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On the distribution and speciation of arsenic in the soil-plant-system of a rice field in West-Bengal, India: A μ-synchrotron techniques based case study

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A B S T R A C T

Worldwide, West-Bengal is one of the areas most affected by elevated levels of arsenic in groundwater (50–3000 μg/l). This groundwater does not only endanger humans owing to its use as drinking water. More and above that, irrigation of rice paddies consumes huge quantities of arsenic contaminated groundwater. Consequently, arsenic accumulates in soil and endangers the nutrition chain via arsenic uptake by plants. Rice is one of the staple foods in this region. Lately, there is a considerable intensification of research on the fate of arsenic in affected agricultural systems with most of them resorting to bulk analytical methods. However, so far, knowledge on the μ-scale distribution of arsenic in soil and plants in such agricultural systems is rather limited.

This case study combined μ-synchrotron studies on soil, rice root and rice grain from a rice paddy irrigated with groundwater containing about 519 μg/L As. The investigation of a soil aggregate has shown that As is mainly associated with Fe and is not equally distributed over the whole aggregate but occurs in local enrichments of few tens μm in size.

In soil, As was mainly associated with Fe-(oxy)hydroxides. Rice root coatings consisted of a similar assemblage of arsenic bearing minerals. Furthermore the incorporation of soil matter in the coating could be shown. On μm-scale, As concentrations in rice root coatings showed an inhomogeneous, patchy distribution (100–2400 mg/kg; median 500 mg/kg) and correlated with Fe concentrations. Some small amounts of arsenic could also be detected in the interior of the root (3–60 mg/kg; median 21 mg/kg). In the rice grain, trace elements such as Zn and Cu were mainly enriched along the grain coating, while As in contrast showed the highest concentrations in the germ and some hot spots in the coating (up to 13 mg/kg). Thus, peeling of rice grain would remove some, but not all of the arsenic.

1. Introduction

The Bengal Delta Plain (BDP) is one of the largest areas worldwide severely affected by high As concentrations in groundwater. Millions of people in West Bengal, India, and in Bangladesh are at risk of poisoning due to consumption of water exceeding the threshold value of 10 μg/L As, as recommended by the WHO (WHO, 2003; Kinniburgh and Smedley, 2001; Smedley, 2003) by 1–2 orders of magnitude. Although the uptake of As with drinking water is one of the major and most obvious pathways (Kinniburgh and Smedley, 2001), additional sources, such as rice consumption, have come into consideration recently.

In West Bengal, more than 90% of the pumped groundwater is used for irrigation, especially of paddy fields accounting for 91% of the cultivated area (Sanyal and Nasar, 2002). With around 92% of the food production, rice is the staple food in the region (Chandrasekharam, 2005). During dry season each harvest requires between 1144 and 1775 mm of irrigation water (Gupta et al., 2002). Hence, there is a potential risk of As accumulation in soil and subsequent uptake by rice plants increasing the health hazard for people living in that area (Correll et al., 2006; Huq et al., 2006; Kile et al., 2007).

Therefore, in the last years, several studies dealt with the accumulation of As in irrigated soils as well as in crops (Abedin

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et al., 2002a,b; Fitz and Wenzel, 2006; Dittmar et al., 2007; Stüben et al., 2007; Neidhard et al., 2012, Norra et al., 2012). However, relatively little is known about the specific processes and predominant mineral phases involved in fixation/adsorption and mobilisation of As in the soil – plant system of rice paddies (McGeehan et al., 1998; Takahashi et al., 2004; Norra et al., 2005; Frommer et al., 2011).

Generally, As in soils can be fixed on surfaces of Fe-, Al-, Mn-(oxy)hydroxides, clay minerals and organic matter (Alloway, 1999; McLaren et al., 2006) as well as on carbonates (Goldberg and Johnston, 2001) and sulphides (Moore et al., 1988). Furthermore, arsenate can act as a mineral forming oxy-anion-complex in Fe-deficient environments (Drahota and Filippi, 2009), but in an environment with excess Fe such compounds play only a subdominant role in soils relative to Fe-(oxy)hydroxides (Chenga et al., 2009; Drahota et al., 2012; Yamaguchi et al., 2011; Smedley and Kinniburgh, 2002). However, the investigation of specific As-bearing minerals in soils irrigated with As- rich water is still in progress, as is also the transfer of As from soil into the root and from root to fruits. Within this system, some plants, such as rice, can develop a coating at the root surface consisting of Fe-(oxy)hydroxides, which precipitate due to the diffusion of O_2 (via aerenchym) from shoots towards the roots, where O_2 passes the root epidermis and enters the plant (Fitz and Wenzel, 2006; Flessa and Fischer, 1992). In the presence of Fe^{2+} as it is common in the reducing environment of irrigated rice fields, the O_2 released from roots oxidises Fe^{2+} leading to the precipitation of Fe(III)-oxyhydroxide plaques (Chen et al., 1980; Crowder et al., 1987; Bigham et al., 2002).

In weakly oxidising to reducing soil water, As can form tri- or penta-valent hydroxo-complexes, while the released O_2 from roots can oxidise As(III) to As(V). Generally it was stated that As(III) is more soluble as As(V) (Yan-Chu, 1994; Bhumbla and Keefer, 1994). The mobility of As(V) and As(III) species adsorbed on Fe-oxides depends on the pH of the environment. Near neutral pH, both arsenate and arsenite are adsorbed with the same efficiency on surfaces of Fe-oxy-hydroxides and Fe-oxides. In alkaline environments arsenite adsorption is more efficient, while under acidic conditions the sorption of arsenate is favoured (Morin and Calas, 2006).

Studies on root coatings of other wetland plants (e.g., *Phalaris arundinacea* and *Typha latifolia)* showed a high potential of Fe-mineral-coatings for sequestering As from aqueous solutions (Otte et al., 1995; Hansel et al., 2002; Keon-Blute et al., 2004). Rice root coatings show elevated As concentrations in cases of irrigation by As contaminated water (Liu et al., 2006; Stüben et al., 2007; Kramar et al., 2007; Vögelin et al., 2007; Frommer et al., 2011). Nevertheless, the specific pathway of As from soil into rice, the involved predominant As bearing mineral phases and the composition of rice root coatings, is not fully understood yet.

In this study, we investigated the As distribution and the As bearing mineral phases in associated soil and rice of a temporarily submerged paddy soil of West-Bengal, India. The same field was already investigated by Norra et al. (2005) mainly using bulk analytical methods. In the present study we combined μ-synchrotron X-ray fluorescence (μ-XRF), μ-synchrotron X-ray absorption near edge structure spectroscopy (μ-XANES) and μ-synchrotron X-ray diffractometry (μ-XRD) to shed light with a micrometric resolution on the chemical and mineralogical speciation of As in a nearly undisturbed soil matrix and the different organs/tissues (roots, seed) of a rice plant growing on it. Though, due to the restricted number of samples, the results cannot be generalized, they provide important basic information on the abundance and distribution of As species in similar soil-plant systems.

2. Materials and methods

2.1. Area of investigation

Sampling took place in two rice paddy fields in Block Kaliachak I, Malda District, West Bengal, India (Fig. 1), as reported by Norra et al. (2005). Kaliachak is located between the Ghanges and Kalindri rivers. Malda is one of 9 districts in West Bengal, which faces severe problems due to high As concentrations in groundwater.

The paddy field in Kaliachak Block was irrigated with water containing 519 μg/L As and 4620 μg/L Fe (Norra et al., 2005). The soil type in the paddy fields investigated was a anthraquic anthrosol developed from fluvisols deposited by Ganges Brahmaputrar.

2.2. Sample collection and preparation

Soil and plant samples were collected at a rice paddy field in Kaliachak, West Bengal, India, as was reported by Norra et al. (2005). For soil sampling a 110 cm deep pit was excavated. Soil samples of 5 cm thick layers were taken up to 30 cm depth. Below 30 cm, soil samples were taken from 10 cm thick layers. Soil samples were air dried and transported in sealed plastic bags before they were oven-dried at 45 °C in the laboratory. Samples for speciation analysis were only air dried.

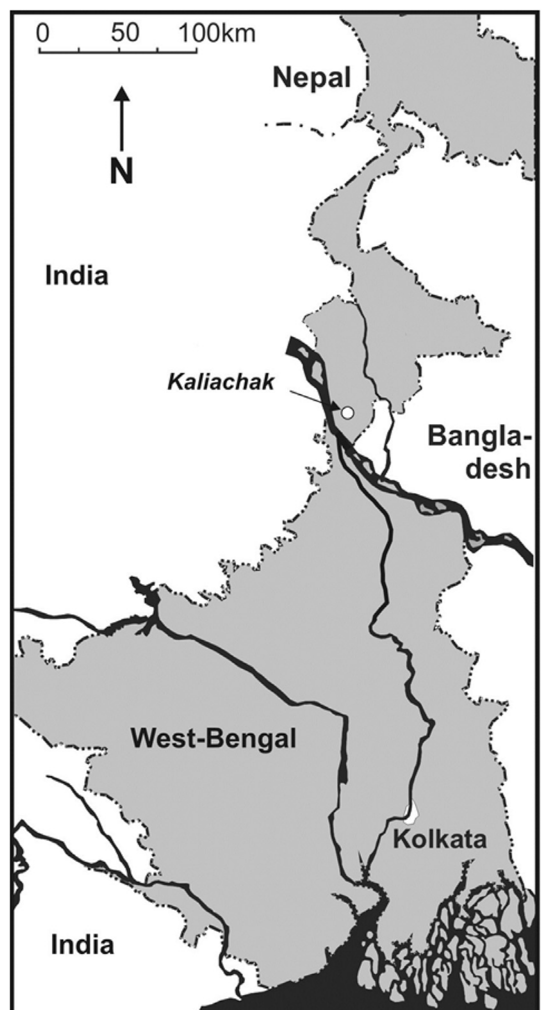

Fig. 1. Map of West-Bengal, India, showing the location of the area of investigation, Kaliachak.