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# Effect of nanomaterials on arsenic volatilization and extraction from flooded soils☆

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## ABSTRACT

Herein, we utilize sequential extraction and high-throughput sequencing to investigate the effects of nanomaterial additives on As volatilization from flooded soils. We reveal that maximum volatilization is achieved in the fourth week and is followed by stabilization. The extent of volatilization decreased in the order of control > nano-zerovalent iron >40-nm hydroxyapatite > nano-$Fe_3O_4$ > 20-nm hydroxyapatite > multilayer graphene oxide > high-quality graphene oxide. The most abundant forms of As in soil corresponded to As-Fe and Al oxides. In soil with low levels of As pollution, the contents of these species increased after treatment with graphene oxides but decreased after treatment with other nanomaterials, with an opposite trend observed for soil with high levels of As pollution. The addition of nanomaterials influenced the activity of soil enzymes, e.g., hydroxyapatites affected the activities of urease and alkaline phosphatase, whereas graphene oxides significantly impacted that of peroxidase ($P < 0.05$). The addition of nanomaterials (which can potentially inhibit microbial growth) affected As levels by influencing the amount of As volatilized from polluted soil. Moreover, As volatilization, enzyme activity, and As speciation were observed to be mutually correlated (e.g., volatilization was negatively correlated to peroxidase activity and the contents of amorphous crystalline hydrous oxides of As-Fe and Al).

## 1. Introduction

Arsenic is a soil pollutant released by rock weathering, mining, burning fossil fuels, and the use of As-containing pesticides (Lyubun et al., 2013; Mestrot et al., 2013). Long-term consumption of As-contaminated water and food can lead to numerous health problems, including cancer. Notably, $As^{III}$ is considered to be more toxic than $As^{V}$ (Zhang and Sun, 2013), and gaseous As compounds have a higher toxicity than those that contain inorganic trivalent As. The generally accepted order of As toxicity is: hydrogen arsenide and derivatives > inorganic arsenite ($As^{III}$) > inorganic arsenate ($As^{V}$) > organic As compounds ($As^{III}$) > organic As compounds ($As^{V}$) > elemental As (Mestrot et al., 2013). In soil, As undergoes biovolatilization and is converted by plants and microorganisms into monomethylarsine, which easily escapes into the atmosphere because of its low boiling point (~50 °C, whereas that of elemental As equals 613 °C). The biological volatilization ability of As is also affected by its concentration. Notably, the emission of gaseous As species increases the range of As contamination, since such species can be readily adsorbed by fine particulate matter and transported over long distances (Finkelman, 1999). The increased toxicity of gaseous arsenicals compared to those of inorganic $As^{III}$ derivatives presents a problem that requires novel pollution management methods (Mestrot et al., 2009). Liu et al. (2006) investigated the volatilities of Hg, As, and Se during underground coal gasification, obtaining a volatility order of Hg > Se > As, and Tang et al. (2017) determined the 260-day accumulation and volatilization of As as 13.2 $mg\,L^{-1}$. Approximately 35% of atmospheric As is thought to originate from its low-temperature volatilization from soil (Frankenberger, 1998), with some investigations showing that as much as 320 ng of As (0.014% of total soil content) can be emitted in a three-week period from fertilized and flooded soils (Mestrot et al.,

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2009). Fungi, bacteria, methanoarchaea, and other eukaryotic microorganisms can also volatilize As (Wang et al., 2014), with water-soluble and exchangeable forms of As significantly inhibiting soil enzymes, as demonstrated by Bhattacharyya et al. (2008). Therefore, the volatilization and fractionation of As in soil are intimately connected with soil enzyme activity.

The increasing volume of nanomaterial production caused by their widespread applications raises concerns related to their potential release into the environment (Bai et al., 2017). Although nanomaterial adsorbents have already been utilized to remove As from soil, their effect on As volatilization is largely unreported. However, several studies have shown that nanomaterials can affect soil properties and microbial activity. Thus, at concentrations of 2.5–25 g $kg^{-1}$ dry soil, nano-zerovalent Fe was reported to efficiently immobilize As in soil with different contents of clay particles and organic matter, with the efficiency of this method increasing with time (Azari and Bostani, 2017). Additionally, the reduction of available As content in soils treated with nano-zerovalent Fe was shown to decrease soil phytotoxicity (Gil-Diaz et al., 2017). Bai et al. (2017) found that graphene oxide (GO) increased the abundance of fungivores, and Chung et al. (2015) indicated that soil enzyme activity was reduced by the entry of GO into soils in the short term. Moreover, Su et al., 2017 showed that conjugated magnetite ($Fe_3O_4$) nanoparticles can be utilized for adsorptive or separative removal of As, among other uses, whereas nano-hydroxyapatite was demonstrated to improve the activity of soil catalase, urease, and acid phosphatase. Ogawa et al. (2015) suggested that the combined application of hydroxyapatite and ferrihydrite could simultaneously immobilize Pb and Sb in shooting-range soil at neutral to alkaline pH. Yang et al. (2016) showed that biochar-supported nano-hydroxyapatite could effectively remediate contaminated soil and restore it to a quality suitable for planting. Thus, nanomaterials might influence the volatilization of As in polluted soil. Herein, we determine the effects of different nanomaterials on As volatilization from soil, clarify the effect and mechanism of As adsorption by these nanomaterials, and provide a theoretical basis for remediating As-contaminated soils.

## 2. Materials and methods

### 2.1. Materials

High-quality graphene oxide (HGO), multilayer graphene oxide (MGO), 20-nm hydroxyapatite ($HA_{20}$), 40-nm hydroxyapatite ($HA_{40}$), nano-$Fe_3O_4$ (n$Fe_3O_4$), and nano-zerovalent iron (nFe) were supplied by Jining Lite Nano Technology Co., Ltd. and Beijing Dekedaojin Technology Co., Ltd. The physical and chemical properties of these nanomaterials are listed in Table S1.

Paddy soil was sampled from two polluted areas in Chenzhou, Hunan Province, China. The As content of soils sampled from “lightly” and “highly” polluted areas equaled 21.7 and 88.0 mg $kg^{-1}$, respectively. During sampling, the top soil layer (0–20 cm) was packed into polyethylene bags, air-dried, passed through a 2-mm sieve, and kept in the dark. The physicochemical properties of the obtained specimens are listed in Table S2.

Silica gel particles (0.5–1 mm) were soaked in 10% aqueous $AgNO_3$ (w/v) (Mestrot et al., 2009) and dried at 70 °C; the whole process was performed in the dark.

### 2.2. Volatilization experiments

Soil samples (100 g) were weighed in porous gas-washing bottles (the top of the conical flask had an empty glass-stoppered core, and two curved branches with small balls were soldered on) and treated with deionized water (100 mL) to simulate flooding. Subsequently, different quantities of nanomaterials (0, 1, and 4 g) were introduced into the system. All experiments were repeated thrice. The gas bottles were connected to an air pump (airflow = 40 mL $min^{-1}$). Capture tubes containing silica gel particles were constantly replaced with new ones, and deionized water was added as required to maintain the water level. Each volatilization experiment lasted seven weeks, and the silica gel particles and glass wool containing volatile As compounds were finally digested with 5 mL of 1% $HNO_3$ in a microwave system (Huang et al., 2012) using the following temperature program: increase to 55 °C over 5 min and maintain for 10 min; increase to 75 °C over 5 min and maintain for 10 min; increase to 95 °C over 5 min, maintain for 30 min, and cool down over 15 min. The digested samples were filtered through 0.22-μm filters into 10-mL tubes, and the As contents of filtrates were determined using a dual-channel atomic fluorescence spectrophotometer (AFS-9760, Beijing Haiguang Instrument Co. Ltd., China).

### 2.3. Sequential extraction

Soil suspensions were centrifuged for 5 min at 5000 g and filtered. The obtained solids were air-dried and passed through a 2-mm sieve. Subsequently, the thus obtained samples (1 g) were weighed in 50-mL centrifuge tubes and treated with 25 mL of extraction agents (Table S3). The resulting mixtures were filtered through 0.45-μm filters into 50-mL tubes for As quantitation (Wenzel et al., 2001).

### 2.4. Determination of enzyme activity

Soil samples (0.1 g) were added to test tubes containing different enzyme extraction agents. The obtained mixtures were centrifuged, and enzyme concentrations were determined from the absorptions of the supernatant at specified wavelengths using an ultraviolet spectrophotometer. Four soil enzymes were quantified, namely catalase (CAT) (Souri et al., 2017), urease (UE) (Li et al., 2017), peroxidase (POD), and alkaline phosphatase (AKP) (Su et al., 2017).

### 2.5. High-throughput sequencing

Based on the characteristics of the amplified 16S regional and the Illumina HiSeq sequencing platform, two-terminal sequencing was constructed using the paired-end method. Filtering of the reads, operational taxonomic unit clusters, and species annotation and abundance analysis revealed sample compositions and differences between different samples (Youssef et al., 2009; Caporaso et al., 2011; Hess et al., 2011).

### 2.6. Statistical analyses

Statistical analyses were performed using SPSS 17.0 for Windows software (SPSS Inc., Chicago, USA). The ANOVA test was used to determine significant differences, with *P*-values less than 0.05 indicating statistical significance.

## 3. Results

### 3.1. Arsenic volatilization

When soil samples were treated with 4 g of nanomaterials (Fig. 1), the volatilization initially increased, reached a maximum in the fourth week, and declined over the next two weeks before finally reaching equilibrium. The extent of volatilization was observed to decrease in the order of control