Biogas slurry application elevated arsenic accumulation in rice plant through increased arsenic release and methylation in paddy soil

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Abstract

Background Rice can accumulate arsenic (As) to relatively high concentrations due to the general flooding practices in rice cultivation, and organic matter in the soil strongly affected As bioavailability to rice plants. The influence of organic matter input on the As transformation in paddy soil and As uptake into rice plants is an area that is rarely investigated.

Methods Biogas slurry (BGS), a commonly used organic fertilizer, was applied to an As contaminated paddy soil, in order to investigate the influence of

organic matter on As transformation in the paddy soil and As accumulation in rice plants.

Results Application of BGS significantly increased the As accumulation in rice plants, especially for methylated As species. Results showed that the concentrations of dissolved organic carbon (DOC) and dissolved Fe(II) in the soil solution were significantly increased by the BGS addition into the paddy soil, and were significantly correlated to the As concentration in the soil solution ($P < 0.01$). The increase of soil pH and the decrease of the soil redox potential (Eh) were observed as well. These alteration of soil characteristics elevated the As release from soil particles to the soil solution under the addition of BGS. The increased concentrations of dimethylarsinic acid (DMAs(V)) and monomethylarsonic acid (MMAs(V)) in the soil solution, and the volatilized As of trimethylarsine (TMAs) from the paddy soil, suggested that As methylation and volatilization in the soil were also enhanced by BGS addition. The concentrations of methylated As species in rice husks and grains were increased by 105.8–105.9 % and 99.7–112.2 %, respectively.

Conclusion These results suggested that the use of organic fertilizer, such as BGS in As-contaminated paddy soil, can significantly alter the behavior of As in soil-rice system and enhance As accumulation in rice plants and should therefore be avoided.

Keywords Arsenic accumulation · Arsenic methylation · Biogas slurry · Dissolved organic matter · *Oryza sativa* L. (rice)

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Introduction

Large areas of paddy soil in the world are contaminated by arsenic (As) from anthropogenic point sources, including irrigation with As contaminated groundwater, use of arsenical pesticides, runoff from mine tailings, and the fertilization of poultry litter containing As-based feed additives, especially in Southeast Asia (Han et al. 2003; Oremland and Stolz 2003; Stroud et al. 2011). Rice is much more efficient in absorbing and accumulating As than other crops due to its usual flooding cultivation, which causes the As release from soil iron minerals to the soil solution under the anaerobic condition (Williams et al. 2007; Xu et al. 2008; Zhu et al. 2008). As a class one carcinogen, arsenic in the soil can present a significant risk to humans through the food chain after its high uptake into rice plants. It has been estimated that rice is the major dietary source of As for populations with rice as the staple food (Meharg and Rahman 2003; Mondal and Polya 2008; Zhu et al. 2008; Li et al. 2011).

Fertilizers, including organic fertilizer such as biogas slurry (BGS), are often supplied in paddy fields to increase the crop yield (Bharde et al. 2003; Holm-Nielsen et al. 2009). Many substances such as silica, phosphate and organic matter as fertilizers can influence As bioavailability and uptake into rice (Guo et al. 2005; Chen et al. 2008; Li et al. 2009). Previous studies have shown that the organic matters, especially in the form of dissolved organic matter in organic fertilizer, increased bioavailable As in sediments and soils by the competition with As for absorption sites and also the mediation of the soil redox condition (Redman et al. 2002; Mladenov et al. 2009; Sharma et al. 2011; Stroud et al. 2011). As a secondary product of bio-energy (biogas) production, BGS from animal waste or crop straw often contains high levels of organic matter, and is thought to be an inexpensive way to reduce environmental pollution by recycling animal waste and crop straw (Terhoeven-Urselmans et al. 2009). Little information is available about whether or to what extent the influence of BGS organic matter application has on the As release and speciation in the paddy fields, especially in relation to the As accumulation in rice.

Microorganisms are engines for biogeochemical cycles of many elements. The input of organic matter into soil has been reported to influence the microbial activity and community related to As transformation,

which facilitate the release and bio-methylation of As (Huang et al. 2012). Therefore the application of BGS containing high levels of organic matter, might influence the microbial and physico-chemical properties, thus the fate of As in the paddy soil, consequently altering the As uptake by rice plants. In this study, BGS was applied to the As contaminated paddy soil as an organic fertilizer, to investigate its impact on As transformation, speciation and bioavailability in the paddy soil, as well as its accumulation and speciation in rice plants.

Materials and methods

Pot experiment for rice harvesting

Soil for the pot experiment was collected from the plow layer (0–20 cm) of a paddy field near a mine at Chenzhou city (Hunan province, China). Total As concentration in the soil was determined to be 69.6 mg kg^{-1} . The soil was air dried, sieved to pass a 2-mm sieve and kept in the dark before use. The fertilizer, phosphorus as $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ at $0.15 \text{ g P}_2\text{O}_5 \text{ kg}^{-1}$, potassium as KCl at $0.2 \text{ g K}_2\text{O kg}^{-1}$, and nitrogen as $\text{CO}(\text{NH}_2)_2$ at 0.2 gN kg^{-1} (as solutions) was added to the soil before the rice planting. BGS was collected from a biogas plant of a green products factory in Beijing, China, fed with chicken dung. Properties of the BGS and soil were given in Table 1.

Seeds of rice (*Oryza sativa* L.) cv. Jiahua-1 were disinfected in 30 % H_2O_2 for 15 min, washed thoroughly with deionized water, and germinated in moist perlite. At three-leaf stage, uniform seedlings were selected and transplanted to PVC pots (1.2 kg soil per pot) with one seedling per pot. The pot was maintained at 3 cm of water above the soil surface for the rice to grow. Three treatments were set: control (no BGS addition), 50 ml kg^{-1} BGS input per pot, and $100 \text{ ml BGS kg}^{-1}$ soil input per pot. BGS was added into the soil at the time of the flowering (~100 days after rice planting) because inorganic As and DMAs (V) was mainly transported into the caryopsis of rice during flowering and grain filling (Zheng et al. 2011). Pots were placed in an environmentally controlled chamber house set with a 10/14-h light/dark photoperiod, and a light density of $300 \mu\text{mol m}^{-2} \text{ s}^{-1}$ in the daytime. The temperature was kept at 25°C during the daytime and 16°C during the nighttime with a relative humidity of 70 %. Rice plants were harvested until the

Table 1 Properties of the soil and biogas slurry

Properties of soil			Properties of biogas slurry		
Total N	g kg ⁻¹	2.98±0.12	Total N	g L ⁻¹	1.91±0.18
Total P	g kg ⁻¹	0.67±0.02	Total P	g L ⁻¹	1.81±0.03
Total K	g kg ⁻¹	8.7±0.4	Total K	g L ⁻¹	1.33±0.02
Total As	mg kg ⁻¹	69.6±2.0	Total Fe	mg L ⁻¹	222.8±8.7
Total Fe	g kg ⁻¹	30.7±1.2	Total Mn	mg L ⁻¹	50.8±1.2
Total Mn	g kg ⁻¹	0.60±0.03	pH		7.51±0.01
pH		6.77±0.01	Solids content	%	1.57±0.01
Organic Carbon	%	4.52±0.21	DOC	g L ⁻¹	1.39±0.01
			Total As	μg L ⁻¹	40.2±1.9
			As(III)	μg L ⁻¹	2.44±0.12
			As(V)	μg L ⁻¹	4.27±0.08
			DMAs(V)	μg L ⁻¹	25.89±0.13
			MMAs(V)	μg L ⁻¹	2.84±0.05

time that the rice grains were mature (~150 days after the transplanting). Rice plants were then separated into root, rice straw, husk and grain. Iron plaque on the root surface was extracted by sodium dithionite-citrate-bicarbonate (DCB) (Liu et al. 2004). The grain, husk, straw and the DCB extracted root were ice dried, grinded to powder and stored in -80 °C.

For the determination of As species, samples of grain and husk (0.2 g) were weighed into 50 ml tubes, with addition of 10 ml 1 % HNO₃, kept for one night, and then digested using microwave digestion system (MARS, CEM Microwave Technology Ltd, USA) as described before (Meng et al. 2011). The temperature was gently raised, first to 55 °C and then to 75 °C, holding for 10 min. Finally the digest was taken up to 95 °C for 30 min before cooling. The extracts were filtered through nylon filter (0.45 μm×13 mm, Membrana, Germany) and kept in the refrigerator (4 °C) until analysis. To determinate the total As concentrations in shoots, DCB extracted roots, husks and grains, frozen-dried milled subsamples (0.1–0.2 g) were weighed into 50 ml digestion tubes, followed by 2.5 ml of nitric acid. The mixtures were stood overnight at room temperature, and digested by microwave digestion system (Meng et al. 2011).

Pot experiment for soil solution sampling and volatile As trapping

Sixteen pots of rice were cultured under the same condition as described above. At the tillering stage (about 60 days after transplantation), randomly four

pots without rice plant and four pots with rice plant were added with 100 ml BGS kg⁻¹ soil (+BGS–Rice and +BGS+Rice). The remaining 8 pots without or with rice plants were added with 100 ml kg⁻¹ distilled water (–BGS–Rice and –BGS+Rice). A rhizo-sampler (Rhizon Soil Moisture Samplers, Rhizosphere Research Products, The Netherlands) with a nylon filter (0.45 μm×13 mm, Millipore, USA) was embedded into the soil in all the 16 pots near the roots at the depth of about 8 cm, with a syringe connected for in situ extraction of soil pore-water. To inhibit the growth of algae in top water, the top of the pots were covered with tinfoil for omitting the light. Several small holes were made in the tinfoil to allow the growth of the rice plants and for As volatilization. The soil solutions were collected every 4 days after the addition of BGS, filtrated with 0.45 μm filter, maintained 1 % HNO₃ and kept at 4 °C for determination of dissolved iron, As speciation, and total As concentration. Redox potential (Eh) of the soil was measured before the soil solution collection by platinum electrodes, using the Ag/AgCl electrodes as references.

Cylindrical chambers made of transparent plexiglass were used to cover the pots and plants to make sure the volatilized As all pass through the trapping tubes (containing silica gel pre-impregnated by 1 % AgNO₃), as described in previous reports (Mestrot et al. 2009; Meng et al. 2011). After 32 days of the BGS addition, silica gel in the tubes was extracted with 5 ml 1 % HNO₃ using microwave digestion system (Mars II, CEM, USA), and then kept at 4 °C until analysis (Huang et al. 2012).

Analysis of iron, organic carbon, total As and its speciation

The concentration of total dissolved Fe and Fe(II) in the soil solution were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 2000 DV, Perkin Elmer, USA) and spectrophotometer respectively, according to the reported method (Wang et al. 2009). The concentration of dissolved organic carbon (DOC) in the soil solution was determined using TOC (Liquid TOC II, Elementar, Germany).

Arsenic species (As(III), As(V), DMAs(V), MMAs(V)) in the soil solution and digestion solution of the plant tissues were separated by an anion-exchange column (PRP X-100, Hamilton, Switzerland). The mobile phase was 10 mM $(\text{NH}_4)_2\text{HPO}_4$ and 10 mM NH_4NO_3 (pH 6.2). Total concentration of As and As speciation were determined using ICP-MS (Agilent 7500, Agilent Technology, USA) and HPLC-ICP-MS (Agilent 1200 series; Agilent 7500, Agilent Technology, USA) respectively, as described in the literature (Huang et al. 2012).

Statistic analysis

Statistical analyses were performed using SPSS software (Version 13.0, SPSS Inc, USA). One-way ANOVA was used to measure the significant differences between treatments. $P < 0.05$ was judged to be statistically significant.

Results

Arsenic concentration and its speciation in rice plants

Total As concentration in different tissues of rice plants followed the order of root >> straw > husk > grain, in consistence with previous reports (Williams et al. 2009). Arsenic concentrations in plant tissues were increased by the addition of BGS into soil (Fig. 1a-d), especially in the treatment with 100 ml kg^{-1} addition. The addition of BGS (100 ml kg^{-1} soil) increased the As concentration by 40.7 %, 22.1 %, 16.8 % and 35.7 % in root, rice straw, husk, and grain than that in the treatment without BGS addition, respectively, although the

Fig. 1 Arsenic concentrations in roots **a**, straw **b** husk **c** and grain **d** of rice plants and As speciation in husk **e** and grain **f**. Data are means $\pm$ SE ($n = 4$). Different letters mean significant differences between three treatments on As concentrations in roots, straw, husk and grain, and on the concentration of As speciation of As(III), As(V), DMAs(V), MMAs(V) in husk and grain, respectively

increases in plant biomass and grain yield were also observed by the application of BGS (Table S1). Four As species, i.e. As(III), As(V), DMAs(V) and MMAs(V) were detected in rice grains and husks, and the predominant species were As(III) and DMAs(V) (Fig. 1e, f), similar to previous reports (Sun et al. 2008). The concentrations of the methylated As species (DMAs(V)+MMAs(V)) in grains and husks were significantly increased in the treatments with BGS addition (Fig. 1e, f). The percentage of methylated As increased as well from 30.4 % to 48.0 % in the grains and from 31.7 % to 41.2 % in the husks in the presence of 100 ml BGS kg⁻¹ soil.

Redox potential, pH, dissolved iron, and dissolved organic carbon in soil solution

The second experiment was conducted to investigate the possible mechanism for the enhanced As

uptake in rice plants under the BGS addition. The BGS addition resulted in an increase of 0.16 and 0.11 in soil pH in treatments with or without rice plants respectively (Fig. 2a). Soil redox potential (Eh) in all pots, decreased in the first 12 days and then remained at a relatively constant level (Fig. 2b). The application of BGS to the paddy soil decreased the Eh regardless of the presence of rice plants or not, and the presence of rice plants increased the soil Eh in both BGS and non-BGS treatments.

After the addition of BGS, concentrations of dissolved iron in soil solution were firstly increased (0–8 days) and then decreased (8–32 days) (Fig. 2c), whereas it was higher in BGS addition treatments than non-BGS addition treatments regardless of rice growth. The dissolved iron in the soil solution was mainly Fe(II), accounting for 89.5–96.1 % of the total Fe in soil solution (Fig. S1). The addition of BGS

Fig. 2 pH **a**, Eh **b** of the soil, dissolved ferrous iron **c**, total dissolved organic carbon (DOC) **d** in the soil solution after BGS addition. BGS, biogas slurry; -BGS-Rice, no BGS amendment and no rice growth; +BGS-Rice, with BGS amendment and

rice growth; -BGS+Rice, no BGS amendment and with rice growth; +BGS+Rice, with BGS amendment and with rice growth. Data are means $\pm$ SE ($n=4$). Different letters means significant differences between the four treatments

elevated the concentrations of DOC in soil solution, perhaps due to the high level of DOC in BGS. Levels of DOC in the soil solution were also much higher in non-rice grown treatments than that in the rice grown treatments, regardless of the BGS addition or not (Fig. 2d).

Total As concentration and As speciation in soil solution

In the soil solution, total As concentrations were much higher in the treatments with BGS addition than the non-BGS addition treatments in both the rice grown

Fig. 3 Total As concentrations **a** and its relationship with ferrous iron (Fe(II)) **b** and dissolved organic matter (DOC) **c**, As speciation (As(III) **d**; As(V) **e**; DMAs(V)+ MMAs(V) **f**) in the soil solution of the different treatments after addition of BGS. BGS, biogas slurry; -BGS-Rice, no BGS amendment

and no rice growth; +BGS-Rice, with BGS amendment and no rice growth; -BGS+Rice, no BGS amendment and with rice growth; +BGS+Rice, with BGS amendment and with rice growth. Data are means $\pm$ SE ($n = 4$)

and non-rice grown treatments. BGS addition not only increased the As concentrations in the soil solution much faster in the beginning (0–8 days), but also much higher during the experiment (0–32 days) (Fig. 3a). The presence of rice plants decreased the As concentrations in soil solution, compared to their control (without rice), respectively, regardless of BGS treatment. Linear regression analysis showed that As concentration was significantly positively correlated to the concentration of the dissolved Fe ($R^2=0.767$, $P<0.001$) (Fig. 3b) and the concentration of DOC ($R^2=0.406$, $P<0.001$) (Fig. 3c) in soil solution. The addition of BGS also influenced As speciation in the soil solution (Fig. 3d–f). The determined As species in soil solution were As(III), As(V), DMAs(V) and small amounts of MMAs(V), of which, the concentrations of As(III) and methylated As species (DMAs(V), MMAs(V)) were much higher in the treatments with BGS addition than that in their respective control (Fig. 3d, f). The percentages of methylated As were higher in BGS addition than that in non-BGS addition treatment, regardless of whether rice was grown in the pot or not (Fig. S2).

Arsenic volatilization

Volatilized As from the pots was trapped after the addition of BGS. The amount of As volatilized from the four treatments was in the order of: +BGS–Rice>+BGS+Rice>–BGS–Rice>–BGS+Rice (Fig. 4), with the speciation being predominant by TMAs (Fig. S3). Addition of BGS into the soil significantly increased As volatilization from the soil as compared to the control, by 178.0 % and 216.7 % in the presence and absence of rice, respectively. The growth of rice plant decreased the As volatilization from the soil compared to the non-rice growth treatments respectively, though there was no statistical significance between the treatments without BGS addition.

Discussion

Biogas slurry application to the As-contaminated paddy soil increased As release from soil particles to soil solution, i.e. elevated As bioavailability in paddy soil, thus increased As uptake into rice plants. The significantly positive relationship of dissolved As with DOC in soil solution indicated the potential relationship of

Fig. 4 Amounts of volatilized As from the pots of different treatments. BGS, biogas slurry; –BGS–Rice, no BGS amendment and no rice growth; +BGS–Rice, with BGS amendment and no rice growth; –BGS+Rice, no BGS amendment and with rice growth; +BGS+Rice, with BGS amendment and with rice growth. Data are means $\pm$ SE ($n=4$). Different letters means significant differences between the four treatments

the dissolved organic matter with As release (Fig. 3c). Both As(V) and As(III) are mainly sequestered by iron minerals (Macur et al. 2004; Islam et al. 2005), and the adsorption and desorption of As from the minerals determines the mobility of As in the soil (Smedley and Kinniburgh 2002). Dissolved organic matter could compete with As for adsorption sites at mineral surface, decrease As(V) and As(III) adsorption and enhanced As release to the soil solution in the paddy soil (Liu et al. 2011; Williams et al. 2011). Organic matters (OM) and OM-Fe complexes bind As on the minerals, which also promote desorption of arsenic from solid phases by altering soil/solution equilibrium, while simultaneously impacting on the bioavailability (Liu et al. 2011; Sharma et al. 2011). Recent studies also gave the direct evidence for the complex of As with humic substance (As-SH) in the natural organic matter enriched peat and in pure solution system (Langner et al. 2011; Mikutta and Kretzschmar 2011). Arsenic can also dissolve from OM-As complexes, providing liable pool for As uptake into rice plants (Liu et al. 2011).

The input of BGS markedly increased Fe(II) concentrations in soil solution (Fig. 1c). It was reasonable to suggest that the organic matter in the BGS, such as amino acid, humic acid (Kurchania and Panwar 2011), enhanced Fe reduction and thus As release. Some microbes could couple the oxidation of fermentation products to the reduction of ferric iron (Li et al. 2011). So the organic matter input will result to an increase of the iron-reducing

organisms which mineralize organic matter with ferric iron as the sole electron acceptor. Poorly crystalline Fe (III) hydroxides thereby were reduced to Fe(II) under the anaerobic condition by these microbes, and potentially lost some As adsorption sites, resulting in the release of As into the solution (Masscheleyn et al. 1991; Weber et al. 2009; Xu et al. 2008), especially when the organic matter was abundant.

The adsorption and desorption of As on soil minerals is also closely related to soil pH and the redox potential (Marin et al. 1993; Masscheleyn et al. 1991). The increase in pH and the decrease of Eh in the paddy soil by BGS application were also causes for the enhanced bioavailability of As. Ghosh et al. (2006) showed that 3–4 times more soluble As were leached by an increase in one unit of pH in the soil. The pH of the BGS is usually alkaline (Table 1) due to the microbial degradation of volatile fatty acid (VFA) to CH₄ and CO₂ (Sommer and Husted 1995). Herein BGS addition into the paddy soil increased the soil pH by 0.11–0.16 (Fig. 1a), and may enhance the As desorption from the minerals. Also, the decreased soil Eh under anaerobic condition contributed to the much higher As release from the soil particles under the addition of BGS (Ascar et al. 2008).

Arsenic species show quite different abilities in toxicity to plant, adsorption and immobilization in soil, translocation and accumulation in rice. The addition of BGS enhanced the As methylation and volatilization in the paddy soil. It has been previously proved that the redox condition of BGS was the proper condition for As methylation by anaerobic microbes (McBride and Wolfe 1971), and this was also supported by the much higher methylated As concentration (accounted for 81.1 % of the total As) in the BGS used in this study (Table 1). The conversion of inorganic As to MMAs(V) and DMAs(V) by microbes in soils at high moisture contents that presumably correspond to anaerobic or low oxygen conditions (Ascar et al. 2008). Mestrot et al. (2011) observed a positive relationship between As volatilization and total soluble As concentration, especially for methylated As and DOC concentrations in the soil solution. More importantly, the As methylation and volatilization was influenced by the activity of relative microbes related to As transformation, altered by the input of organic matters into the soil (Huang et al. 2012). It was most likely that the methylated As species in rice plants was originated from the rhizosphere under the active of

relative methylating microbes in the soil (Arao et al. 2011; Lomax et al. 2011), so the methylated As species in the soil solution was absorbed into rice plants, especially in the BGS addition treatments. The extent of the increase of methylated As was much higher than the inorganic As in the rice grain and husk, due to the fact that methylated As were more liable translocating from roots and shoots to the grains (Carey et al. 2011). Though the MMAs(V) and DMAs(V) are less toxic than inorganic As species, it is newly suggested that the pentavalent methylated As can be reduced to the high toxic trivalent methylated As species in the digestion system due to the activities of intestinal microbes and potentially pose a risk to human health (Sun et al. 2012).

In conclusion, this study emphasized the enhancement of As methylation and bioavailability in the paddy soil under the addition of organic fertilizer. The relationship between As and organic matters warrants greater consideration in the controlling of As uptake into rice. The input of organic matter, especially easily degradable organic matter into the paddy soil resulted to reducing conditions, which will facilitate the As mobilization to the soil solution. Given that As accumulation in rice was increased by BGS addition and there were large areas of As contaminated paddy soil, the use of organic fertilizers in the As contaminated soil would raise human health risks and is well worth careful considerations.

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