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Dynamic arsenic aging processes and their mechanisms in nine types of Chinese soils

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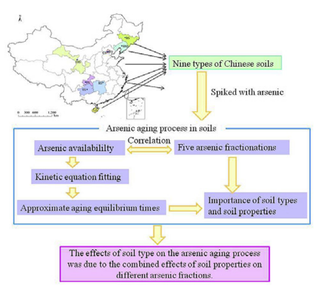
HIGHLIGHTS

- Changes in available As content during aging fit best with the pseudo-second-order model in all soil types.
- In spiked soils, As easily became less toxic and less available in low pH soils compared to high pH soils.
- The shortest equilibrium time of As aging was 28 d in latosol soils.
- Available As fractionations tended to transform to stable fractionations in all soils during aging.

GRAPHICAL ABSTRACT



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ABSTRACT

Although specific soil properties controlling the arsenic (As) aging process have been studied extensively, few investigations have attempted to determine how soil types influence As bioavailability and fractionations in soils. Nine types of soil were selected from typical grain producing areas in China, and the bioavailability and fractionations of As during aging were measured. Results showed that available As in all soils rapidly decreased in the first 30 days and slowly declined thereafter. In spiked soils, As easily became less available and less toxic in low pH soils compared to high pH soils, demonstrating the importance of soil pH on As availability. Results from fitting kinetic equations revealed that the pseudo-second-order model described the As aging processes well in all soils (R^2 = 0.945–0.999, $P < 0.01$, SE = 0.09–4.25), implying that the mechanism for As aging combined adsorption, external diffusion, and internal diffusion. Fe oxides were more important than Al oxides for determining the As aging rate ($|k|$). Based on these results, we are the first to propose the approximate aging equilibrium time (T) for As, which was mainly influenced by soil clay content. The shortest time for approximate stabilization of As aging was 28 d in latosol soils (LS), while the longest approximate equilibrium time was 169 d in cinnamon soils (CS). Individual soil properties controlling the variation in different As fractionations further confirmed that the influences of soil types on As aging were the result of the combined effects of soil properties and a time-consuming redistribution process.

1. Introduction

Arsenic (As) is a widely distributed toxic metalloid in many environments. In 2014, a joint survey report presenting the current

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status of soil contamination in China was issued by The Ministry of Environmental Protection (MEP) and Ministry of Land and Resources (MLR) of the People's Republic of China (http://www.mep.gov.cn/gkml/hbb/qt/201404/t20140417_270670.htm). Unexpectedly, the report found that 16.1% of all investigated soils exceeded China's soil environmental quality limits and that agricultural soils accounted for 19.4% contaminated soils. Soils contaminated with heavy metals and metalloids are of particular concern. Arsenic is the third most common contaminant in soil samples (2.7%), exceeding the MEP limit. As contamination is not only a serious phenomenon in southern China, where total As in the soil can be three or four times higher than that in non-contaminated soils (Yang et al., 2015; Tang et al., 2016), it is also a widespread threat to most of the cultivated soil throughout the country. As contaminated soil ultimately affects human health because As in soils can be absorbed by plants and thus decreases food safety (Zhu et al., 2014). Nevertheless, the total metalloid concentration in soils is a poor indicator of the potential biological availability of As, because it overestimates the risks for assessing toxicity (Huang et al., 2016a). Crop plants easily take up As fractions that are bioavailable and mobile, leading to negative effects on human health when contaminated plants are consumed (Karak et al., 2011). Due to the aging effect, As could transform more labile As fractions into less mobilizable fractions and cause As bioavailability to decrease over time. Hence, a better understanding of the aging process and its influence on As bioavailability is necessary when assessing the ecological risk and reasonable use of As contaminated soil.

In recent decades, many researchers have studied China's soil quality, especially in farmland soil. China is a geochemically diverse country that covers a large span of latitude and longitude, and cultivated soils in different regions of China can be classified into various soil types based on the influence of many factors such as the soil parent materials, pedogenetic processes, climatic characteristics, and human activities. Different types of soil have unique properties that influence crop production in China. For example, highly leached red soils (RS) are generally classified as ferralosols and ferrosols, occasionally as argosols and isohumosols and even as cambosols (Cui et al., 2014). They are widely distributed in tropical and subtropical regions and have a low pH value and high levels of iron (Fe) and aluminum (Al) hydroxides. Black soils (BS), designated as isohumosols and dark chernozems, are mainly distributed in northeast China (Liu et al., 2015). They are widely recognized as inherently productive and fertile and are famous for high soil organic matter content. Purplish soils (PS) are classified as primosols, and develop from purple or red sedimentary rocks from the Trias-Cretaceous system. Those rocks are prone to physical weathering, which results in lithologic soils that are difficult to distinguish based on pedogenic horizons. This type of soil is mainly found in Southwestern China in the Sichuan Basin (Zhou et al., 2014).

Although some specific soil properties controlling the aging process of As in soils such as Fe or Al oxide content, organic matter content, pH value, soil parent matter, and clay content have been investigated extensively (Yang et al., 2002, 2005; Jiang et al., 2005; Quazi et al., 2010; Liang et al., 2014; Wang et al., 2015), only a few studies have focused on mechanisms of As aging in different types of soils. Because of the aging effect, the bioavailability of As greatly declines in some soil types such as argosol, isohumosol, and ferrosol, but the aging effect was not significant in cambosols and ferralosol soils (Tang et al., 2007; Juhasz et al., 2008). These results mean that the As aging process depends on soil type. Therefore, it is important to investigate changes in fractionation and bioavailability of As in soils that are classified into different soil types and distributed in typical crop production regions of China.

In this study, nine types of cultivated soils selected from crop production areas in China were spiked with As and incubated at the same conditions. Changes in fractionation and bioavailability of As over time in the soils were measured using sequential extractions and the $NaHCO_3$ extraction method. The purpose of this study was to investigate: (1) the effect of aging on fractionation and bioavailability of As in different types of soil and their aging mechanisms; (2) the importance and function of individual soil properties on different As fractions during the aging process; and (3) the correlation of sequentially extracted As fractionations with available As. The results are beneficial for explaining the specific progress of As aging in typical regional soils in China and for proposing appropriate remediation strategies for ensuring food security in As contaminated soils.

2. Materials and methods

2.1. Soil samples and soil physicochemical properties

A total of nine types of soil were collected from 0 to 20 cm in cultivated sites throughout China in various cities or provinces including Beijing, Jilin, Shenyang, Guizhou, Hunan, Hainan, Gansu, and Sichuan. These soils have different physicochemical properties and represent typical soils in different geological regions in China including fluvo-aquic soils (FS), cinnamon soils (CS), black soils (BS), brown soils (BNS), yellow soils (YS), red soils (RS), latosol soils (LS), irrigated desert soils (IDS), and purplish soils (PS). All soils were air-dried, homogenized, and passed through a 2 mm nylon sieve before the incubation experiment.

Some soil properties, such as pH, soil organic matter (SOM), pH, soil total phosphorus (TP), available P (Olsen-P), cation exchange capacity (CEC), amorphous and free Fe, Al, and Mn oxides, and soil particle size composition were measured in duplicate. Details of methods for each assay are shown in the Supplemental Section.

2.2. Soil aging incubation

The nine soils were spiked with the same volumes of $Na_3AsO_4 \cdot 12H_2O$ (As, 1000 mg L^{-1}) solution to make up added water-soluble As concentration of 100 mg kg^{-1}. Then, appropriate volumes of double-distilled water were added to adjust the soil moisture to 60% of the water holding capacity and the soils were mixed thoroughly. A uniform concentration of exogenous available As was selected to simulate different types of soils contaminated by labile As under similar conditions. Samples were prepared for incubation according to the methods in Wang et al. (2015), except that soil moisture was maintained to 60% of water holding capacity. The process of sampling during incubation also followed that of Wang et al. (2015).

2.3. Available As and As fractionations

A 0.5 M $NaHCO_3$ chemical extraction method was used to determine the concentration of available As in soil (Peryea, 2002; Wang et al., 2014, 2015; Su et al., 2015). Detailed methods for this procedure are shown in the Supplemental Section. A sequential extraction procedure modified from Wenzel et al. (2001) was used to determine As fractionations in spiked, aged soil. Reagents with increasing dissolution strength, including 0.05 M $(NH_4)_2SO_4$, 0.05 M $NH_4H_2PO_4$, 0.2 M NH_4-oxalate, 0.2 M NH_4-oxalate, and 0.1 M ascorbic acid and aqua regia, were employed to extract As associated with non-specifically adsorbed As (F1), specifically adsorbed As (F2), amorphous and poorly-crystalline Fe/Al oxides (F3), well-crystalline Fe/Al oxides (F4), and residual As fraction (F5). After each extraction, suspension samples were centrifuged at 8000 rpm for 5 min before being filtered through a 0.45 μm filter for As