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# Experimental constraints on redox-induced arsenic release and retention from aquifer sediments in the central Yangtze River Basin

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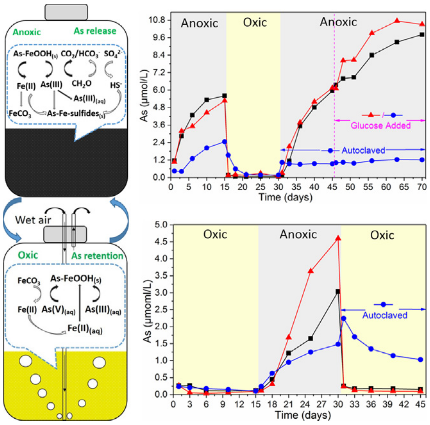
## HIGHLIGHTS

- Incubations were conducted under varying redox conditions to decipher the cause of seasonal variations in As concentration.
- Anoxia is a prerequisite for As mobilization into groundwater from Yangtze River Basin sediments.
- Alternating redox conditions resulted in Fe minerals dissolution and precipitation, and subsequent As release and retention.
- Arsenic released through multiple redox cycles without exogenous electron donors.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The consumption of arsenic (As) contaminated groundwater affects the health of almost 20 million people in China. Unlike the preponderance of observations within the deltas of South and Southeast Asia, groundwater As concentrations in the central Yangtze River Basin, China, vary by up to an order of magnitude seasonally. In order to decipher the cause of seasonal release and retention of As between sediments and groundwater, we conducted batch sediment incubations under varying (imposed) redox conditions. Incubations were conducted under both $N_2$ and $O_2$ gas purges to simulate conditions observed within the field. In all cases, anoxic conditions resulted in As release to solution while As was removed from solution under oxic conditions. These experiments confirm that anoxia is a prerequisite for As mobilization into groundwater from Yangtze River Basin sediments. Alternating redox conditions resulted in Fe minerals dissolution, transformation, crystallization, and precipitation, and subsequent As release and retention in the system. More importantly, aquifer sediments at depths >15 m release As through multiple redox cycles without an exogenous electron donor (carbon source), organic matter in the sediments is sufficiently reactive to support microbial reduction of As(V) and Fe(III).

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These results provide direct evidence for previously described mechanisms explaining the observed seasonal variation of groundwater As concentrations in the central Yangtze River Basin, where seasonal changes in surface and groundwater levels drive changes in redox conditions and thus As concentrations.

## 1. Introduction

High arsenic (As) concentrations in groundwater have been reported worldwide putting millions of people at increased risk of a variety of cancers and diseases (Berg et al., 2007; Nordstrom, 2002; Rodríguez-Lado et al., 2013; Smedley and Kinniburgh, 2002). Across Asia, where groundwater As problems are most acute, weathering of Himalayan rock leads to sediment deposition in deltas and inland basins across the continent (Fendorf et al., 2010). Arsenic contained in these sediments is released to the deltaic aquifers of Asia under strong reducing conditions, resulting from microbial utilization of organic carbon linked to dissimilatory As(V) and Fe(III) reduction. Several field experiments (Harvey et al., 2002; Neidhardt et al., 2014; Stucker et al., 2014) and laboratory microcosm-based batch incubations under anoxic conditions (Akai et al., 2004; Anawar et al., 2006; Freikowski et al., 2013; Gault et al., 2005; Islam et al., 2004; Postma et al., 2010; van Geen et al., 2004) have shown that addition of labile organic matter (OM), such as glucose, to aquifer sediments leads to greater rates of arsenic release to groundwater, although it is now clear that the form of Fe(III) oxide hosting As needs to be considered along with OM (Stuckey et al., 2016). By contrast, it is rare that addition of exogenous carbon sources such as glucose does not lead to increased As dissolution from sediments (Héry et al., 2010; Polizzotto et al., 2006; Radloff et al., 2007).

Within the Jianghan Plain, a major inland basin along the central portion of the Yangtze River, As concentrations exhibit appreciable seasonal variations, with lower concentrations corresponding to lower water levels during the dry season and higher concentrations with increased water levels during the rainy season (Duan et al., 2015). Large changes in dissolved As, Fe(II), and $S^{2-}$ occurred over months, ruling out potential mechanisms such as dilution that would require unreasonable flow and mixing rates in the aquifer, as well as distal sources of both contaminated and As-free water adjacent to the well field (Schaefer et al., 2016). Field data and reactive transport modeling support reductive dissolution of Fe(III) oxides as the dominant mechanism of As release to the aquifer (Schaefer et al., 2017; Huang et al., 2018), but the details of how As cycles between solid and aqueous phases in deep sediment, resulting in seasonally variable As concentrations, are not fully understood.

We previously reported a source of As and OM at ~20 m depth is capable of releasing significant amounts of As to adjacent groundwater (Schaefer et al., 2017). We hypothesized that sediments in this layer are responsible for the seasonal changes in groundwater As concentrations, but have previously only speculated on an oxidative pathway for seasonal As removal from solution. To test this hypothesis and determine whether arsenic release and retention are sustained through multiple cycles of redox transitions, we performed laboratory incubations in which sediments were cycled between oxic and anoxic conditions, simulating redox changes observed within the field.

## 2. Materials and methods

### 2.1. Field area and samples collection

The Jianghan Plain is an alluvial plain in the middle reaches of the Yangtze River. The study area was constructed in Shahu Village, where the first case of arsenic poisoning in the Jianghan Plain was reported and where groundwater As concentrations may exceed 16 μM (1200 μg $L^{-1}$) (Duan et al., 2015; Schaefer et al., 2016). The site was chosen because it is typical in terms of regional hydrogeological conditions and land use. The field area is bounded by four rivers (Tongshun River, Dongjing River, Kuige River, and Lüfeng River), and covered by other abundant surface water bodies such as ponds, irrigation canals, and wetlands. Strong surface water-groundwater interactions were previously observed at the site (Duan et al., 2015; Schaefer et al., 2016). More than 70% of the 10 $km^2$ site is fertile farmland cultivated with rice, corn, cotton, and vegetables, and about 15% is pond for aquariculture.

Sediment samples were collected from a borehole located between two existing well nests (SY03 and SY07, additional details in Duan et al., 2017) at N 30°09′18.62″, E 113°40′21.03″. A rotary drill rig and split-tube sampler with a stainless steel tube (17.5 cm length, 3.8 cm diameter) were used to obtain depth-specific sediment samples. After sample collection, both ends of the tubes were covered with polytetrafluoroethylene caps and sealed with paraffin wax, vacuum sealed in a vacuum bag (FoodSaver V3240) and placed in a gas-tight box containing anoxic pouches (MGC AnaeroPack Series). Samples were then frozen and shipped to Stanford University, where they remained frozen until further analysis. Two sediment samples recovered from the borehole were used throughout this study: (1) shallow clay (referred to as shallow) sampled at 3.8 m below ground level and (2) deeper silty sand (referred to as deep) from 18.5 m below ground level.

### 2.2. Sediment characterization

Sediment cores were opened under an $O_2$-free (<1 ppmv) $N_2/H_2$ atmosphere, thawed and homogenized by manual mixing. Half of the homogenized subsamples were directly used for incubation experiments, and the other half were dried under anoxic conditions prior to bulk characterization. Soil water content was determined by weighing a small amount of homogenized sediment before and after oven drying at 105 °C for 48 h. Sediment pH was measured in a 1:2 sediment: liquid slurry using 0.01 M $CaCl_2$ (Dittmar et al., 2007). Total C and N contents were measured by combusting 18–20 mg of sediment and measuring combustion products $CO_2$ and $N_2$ on a Carlo-Erba NA 1500 Elemental Analyzer. Samples were acid fumigated using concentrated (12 *M*) HCl prior to combustion to remove carbonates for determination of OC (Harris et al., 2001). The bulk element composition before and after incubation was determined using a Spectro Xepos X-ray fluorescence spectrometer (XRF). Measurements were performed in a He atmosphere and bulk elemental abundance was calculated based on the intensity of the characteristic fluorescent X-rays of each element (Schaefer et al., 2017).

Synchrotron X-ray diffraction (sXRD) was performed at beam line 11-3 at the Stanford Synchrotron Radiation Lightsource (SSRL). Radial integration was performed using fit2d and peak identification was performed using the software and mineral library of HighScore Plus. Arsenic K-edge X-ray absorption near edge structure (XANES) spectroscopy was performed at beamline 11-2 at SSRL. Samples were packed between Kapton tape. Energy selection was maintained by a Si (220) monochromator calibrated to 11,874.0 eV for the As K-edge of $Na_3AsO_4$ and fluorescent X-rays were measured with a 100-element Ge detector (Canberra). $HxAsO_4^{3-x}$ adsorbed on ferrihydrite and $H_3AsO_3$ adsorbed on ferrihydrite were used as $AsO_4^{3-}$ and $AsO_3^{3-}$ standards, As-sulfides were calculated as the sum of the relative area of arsenopyrite, arsenian pyrite, and realgar, which were used as standards