The influence of irrigation-induced water table fluctuation on iron redistribution and arsenic immobilization within the unsaturation zone

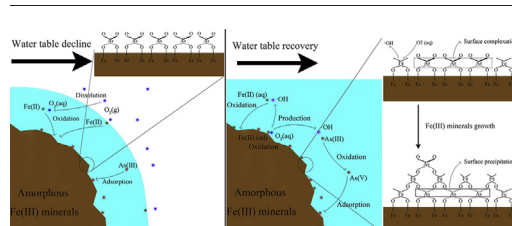Zeyong Chi [a], Xianjun Xie [a,*], Kunfu Pi [b], Yanxin Wang [a], Junxia Li [a], Kun Qian [a]

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HIGHLIGHTS

- As and Fe accumulation within the unsaturation zone during irrigation is studied.
- Oxygen is more likely exists in gaseous-phase at LWP but dissolved oxygen at HWP.
- As and Fe immobilization ratio is slow at LWP but accelerated by •OH at HWP.
- Combined state of fixed As and Fe changed with the growth of Fe(III) minerals.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Given the long-term potential risk of arsenic (As)-contaminated agricultural soil to public health, the redistribution of iron (Fe) and immobilization of As within the unsaturation zone during irrigation and consequent water table fluctuations were studied via a column experiment and corresponding geochemical modeling. Experimental results show that As and Fe accumulated significantly at the top of the column during irrigation. A tremendous increase in As and Fe accumulation rates exists after water table recovery. It was deduced that Fe(II) and As(III) were oxidized directly by O_2 at the period of low water table. But the production of hydroxyl radical (•OH) was promoted at the period of high water table due to the oxidation of adsorbed Fe(II). The generated •OH further accelerate the oxidation of Fe(II) and As(III). Moreover, the combination of As and Fe is more stronger at the top of the column due to the transformation of combined states of As from surface complexation into surface precipitation with the growth of Fe(III) minerals. This study details the processes and mechanisms of As and Fe immobilization within the unsaturation zone during different irrigation periods and accordingly provides some insights to mitigate As accumulation in topsoil.

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1. Introduction

Irrigation using arsenic (As)-contaminated groundwater may cause a potential threat to public health via daily diet (Mandal and Suzuki, 2002; Meharg et al., 2009; Sun et al., 2009). Ingestion of As via drinking water was the first noted pathway that leads to arsenism. More recent studies have shown that consumption of As-contaminated foods became an alternative human exposure pathway for As (Fransisca et al., 2015). For instance, the inorganic As from cooked rice can be well assimilated into the human body (Rahman and Hasegawa, 2011). This poses a potentially considerable risk to public health since around half of the world's population consumes rice as their staple food (Meharg et al., 2009). Actually, As compounds in crops come primarily from soil and irrigation water. As uptake in crops occurs when agricultural soil or irrigation water contains a high concentration of As, especially in anaerobic conditions (Zhao et al., 2010). However, there remain many regions that exploit As-contaminated groundwater for

agricultural usage due to water resource shortages and high demands for agricultural water (Meharg and Rahman, 2003; Ninno and Dorosh, 2001; Xie et al., 2012). As a result, the As content in soil can reach up to 83 μg·g^{-1}, which far exceeds the background level or safety level for agricultural soil (Williams et al., 2006). Given the potential risks to public health, it is imperative to comprehend the transport and transformation processes of As during irrigation, which may be responsible for the possibility of As uptake by crops and may further threaten public health.

Irrigation practices can remarkably change the behaviors of As in both aquifer and surface soil. The Fe(III)-SO$_4^{2-}$ redox cycling and consequent As mobilization/immobilization inside aquifers might be the result of periodic irrigation practices (Xie et al., 2015). High As levels in groundwater extracted from deep aquifers to the surface for irrigation can cause the accumulation of As in topsoil and/or near-surface sediments (Harvey et al., 2006; Saha and Ali, 2007). Then, the immobilized As in topsoil can be released again via biogeochemical and hydrological ways, and the liberated As ultimately concentrates in shallow groundwater (Kocar et al., 2008; Polizzotto et al., 2008).

Iron (Fe) oxide/hydroxide is one of the most important natural As pools in sediments and/or soils, and As behaviors are always associated with Fe minerals (Bissen and Frimmel, 2010; Bose and Sharma, 2002; Smedley and Kinniburgh, 2002). For instance, As release and immobilization is always synchronized with the dissolution and precipitation of Fe minerals (Xie et al., 2015). Naturally geogenic As-contaminated groundwater tends to contain high levels of Fe(II). The maximum Fe(II) concentration within the Bengal basin, Red river delta and Datong basin (northern China) in groundwater can be up to 30, 20 and 5 mg·L^{-1}, respectively (Eiche et al., 2008; Nickson et al., 2000; Xie et al., 2008). Such groundwater can generate obvious Fe precipitation after air aeration. Thus, Fe components may also play an important role in As fate within the unsaturation zone during irrigation (Nitzsche et al., 2015).

A reductive high-As aquifer generally maintains an anaerobic environment, and contains a low level of dissolved oxygen (DO). However, irrigation-induced groundwater table fluctuation may entrap air and deliver oxygen into the subsurface (Farnsworth et al., 2012; Tong et al., 2016). This will result in a series of redox reactions within the pore water that include elemental Fe and As (Tong et al., 2016).

Previous studies have demonstrated that irrigation practices can result in the redistribution of As, but most studies were focused on the As redistribution results from a more macro standpoint (Kocar et al., 2008; Polizzotto et al., 2008; Saha and Ali, 2007). Therefore, the purposes of this study are to explain how the Fe redistribution occurred and how it will affect the fate of As within the unsaturation zone during irrigation and consequent water table fluctuation. To achieve these goals, a column experiment and geochemical modeling were carried out. In the column experiment, the groundwater and soil were replaced by deoxidized As(III)-Fe(II) solution and acid-washed quartz sand to avoid the multiple solutions of experiment, although this may result in the distortion of result to some extent compare with the natural condition. The external environment of this experiment is primarily maintained in anaerobic conditions. The microbial processes are not considered in this study, and the only artificially controllable factor is water table levels.

2. Materials and methods

2.1. Column experiment

The experimental setup primarily consists of inorganic glass pipes with a 4.65-cm inner diameter and a 70-cm length (Fig. 1a). Two plastic screw caps were installed on the ends of column and sealed with a rubber O-ring between the pipe and caps. The column was equipped with a ventilation valve 7.5 cm from the column top. In addition, a filter, peristaltic pump and a 10-L reservoir were connected to the upper cap by latex tubing. The reservoir was placed in an anaerobic glove box to separate it from the oxygen. At the other end of the column, a T valve and a small flow cell were installed and used for sampling and measurement of pH, ORP, EC and DO. An atmosphere-connected 3-way splitter was added to the end of the setup, and the height of the splitter controlled the height of water table inside the column.

Quartz sand (particle size: 0.30–0.85 mm) was soaked in the 5% hydrochloric acid for 24 h to remove the Fe-bearing mineral. The acid-soaked quartz sand was washed with deionized water and completely dried. The components of influent solution were 1.0 mg·L^{-1} Fe(II) and 550 μg·L^{-1} As(III). The deoxygenated water was prepared before the preparation of influent solution by bubbling N$_2$ into the deionized water for 2 h. The N$_2$-sparged water was put into an anaerobic glove box immediately. The N$_2$ inside the glove box was replaced every 12 h until a gas-liquid equilibrium was achieved and the DO concentration was under the detection limit (HACH, HQ 40-d). Then, the influent solution was prepared using FeSO$_4$·7H$_2$O, NaAsO$_2$ and deoxygenated water inside the glove box. The sand filled 60 cm of the column with a porosity of 45.5%. The filled column was flushed in down-flow mode with N$_2$ for 2 h to drive oxygen out of the column. And the As(III)-Fe(II) solution was injected from the bottom cap and filled 62 cm of the column. The column was then switched from up-flow to down-flow, and the As(III)-Fe(II) solution was injected continually with an average flow rate of 40 mL·h^{-1}. During these stages, the ventilation valve was closed. The system was equilibrated for 65 h.

Once the dissolved oxygen was under 0.2 mg·L^{-1}, the ventilation valve was opened, and the flow rate was switched to 2 mL·h^{-1} (Fig. 1b). The water lever inside the column was lowered from approximately 62 to 30 cm immediately through decreasing the splitter height. The low water table period (LWP) maintained for a total of 198 h. The water table was then raised again by restoring the splitter height. The high water table period (HWP) maintained for a total of 171 h. The ventilation valve was opened during the experiment, allowing the gas to exchange between the atmosphere and the pore volume.

2.2. Analytical methods

Effluent samples were taken directly from the T valve on the bottom of column and filtered using 0.45-μm syringe-driven filter units. We sampled once a day during the experiment. A total of sixteen water samples were collected from the valve. The samples were partially used for ferrous and total Fe concentration measurements using a portable spectrophotometer (HACH, DR2800). Remainder of the sample was separated into two As species using a solid phase extraction cartridge (CNW Technologies, SAX). The detached solution was acidified to pH < 2 using hydrochloric acid (36–38%, GR). The acidified samples were then stored at 4 °C in the dark for the measurements of the As concentration.

At the end of the experiment, the column was flushed with N$_2$ to dry the sand inside the column under an anaerobic atmosphere, and the sand was then sampled every 6 cm. Thus, a total of 10 solid samples were collected after the column experiment. The samples were then placed in 50-mL centrifugation tubes for As and Fe sequential extraction in different solid-to-liquid ratios. The methods of sequential extraction are described in Table 1 (Keon et al., 2001; Norra et al., 2005). The blank values were obtained through the As and Fe extraction of acid-washed sand using the same methods.

The total Fe concentration was measured by the phenanthroline method after the Fe(III) was reduced to Fe(II) by the hydroxylamine hydrochloride. The As concentration of the samples was determined using an atomic fluorescence spectrometer (AFS-9700, Beijing Haitian Instruments). The detection limit of the spectrometer for determining the ferrous ion concentration is 0.01 mg·L^{-1}, and the atomic fluorescence spectrometer which was utilized for determine the As concentration is 0.1 μg·L^{-1}. The sample replicate concentrations usually differed from each other by <5%.