and stability of As chemical forms in solution was determined and related to uptake and translocation of As in the plants. We also investigated the redox stability of monomethyl arsenic acid in soil suspensions and its bioavailability and phytotoxicity to rice.

Materials and methods

Soil

Crowley silt loam soil (Typic Albaqualf) was collected from a rice farm, with a history of straighthead disease, in Cameron Parish, LA (USA). The oxidized soil had a pH = 5.2, 1.2% organic matter, and a total As content of $3.2 \, \text{mg kg}^{-1}$ dry soil. The soil was air-dried, screened through a 6 mm hardware cloth, and well mixed.

Redox control system – plant microcosms

Five hundred gram soil (amended with 0.2% (w/w) ground dried rice straw) was added to 2 L deionized water and equilibrated in laboratory microcosms under controlled redox-pH conditions. The apparatus used (Fig. 1) is a modification of the redox-pH control system developed by Patrick et al. (1973). It consists of a dessicator, a plexiglass plate designed to support the rice seedlings, pH and platinum electrodes, a
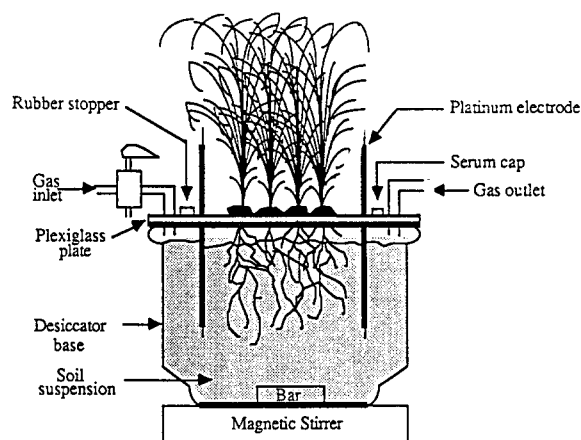

Fig. 1. Experimental setup used in the plant growing experiment under controlled redox and pH conditions.

calomel half cell, and a gas inlet and outlet. The soil is kept in suspension by a magnetic stirrer. The pH and platinum electrodes, the calomel half cell, and the gas inlet and outlet are fitted into holes on the plexiglass plate. The plate covers the desiccator and is sealed with silicone rubber sealant. The outer surfaces of both the desiccator and plexiglass plate are painted with silver paint to prevent exposure of the soil suspension to light.

In a first experiment, 12 equilibrations were performed and the following redox-pH combinations were used: redox −200, 0, +200, and +400 mV; pH 5.5, 6.5, and 7.5. In the redox control systems the soil redox potential is maintained at a preset value automatically (Patrick et al., 1973). Sodium hydroxide (2N) or HCl (2N) were added to the plant microcosms with a syringe and needle as required to adjust pH. Soil suspensions were equilibrated under the controlled redox-pH conditions for 3 days prior to the plant growing experiment.

In the second experiment, the soil was amended with 4 mg monomethylarsonic acid-As per kg dry soil prior to equilibration under specific soil redox-pH conditions. As was observed in a previous field (Marin, 1989) and hydrophonic (Marin, 1992) study, application of $4 \, \text{mg MMAA kg}^{-1}$ dry soil is expected to affect plant As uptake. Soil redox-pH conditions used were the same as in the first experiment. Plant As uptake was examined in relation to the

redox-pH stability and solubility of amended MMAA.

Plant material

Rice (*Oryza sativa*, L.) seeds from the cultivars Lemont and Mercury were germinated in sterilized sand. Lemont, an early maturing semidwarf, long grain cultivar, and Mercury, an early maturing, semidwarf, medium-grain cultivar are considered to be moderately tolerant (Bollich et al., 1985) and very susceptible to As toxicity (McKenzie et al., 1988), respectively. Eight days after germination uniform seedlings were selected and grown in a nutrient solution (Yoshida et al., 1976) for two weeks.

Plant growing experiment

Seedlings were transplanted in soil suspensions equilibrated under controlled redox-pH conditions. A single microcosm, representing one specific soil redox-pH condition, contained 6 seedlings from each cultivar (Fig. 1). Plants were placed through holes in the plexiglass plate. Some cotton wool was placed around the seedlings and held the seedlings in place. Every other day deionized water was added to the microcosms to replace the water lost through evapotranspiration. Plants were grown in the redox control-plant microcosms until they were 56 days old.

The plant growing experiment was conducted with the native soil and with the MMAA amended soil.

No symptoms of vegetative injury could be observed during the plant growing experiments.

Sampling procedures

During the growing period under controlled redox-pH conditions the concentration and chemical forms of As present in the soil suspensions were determined weekly. Thirty mL soil suspensions were withdrawn from the microcosm, centrifuged, and filtered through a 0.45 μm micropore filter; under an inert N_2 stream for the reduced treatments (Patrick and Henderson, 1981). Concentrations of As(III), As(V), MMAA, and DMAA in the supernatants

were determined using the As speciation technique described by Masscheleyn et al. (1991a).

At the end of the growing period plants were harvested. Eight seedlings (4 of each variety) were randomly selected for tissue analysis. Roots were carefully washed with tap water, rinsed with 0.1 N HCl solution followed by 3 rinses with deionized water. Roots and shoots were separated and dry matter yields determined after drying at 65°C for 48 hr. Dried samples were ground in a stainless-steel Wiley mill to pass a 20 mesh sieve. Plant tissue samples (1 and 0.5 g for shoot and root samples, respectively) were digested with 5 mL conc. HNO_3 (AR select, Mallinkrodt Inc.) for 4 hr at 130°C. Digested samples were filtered (Whatman #42) and diluted with deionized water to 50 mL. Arsenic, as well as nutrients (Ca, Mg, Ca, Na, K, Fe, Mn, Cu, and Zn) in the extracts were determined with a Jarrel Ash (Atom Comp 800 series) ICP. The detection limit of our ICP for As is 15 μg L^{-1}.

Statistical analyses were performed using the PROC CORR and PROC GLM procedures from SAS (SAS, 1987).

Results and discussion

Effect of soil redox-pH condition on arsenic speciation and solubility

In the experiment with the unamended soil, redox potential and pH greatly affected the speciation and solubility of indigenous As. Figure 2 shows the amount of watersoluble As chemical forms at four redox levels (−200, 0, +200, and +400 mV) in combination with three pH levels (5.5, 6.5, and 7.5). Results represent the average concentration of soluble As chemical forms, calculated from the weekly analyses of the soil suspensions, and represent the As concentration and chemical forms available for uptake by the rice plants during the growing period.

Watersoluble As concentrations were inversely related to redox and pH. At the lowest redox potential studied (−200 mV) 7.3, 2.2, and 1.4% of the total As in the soil (3.2 mg kg^{-1} dry soil) became watersoluble at a pH 5.5, 6.5, and 7.5, respectively. Irrespective of soil redox potential,
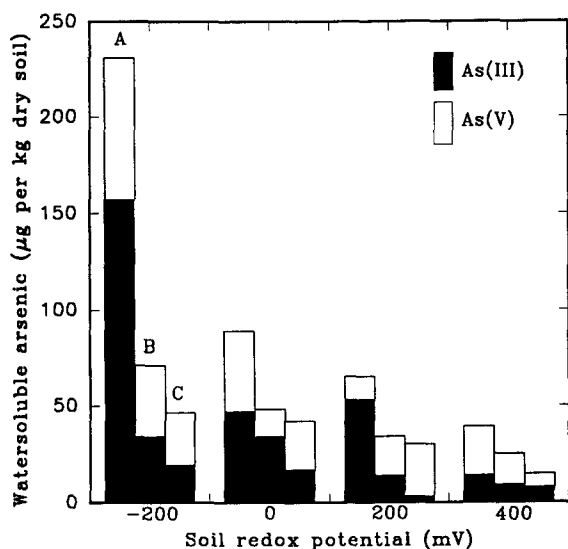
Fig. 2. Speciation and solubility of indigenous As as affected by redox condition for soil equilibrated at A) pH 5.5, B) pH 6.5, and C) pH 7.5.

most watersoluble As was found at pH 5.5. The effect of pH on As solubility was most pronounced at a soil redox condition of -200 mV. At redox potentials of $+400$ and $+200$ mV, As(V) was the major dissolved As species constituting from 51 to 90% of the total dissolved As. Except at pH 7.5, As(III) became the dominant As chemical form in solution upon reduction (0 and -200 mV) of the soil suspensions. Although thermodynamically unstable a considerable amount of As(V) remained in solution under reduced conditions. It is interesting to note that both the amount of watersoluble As(III) and As(V) increased with decreasing redox. For the experiment conducted at pH 7.5, the As(III)/As(V) concentration ratio increased with decreasing redox but As(V) remained the most important As species in solution at all times. No watersoluble organic arsenicals could be detected. Our data illustrate that a decrease in pH and/or a decrease in soil redox level will result in an increased As availability to plants.

According to Livesey and Huang (1981) soluble As concentrations are controlled by sorption/ desorption reactions rather than through precipitation/dissolution reactions. Convincing evidence for a species specific sorption behavior of As on soils and mineral phases has been pre-

sented (Pierce and Moore, 1982). Under the redox-pH conditions encountered in this study As(V) will be negatively charged (as $H_2AsO_4^-$ or $HAsO_4^{2-}$) while As(III) will be predominantly present as the uncharged H_3AsO_3 chemical form (Masscheleyn et al. 1991b). As the soil pH will increase, hydroxyl ions will replace As on the soil sorption sites and As will be released into solution. Furthermore, the increasing negative soil surface charge with increasing pH will facilitate desorption of As anions. Deuel and Swoboda (1972) reported an increase of total soluble As under reduced soil conditions and attributed this increase to the reduction of ferric arsenate compounds. More recently, Masscheleyn et al. (1991b) found the influence of redox on As solubility in soils to be governed by 1) reduction of As(V) to As(III) followed by desorption, and 2) the dissolution of Fe-oxyhydroxides and concurrent release of coprecipitated As(V). Results of our study are apparently in accordance with the latter findings. Watersoluble Fe concentrations were highly correlated ($p < 0.001$) with dissolved total As (r = 0.86), As(III) (r = 0.83), and As(V) (r = 0.62) concentrations suggesting the relation between the reduction of Fe-compounds and the solubility of As. Furthermore, an increase in dissolved total As was generally associated with an increase in the As(III)/As(V) concentration ratio (Fig. 2). For example, in the equilibrations at pH 7.5 the observed increase in dissolved As concentration was due to the reduction of As as the amount of reduced (watersoluble) Fe remained approximately the same for all redox levels studied.

When the soil was amended with MMAA (at a rate of 4 mg As kg^{-1} dry soil) soil physicochemical condition, as indicated by redox potential and pH, affected the speciation and solubility of both inorganic As and MMAA, the organic arsenical added (Fig. 3). Considering the addition of MMAA as main effect, the amount of watersoluble AS(III + V) increased significantly ($p < 0.05$) in the MMAA amended soil (Table 1) as compared to the unamended soil. This was associated with a significant increase in dissolved As(V). At pH 6.5 and 7.5, As(V) remained the dominant inorganic As species in solution even under strongly reducing (0, and -200 mV) conditions. In the MMAA amended soil watersoluble
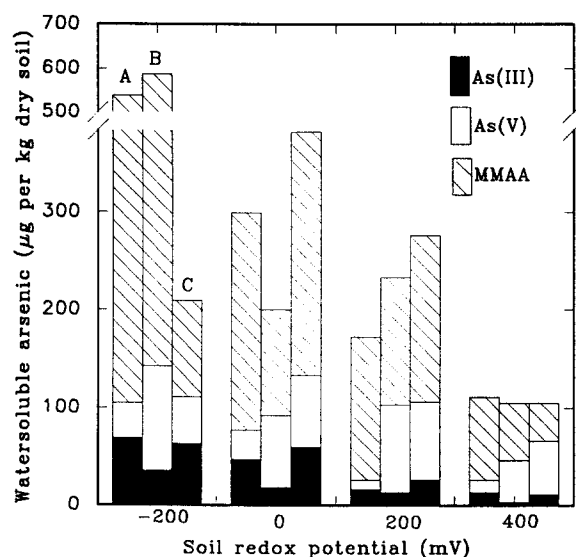
Fig. 3. Arsenic speciation and solubility in the MMAA amended soil suspensions as affected by redox condition for soil equilibrated at A) pH 5.5, B) pH 6.5, and C) pH 7.5.

Table 1. Effect of MMAA addition on soil arsenite and arsenate content

MMAA applied	As(III + V)	As(III)	As(V)
	(μg kg^{-1} dry soil)		
Yes	83.4a*	30.3a	53.1a
No	55.3b	31.4a	23.9b

* Means followed by the same letter do not differ at the 5% confidence level (Duncan's Multiple range test).

Fe concentrations were not significantly correlated with dissolved As(III + V), As(V), and MMAA. However, dissolved Fe concentrations were correlated ($p < 0.001$) with soluble As(III) ($r = 0.61$). Although other soil biogeochemical processes – such as sorption/desorption and/or microbial mediated oxidation/reduction reactions – may be involved, the observed increase in As(V) concentration may be due to demethylation of amended MMAA. The rupture of C-As bonds and production of As(V) from MMAA has previously been observed by Dickens and Hiltbold (1967), Von Endt et al. (1968), and Odanka et al. (1985a,b). Methylation of the amended MMAA and dimethyl arsenic acid (DMAA) formation was not observed in our experiments. Higher soil redox levels led to lower dissolved MMAA concentrations. The effect of pH on watersoluble MMAA concen-

trations was less clear. As for the inorganic As chemical forms (Livesey and Huang, 1981; Pierce and Moore, 1982) Fe-oxides have been implicated in the sorption of MMAA by soils (Holm et al., 1980). The observed responses of MMAA solubility to redox and pH are likely due to reduced sorption capacity of the soil caused by decreasing redox or increasing pH.

Some questions remain concerning the persistence of As(V) under reducing soil conditions (Figs. 2, 3). Although the ratio As(III)/As(V) generally increased with decreasing redox the observed As(III)/As(V) ratios do not agree with equilibrium thermodynamic considerations. Under the redox-pH conditions encountered in our experiments $H_2AsO_4^-$ and H_3AsO_3 are the thermodynamically stable As(V) and As(III) chemical forms, respectively (Masscheleyn et al. 1991b). The As(V) to As(III) reduction can thus be written as $H_2AsO_4^- + 3H^+ + 2e^- = H_3AsO_3 + 2H_2O$. If we assume thermodynamic equilibrium and an equilibrium constant $= 10^{-11}$ (Masscheleyn et al. 1991b), the As(III)/As(V) concentration ratio should follow the equation: $\log[As(III)/As(V)] = 22 - 2[pe + 3/2pH]$. Clearly, the observed As(III)/As(V) concentration ratios do not conform to this equation suggesting that chemical kinetics could play an important role in the conversion of As(V) to As(III). The presence of the rice plants in the soil suspensions could have been another important factor altering the As(III)/As(V) concentration ratio.

Recently, Marin et al. (1992) illustrated the importance of the chemical form of As in the uptake of the element from nutrient solutions by plants. It was shown that, in nutrient solutions, As(III) is the As chemical form most readily taken up by rice plants. Assuming the same is true in soil suspensions, the rice plants would selectively remove As(III) thereby altering the As(III)/As(V) concentration ratio's in the soil suspensions.

Arsenic uptake by rice as affected by soil redox-pH condition and MMAA application

As soil redox-pH conditions affected the specification and solubility of As in the soil one could expect soil redox-pH to also determine As

phytoavailability and phytotoxicity. We found soil physicochemical (redox-pH) condition and application of MMAA to affect plant growth and tissue As concentration. There were no significant differences in dry matter production and tissue As concentration due to cultivar effect. Therefore, cultivar could be used as subsample in the statistical analysis.

In the experiments with the native (un-amended) soil tissue As concentration increased with decreasing redox and pH (Table 2). Arsenic absorbed by the plants was accumulated in the roots. Shoot As was only detected at the lower redox levels. When the pH was 6.5 and 7.5 in the unamended soil (Table 2), plants did not take up any As at the highest soil redox level ($+400$ mV) studied. Under this soil redox-pH condition As solubility was lowest and the major part of soil As was present as As(V) (Fig. 2). Arsenic tissue concentrations were highest at pH 5.5. This in agreement with the higher As solubility in the soil at pH 5.5 (Fig. 2). Root As concentration were significantly ($p < 0.001$) correlated with As(III) ($r = 0.76$), and As(V) ($r = 0.76$) concentrations in solution. Total plant As uptake, calculated by multiplying tissue As concentrations with the dry weight of the corresponding plant part, was also affected by soil redox-pH

condition (Fig. 4A). Due to the low dry matter production at the 200 mV − 5.5 and 0 mV − 5.5 soil redox-pH conditions the total plant As uptake was low under these physicochemical soil conditions. Plant As uptake was not correlated with soluble As(III), nor with soluble As(V) concentrations. Plant As uptake from soil suspensions agreed with what we observed in a previous reported hydrophonic study (Marin et al. 1992). When plants were grown in nutrient solutions amended with As(III) the element was readily taken up and stored in the root. In the soil suspensions under reduced conditions, As(III) was the dominant chemical form present. A considerable amount of As(III) was taken up by the plants and the major part remained in the root (Table 2). Roots from plants grown in the reduced soil suspensions were coated with a brownish precipitate, indicating the formation of an iron plaque, due to the oxidizing activity of rice roots. Leaching roots in a 1 M oxalic acid solution removed the precipitate and chemical analysis of the obtained extracting solution revealed the presence of both Fe and As. Unfortunately, present analytical techniques do not allow for the determination of As chemical form present in the plant. Possibly, As(III) may have been immobilized due to oxidation to As(V),

Table 2. Tissue arsenic concentrations as affected by soil redox-pH condition

| MMAA added	Redox	Plant part	pH 5.5	pH 6.5	pH 7.5
			($mg\,kg^{-1}$ dry plant material)		
No	−200 mV	Root	107*	78.5	74.5
		Shoot	1.0	2.0	1.0
	0 mV	Root	59.5	37.5	17.5
		Shoot	1.5	N.D.**	0.5
	+200 mV	Root	49	8.5	6.5
		Shoot	1.0	N.D.	N.D.
	+400 mV	Root	35.5	N.D.	N.D.
		Shoot	N.D.	N.D.	N.D.
Yes	−200 mV	Root	277.5	176.5	168
		Shoot	28.5	11.5	6.0
	0 mV	Root	228	117	80
		Shoot	20.5	7.0	7.0
	+200 mV	Root	128	54.0	27.5
		Shoot	5.0	0.5	1.0
	+400 mV	Root	102.5	18.0	16.5
		Shoot	N.D.	0.25	N.D.

* Mean of n = 2.
** Not detectable.
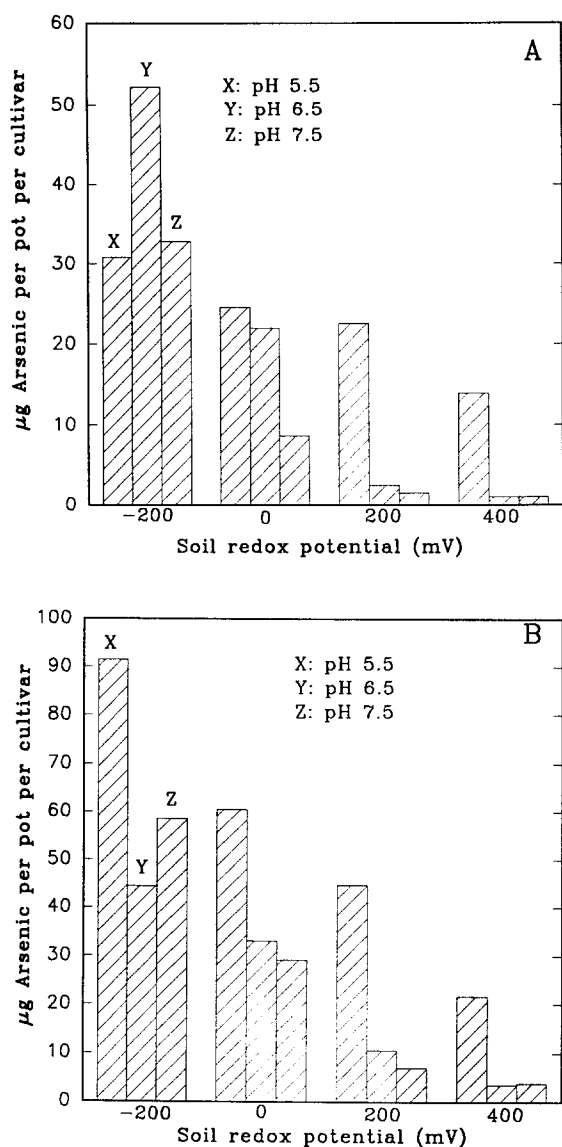
Fig. 4. Total plant As uptake as affected by soil redox-pH condition in A) the native soil, and B) the MMAA amended soil.

and subsequent sorption onto Fe-oxyhydroxides coating the roots, in the rhizosphere of the plant roots. This mechanism of detoxification was suggested by Otte (1991) to control As uptake in salt marsh plants and could have controlled As uptake by rice as well.

When As was added as MMAA at a rate of 4 mg As kg^{-1} dry soil, a significant $(p < 0.05)$ decrease in total dry matter production was observed reflecting the negative impact of MMAA on plant growth. Although application of MMAA resulted in lower dry matter production the total As uptake by the plants significantly increased (Table 3). On the average, the addition of MMAA resulted in approximately a two fold increase in total As uptake. When plants were grown in the MMAA amended soil suspensions the tissue As concentration ratio (shoot As concentration/root As concentration) and As uptake ratio (shoot As uptake/root As uptake) significantly increased. This suggests that when more As is taken up by the plant in the MMAA form, a large part of As is translocated to the above ground plant parts. However, most As remained stored in the root resulting in a As concentration ratio <1. This in agreement with the findings from our previous study (Marin et al. 1992) where plants were grown in MMAA-amended nutrient solutions. Monomethyl acid was shown to be the As chemical form most phytotoxic.

Addition of MMAA also affected Zn and Cu phytoavailability. In our experiments, application of MMAA caused a significant decrease in Zn tissue concentration, uptake, and translocation to the rice shoot. Due to the addition of 4 mg As (as MMAA) kg^{-1} dry soil the Zn concentration and uptake ratios decreased from 1.32 and 3.88 to 0.71 and 2.35, respectively.

Table 3. Effect of MMAA addition on plant dry weight and tissue As concentration

MMAA addition	Total dry weight (g plant^{-1})	As uptake			As conc. ratio	As uptake ratio
		Shoot	Root	Total		
		(μg pot^{-1})				
Yes	1.02b*	5.04a	29.1a	34.1a	0.04a	0.123a
No	1.60a	0.64b	16.9b	17.6b	0.01b	0.028b

* Means followed by the same letter do not differ at the 5% confidence level (Duncan's Multiple range test).

Solubility of Zn in the soil suspensions was not influenced by soil redox-pH condition. The observed antagonistic effect of As on Zn absorption may have been another factor related to the consistent negative effect of solution MMAA on plant growth. A similar antagonistic MMAA-Zn interaction was observed before in rice (Marin, 1989; Oh and Sedberry, 1974) and in peaches (Batjer and Benson, 1958; Thompson and Batjer, 1950). Besides Zn, addition of MMAA also influenced Cu solubility in the soil. Soil Cu concentrations significantly decreased due to MMAA. The reason for the decreased Cu solubility is still unclear. As a consequence of the effect of MMAA on Cu solubility several Cu plant uptake parameters were negatively correlated with As uptake and soil As solubility. For example, plant Cu and As uptake ($r = -0.67$; $p < 0.001$), plant Cu uptake and soluble inorganic As content ($r = -0.55$, $p < 0.01$), and root Cu and root As uptake ($r = -0.66$, $p < 0.001$) were all negatively correlated. As soil redox status did not affect soil Cu solubility, the observed decrease in Cu uptake with decreasing soil redox level could be attributed to the increased As absorption by the plants.

The effect of soil redox-pH condition on tissue As concentration and plant As uptake in the experiments with the MMAA amended soil suspensions are given in Table 2 and Figure 4b, respectively. Both plant As root and shoot concentrations were significantly ($p < 0.001$) correlated with the amount of As(III) ($r = 0.71$ and 0.83) and MMAA ($r = 0.59$ and 0.61) in solution. In contrast to the unamended soil, plant As concentrations were negatively correlated with the amount of As in solution present as As(V). Seedlings subjected to MMAA accumulated As in their tissues at all soil redox-pH conditions studied (Fig. 4B). The lower the pH and redox the higher the amount of As accumulated by the rice plants. A decrease in soil redox level from $+400$ to -200 mV caused approximately a 4, 13, and 15 fold increase in plant As uptake for soils equilibrated at pH 5.5, 6.5, and 7.5, respectively. Application of MMAA affected the As shoot/ root uptake ratio, as mentioned above. Except for the $+400$ mV treatments, part of the As taken up by the plants was translocated to the shoot.

In summary, soil redox potential and pH were shown to affect As speciation and solubility, thereby determining As phytoavailability and phytotoxicity to rice. The lower soil redox potential and pH the higher the amount of watersoluble As. Although As(III) became the major As species in solution under reduced conditions, some As remained present as As(V). Plant As tissue concentrations and uptake were highest under reduced soil conditions. Flooding a rice soil will lead to higher dissolved As concentrations and the presence of As(III) will enhance As uptake by the plants. In our plant growing experiments under controlled redox-pH conditions most As taken up by the rice plants remained in the roots. As was illustrated, soil residues of MMAA – a herbicide widely used for postemergence weed control in cotton as a direct spray – will be readily taken up by rice plants and can cause damage to the succeeding rotational rice crop. Although most MMAA-As will remain in the root, part is translocated to the rice shoots. In our experiment, addition of 4 mg MMAA-As kg^{-1} dry soil inhibited plant growth but resulted in significant higher plant As concentrations and uptake. Low soil redox conditions increased the solubility and phytoavailability of MMAA. Monomethyl arsonic acid also affected the absorption of Zn and Cu.

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