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Arsenic accumulation in the roots of *Helianthus annuus* and *Zea mays* by irrigation with arsenic-rich groundwater: Insights from synchrotron X-ray fluorescence imaging

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ABSTRACT

The aim of this study was to investigate the accumulation of arsenic (As) in and on roots of *Zea mays* (maize) and *Helianthus annuus* (sunflower) by means of synchrotron-based micro-focused X-ray fluorescence imaging (μ-XRF). Plant and soil samples were collected from two field sites in the Hetao Plain (Inner Mongolia, China) which have been regularly irrigated with As-rich groundwater. Detailed μ-XRF element distribution maps were generated at the Fluo-beamline of the Anka synchrotron facility (Karlsruhe Institute of Technology) to assess the spatial distribution of As in thin sections of plant roots and soil particles. The results showed that average As concentrations in the roots (14.5–27.4 mg kg^{-1}) covered a similar range as in the surrounding soil, but local maximum root As concentrations reached up to 424 mg kg^{-1} (*H. annuus*) and 1280 mg kg^{-1} (*Z. mays*), respectively. Importantly, the results revealed that As had mainly accumulated at the outer rhizodermis along with iron (Fe). We therefore conclude that thin crusts of Fe-(hydr)oxides cover the roots and act as an effective barrier to As, similar to the formation of Fe plaque in rice roots. In contrast to permanently flooded rice paddy fields, regular flood irrigation results in variable redox conditions within the silty and loamy soils at our study site and fosters the formation of Fe-(hydr)oxide plaque on the root surfaces.

1. Introduction

Depending on the prevailing geochemical conditions, soils can either act as a source or sink for the toxic metalloid arsenic (As). There are numerous possible pathways through which As can enter agricultural soils, for example through the application of As-containing pesticides and fertilizers or pollution by industrial activities that release As via acid mine drainage, waste water or exhaust air (Gomez-Caminero et al., 2001). Irrigation with As-rich groundwater presents another important pathway and constitutes an increasing problem, especially in the densely populated delta areas of Asia (Dittmar et al., 2007; Nath et al., 2008; Roberts et al., 2007; van Geen et al., 2006). Here, the occurrence of As-rich groundwater is a common feature in shallow aquifers and is closely linked to biogeochemical processes in the young (Holocene to Pleistocene) aquifer sediments, i.e. the microbially mediated reduction of inorganic As and the reductive dissolution of As-bearing Fe-mineral phases (Islam et al., 2004; Tufano et al., 2008). The resulting enrichment of As in shallow groundwater directly threatens the health of millions of people who depend on groundwater as drinking water source (Charlet and Polya, 2006). Furthermore, As-rich groundwater is often used for irrigation (especially during the dry season), which constitutes an additional pathway of As into the food chain (Nath et al., 2008). Further information regarding the occurrence and biogeochemistry of As in groundwater is provided elsewhere (Matschullat, 2000; Murcott, 2012; Smedley and Kinniburgh, 2002).

Irrigation with groundwater containing As may result in the accumulation of As in soils and its transfer into crops, thereby raising the risk of an increased As uptake by consumers (Halder et al., 2013; Martínez-Villegas et al., 2013; Meharg, 2004; Norra et al., 2005, 2012). In general, the mobility and plant availability of As in agricultural soils depends on a complex interplay of interdependent abiotic and biotic factors, such as microbially mediated redox processes, pH influenced sorption/desorption processes, and the presence of As-adsorbing mineral phases like Fe-(hydr)oxides or sulphides (Bar-Yosef et al., 2005; Blute et al., 2009; Fedotov et al.,

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2012; Marin et al., 1992, 1993; O'Day, 2006; Vamerali et al., 2011). This complex interplay is particularly evident in the biogeochemical cycling of Fe, which is in turn closely linked with the mobility of As (Borch et al., 2010). Fe represents a key nutrient for plants and microbes, but the solubility of Fe(III)-minerals is extremely low under aerobic and circum-neutral pH conditions. To overcome this limitation, many bacteria and fungi excrete low-molecular compounds, siderophores, to complex and mobilize Fe(III) (Konhauser et al., 2011). Under waterlogged conditions, anaerobic and reducing conditions prevail, resulting in the reductive dissolution of Fe(III)-minerals and the concomitant release of adsorbed or incorporated As (Roberts et al., 2010). In the case of long-term irrigation with As-rich water, As can also accumulate in the soil, which results in a loss of yield as soon as plant-specific threshold values are exceeded (Heikens et al., 2007).

Most studies investigating the distribution and accumulation of As in plants have focused on rice (*Oryza sativa*), one of the world's most important cereal crops (Duan et al., 2013; Meharg, 2004). In general, the uptake and enrichment of As by plants depends on the individual physiology of each plant species as well as on the overall bioavailability of As in the surrounding soil (Mallick et al., 2011). In soils, As is mainly present as inorganic As(III) and inorganic As(V), and the oxidation state crucially determines the As mobility as well as the potential plant uptake pathways. Due to a high chemical similarity with phosphorous (P), many plant species transport As(V) into the cytoplasm by the phosphate transfer system, which causes competition between P and As(V) (Meharg and Hartley-Whitaker, 2002). In rice paddy fields, the mobility and plant uptake of As is further closely linked to the biogeochemical cycling of iron (Fe) (Roberts et al., 2010). In the case of wet rice cultivation, permanent waterlogged conditions foster a rapid depletion of oxygen (O_2) through microbial decomposition of organic matter and therefore the development of reducing redox conditions. As a consequence Fe-(hydr)oxides dissolve, which increases the concentration of dissolved Fe(II) in the pore water (Takahashi et al., 2004). Since Fe-(hydr)oxides constitute important sinks for As in soils and sediments, the reductive dissolution of Fe-minerals is accompanied by the release of adsorbed and/or incorporated As (Norra et al., 2012; van Geen et al., 2006). At the same time, rice roots are known to release O_2 via aerenchyma (similar to other wetland plants) into the rhizosphere (Zhao et al., 2010), the zone where root–soil interactions take place. This O_2 release results in the formation of amorphous to crystalline Fe-(hydr)oxides around the roots, so-called Fe plaque (Bacha and Hossner, 1977; Liu et al., 2006).

Similar to rice, *Zea mays* (maize) and *Helianthus annuus* (sunflower) constitute economically important crops which are traditionally cultivated in many countries all over the world. In contrast to rice, different plant physiology (especially the absence of aerenchyma in the roots) and cultivation methods (regular irrigation instead of permanent wet-field cultivation) create different conditions for the uptake of As. Using hydroponic pot experiments, Gulz et al. (2005) showed a significant As(V) accumulation in plants known for a high P demand, including *Z. mays* and *H. annuus*. In higher plants, As(III) enters the plant system mainly via aquaporins in non-ionic form (H_3AsO_3 at pH < 9.2) while the As(III) uptake by *O. sativa* is linked to the silicic acid (H_4SiO_4) uptake pathway (Zhao et al., 2010). Lyubun et al. (2002) used As(III) spiked soil samples with concentrations of 10–100 mg kg^{-1} to investigate the resulting influence of As on *H. annuus*, revealing a linear correlation between the soil's As concentration and the plant uptake and an accompanying reduction of the biomass production of up to 50%. In general, some plant species are tolerant to high As concentrations (e.g. *Pteris vittata* up to 1.5 g kg^{-1}) and have succeeded in developing physical strategies to either reduce the As uptake or to prevent physical damage (Ma et al., 2001; Mallick et al., 2013; Meharg and Hartley-Whitaker, 2002; Raab et al., 2007). One successful strategy to detoxify As(III) is the complexation with thiol-rich proteins like glutathione or phytochelatins, which has been observed for example in *H. annuus* (Raab et al., 2007). This mechanism can be further combined with a preceding enzymatic reduction of As(V) as observed for *Brassica juncea* (Pickering et al., 2000). The inoculation of plant roots with arbuscular mycorrhizal fungi appears to further influence the soil–plant system and may reduce uptake as well as the toxic effects of As in the cases of *Z. mays* and *H. annuus* (Ultra et al., 2006; Yu et al., 2009). It was further reported that roots of *Z. mays* might cause a significant acidification in soil close to the elongation zone, which is likely to affect the mobility of trace metals at small scale (Blossfeld et al., 2010). The uptake of nutrients and potentially phytotoxic elements such as cadmium (Cd) and uranium (U) by *H. annuus* shoots was recently predicted by Kötschau et al. (2014), combining numerical modelling and specific soil extractions methods. However, similar modelling approaches are lacking regarding the plant uptake of As.

Our previous investigations revealed that irrigation with As(III)-rich groundwater caused an accumulation of As in the roots of *Z. mays* and *H. annuus* grown at our study site in the Inner Mongolia Autonomous Region (Neidhardt, 2008; Neidhardt et al., 2012). Considering the practice of periodic flooding, we propose that similar processes and mechanisms are likely to occur in the field soil that influence the cycling of As and Fe in riparian soils and constructed wetlands (Blute et al., 2004; Hansel et al., 2002; Voegelin et al., 2007). As a result, iron plaque has likely formed around local plant roots as it is known from plants growing within the riparian zone (Voegelin et al., 2007).

In our present study we used synchrotron-based micro-focused X-ray fluorescence imaging (μ-XRF) to further assess the spatial distribution of As, Fe and other elements in roots and soil particles at the micrometre scale. This analytical approach combines an advanced spatial resolution at the micrometre scale with lower detection limits at a sub-mg kg^{-1} level for most trace elements than other commonly used methods, such as electron microprobe with energy-dispersive XRF or laser ablation-inductively coupled plasma mass spectrometry (Lobinski et al., 2006; Reed, 2005). Only few studies have thus far been conducted in relation to the distribution of As in the soil–plant-system of crops using μ-XRF in general (Kashiwabara et al., 2010; Norra et al., 2012). Our study presents the first detailed μ-XRF studies of As in *Z. mays* and *H. annuus* roots and the results provide valuable insights into the soil–plant transfer of As in *Z. mays* and *H. annuus*.

2. Sampling and analytical methods

2.1. Field site and sampling

Our field site was located in the Hetao Plain, situated in the western part of the Inner Mongolia Autonomous Region, China (Fig. 1). This fertile plain is known as one of the oldest crop-producing areas in China and is based on flood irrigation using water from the adjacent Yellow River. The area is influenced by an arid desert climate with a low annual rainfall of 130–220 mm (mainly during July to September), an annual potential evaporation of about 2000–2500 mm, and average annual temperatures between 5.6 and 7.8 °C (Guo et al., 2008). Due to higher operating costs, some farmers have recently decided to irrigate their fields with groundwater instead of surface water. Unfortunately, the local groundwater often contains high concentrations of dissolved As, which raises the risk of As accumulation in agricultural soils and the food chain (Guo et al., 2008). Two fields near the small farming village of Yongming which have been irrigated with As-rich groundwater for three years (Fig. 1), were chosen for sampling (40° 51′ 49.90″ N;