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Natural degradation of roxarsone in contrasting soils: Degradation kinetics and transformation products

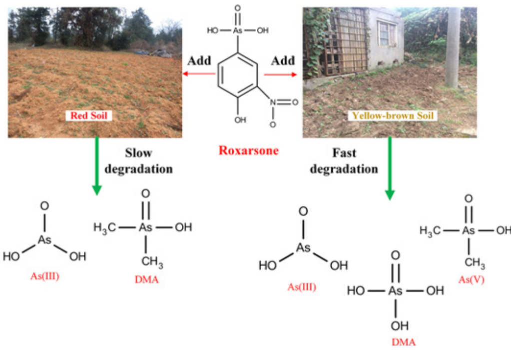
Qing-Long Fu [a,b], Lee Blaney [c], Dong-Mei Zhou [a,*]

[a] *Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, PR China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, PR China*
[c] *Department of Chemical, Biochemical and Environmental Engineering, University of Maryland Baltimore County, 1000 Hilltop Circle, Baltimore, MD 21250, USA*

HIGHLIGHTS

- Extractable ROX was degraded faster in yellow-brown soil compared to red soil.
- Soil moisture and exogenous glucose facilitated ROX degradation in soil.
- DMA was the predominant As species in yellow-brown soil extracts.
- Soil properties affect the degradation and environmental fate of ROX in soils.

GRAPHICAL ABSTRACT



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ABSTRACT

Roxarsone (ROX) is transformed to more toxic arsenicals after land application of ROX-containing poultry litter to agricultural soils. To date, no reports have compared ROX degradation in soils with contrasting properties. In this study, the impact of different incubation conditions on ROX degradation was investigated in red (C-Soil) and yellow-brown (H-Soil) soils. The degradation half-lives of extractable ROX in C-Soil and H-Soil were found to be 130–394 d and 4–94 d, respectively, indicating that the extractable ROX degraded faster in H-Soil. This result stems from the higher organic matter content, more abundant soil microbes, and lower ROX sorption capacity of H-Soil compared to C-Soil. Degradation of extractable ROX in both C-Soil and H-Soil was significantly promoted by soil moisture and exogenous glucose. Exogenous P(V) facilitated degradation of extractable ROX in C-Soil, but limited effects were observed for H-Soil. HPLC-ICP-MS analysis confirmed that ROX and dimethylarsinic acid were the predominant As species in soil extracts from 119-day incubated C-Soil and H-Soil, respectively. Ultimately, minimal transformation of extractable ROX was observed in C-Soil, but the majority of extractable ROX in H-Soil was biologically transformed. The differences in degradation of extractable ROX in C-Soil and H-Soil highlight the key roles of soil properties on the environmental fate of ROX and associated arsenicals. Results from this study inform the need for comprehensive evaluation of the ecological risks in organoarsenical-contaminated soils.

1. Introduction

Roxarsone (4-hydroxy-3-nitrophenylarsonic acid, ROX) is a water-soluble organoarsenic feed additive used in animal feeding operations

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[*] Corresponding author.
E-mail addresses: fuqinglong09@mails.ucas.ac.cn (Q.-L. Fu), blaney@umbc.edu (L. Blaney), dmzhou@issas.ac.cn (D.-M. Zhou).

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to control intestinal parasites, improve feed efficiency, and promote poultry growth (Liu et al., 2017; Mangalgiri et al., 2015). ROX is minimally metabolized in animal bodies, excreted unchanged in fresh litter (Garbarino et al., 2003), and introduced to soils through land application of ROX-containing poultry litter (Fu et al., 2016e; Mangalgiri et al., 2015). For context, the ROX content in poultry manure from Guangdong province, China was reported as 10.7 mg As/kg (Yao et al., 2009b). In the environment, ROX is transformed through biotic and abiotic mechanisms into arsenate (As(V)), arsenite (As(III)), and methylated arsenicals (Adak et al., 2015; Fisher et al., 2015; Garbarino et al., 2003; Liang et al., 2014; Stolz et al., 2007), causing arsenic (As) contamination of soil and water. The total As content in the surface soil of concentrated animal feeding operations in the Pearl River Delta, China ranged from 3.44 to 36.41 mg/kg with an average of 15.95 mg/kg (Liu et al., 2015). Due to potential risks to human and environmental health, ROX was banned from feed additives in the European Union, Canada, and United States in 1998, 2011, and 2013, respectively (Fu et al., 2016e; Mafla et al., 2015). However, ROX is still being used in many other countries, including Brazil, China, Malaysia, Mexico, Pakistan, the Philippines, and Vietnam, among others (Fu et al., 2016e; Mafla et al., 2015). For example, approximately 1200 tons of ROX was used in the Chinese animal industry in 2003 (Zhu, 2013).

The ecological risks of As in organoarsenical-contaminated sites are highly dependent on soil processes that govern arsenic speciation and distribution (Fu et al., 2016b; Fu et al., 2016c; Liang et al., 2014; Liu et al., 2017). The transformation of organoarsenic feed additives to more toxic inorganic and/or methylated arsenicals may cause stress responses to soil organisms (Fu et al., 2016e). Accumulation of organoarsenicals in plants, and the corresponding responses, have been previously documented (D'Angelo et al., 2012; Fu et al., 2016a; Geng et al., 2017; Huang et al., 2013; Yao et al., 2009a; Yao et al., 2009c). In addition, organoarsenical accumulation in food crops like rice can pose potential health risks to consumers (Yao et al., 2016). For these reasons, it is essential to study the dynamic changes of extractable ROX content in soils.

Microbial degradation is the main process responsible for transformation of organoarsenic feed additives in soils (Liang et al., 2014; Liu et al., 2017; Ma, 2009; Sun, 2012). *Bacillus* spp., *Paenibacillus* spp., *Arthrobacter* spp., *Lysobacter* spp., and *Alkaliphilus* spp. were reported to be involved in the degradation of ROX in brown soil (Liu et al., 2017). The quarter-life of ROX in non-sterilized soil was approximately half of that in sterilized soil, indicating that ROX degradation was dominated by the biotic mechanism. Stolz et al. (2007) reported that microbial degradation of ROX involved reduction to 3-amino-4-hydroxyphenylarsonic acid (HAPA) followed by loss of the amine group to form 4-hydroxybenzene arsonic acid. Then, the arsenate group was released. As(V) can be further reduced to As(III) or methylated to monomethylarsonic acid (MMA) or dimethylarsinic acid (DMA) through abiotic and biotic processes. The abiotic mechanism is also responsible for the degradation of organoarsenic feed additives in some environmental circumstances (Menahem et al., 2016; Wang and Cheng, 2015). Recently, Wang and Cheng (2015) reported that the *p*-arsanilic acid (*p*-ASA) organoarsenical could be transformed by metal oxides (δ-MnO_2). In this case, As(III) was released following cleavage of the *As*-phenyl ring in *p*-ASA radicals, which were formed from a precursor complex of *p*-ASA and the δ-MnO_2 surface through single-electron transfer to δ-MnO_2, and oxidized to As(V) (Wang and Cheng, 2015). Inorganic arsenicals can also be transformed to MMA and/or DMA by microbial communities in soil environments (Fu et al., 2016e; Huang et al., 2011).

The environmental fate of ROX in soils is profoundly affected by soil incubation conditions (Liang et al., 2014; Ma, 2009; Sun, 2012) and physicochemical properties (Arroyo-Abad et al., 2011; Fu et al., 2016c). Soil microbial activity can be stimulated by moisture, exogenous phosphate, and exogenous glucose, leading to elevated microbial degradation rates for organic contaminants in soils (Frkova et al., 2016; Liang et al., 2014; Ma, 2009; Sun, 2012). Previous studies have reported positive correlations between ROX degradation, soil moisture, and incubation temperature in brown soil (Ma, 2009; Sun, 2012; Liang et al., 2014). However, only loam and brown soils were investigated in the aforementioned studies. ROX degradation in soils with different, or contrasting, properties has not been investigated.

A variety of soil types have been identified in agricultural regions of China that contain concentrated animal feeding operations. For example, red soil and brown soil are dominant in the Pearl River Delta and Jiangsu province, respectively (Liu et al., 2015; Wang et al., 2013). Compared to brown soil, red soil has a higher iron content but lower organic matter content. In a previous study, ROX strongly sorbed to red soil with a sorption capacity of 4.12 mg/g due to the high crystalline iron content (Fu et al., 2016c). In contrast, ROX was rapidly degraded in the brown soil (Liu et al., 2017; Ma, 2009; Sun, 2012). Soil properties are also critical for ROX degradation in soils. The mobility of ROX and its inorganic metabolites in soil is significantly controlled by iron oxyhydroxides, which have high sorption affinities for arsenicals (Arroyo-Abad et al., 2011; Brown et al., 2005; Fu et al., 2016c; Mangalgiri et al., 2015). Soil organic matter simulates microbial activity, generates anaerobic conditions, and facilitates biological reduction of iron oxyhydroxides in soils (Weber et al., 2010). However, organic matter can also complex with and desorb arsenicals from soils (Fu et al., 2016c; Mangalgiri et al., 2015), increasing the mobility of ROX and its inorganic metabolites in soils. For these reasons, a comparison of ROX fate in contrasting soils with high sorption capacity or microbial activity will provide important insights for diverse agricultural soil environments.

The toxicity of arsenicals is species-dependent. ROX is less toxic to plant metabolism and microorganism growth compared to its inorganic metabolites, As(III) and As(V) (Fu et al., 2016a; Jiang et al., 2013). For instance, the median effective concentration (EC_{50}) for ROX inhibition of wheat root elongation was approximately 29 and 8 times that of As(V) and As(III), respectively (Fu et al., 2016a). Arsenic speciation changes in ROX-contaminated soils are, therefore, critical for risk assessment of poultry litter-amended soils. Nevertheless, few studies have focused on As speciation and the associated environmental risks in ROX-contaminated soils. Besides As(III) and As(V), other As-containing compounds were detected in equilibrium solutions of ROX after 24 h of contact with soils (Arroyo-Abad et al., 2011). Liang et al. (2014) reported that As(V) content gradually increased with incubation time, temperature, and soil moisture. HAPA was also identified as the primary degradation product of ROX (Liu et al., 2017). Liu et al. (2009) found that ROX in soil solution was completely transformed into inorganic and methylated arsenicals in flooded paddy soil within 7 d; furthermore, the presence of ROX and its degradation products significantly decreased the tiller number, 1000-grain weight, and grain yield of rice. The aforementioned results indicate that the environmental fate of ROX differs between soil types and conditions, but a controlled study of these differences has not been previously conducted.

In the present study, the effects of ROX concentration, soil moisture, exogenous phosphate, and exogenous glucose on ROX degradation were investigated in red and yellow-brown soils. In addition, the four common ROX metabolites, namely As(III), As(V), MMA, and DMA, were measured and compared in these contrasting soils to reveal the impacts of soil properties on ROX degradation mechanisms.

2. Materials and methods

2.1. Chemicals

ROX (≥98%) was obtained from Acros Organics (USA). As(III), As(V), MMA, and DMA standards were purchased from the National Institute of Metrology, China. NH_4NO_3 and glucose were of analytical grade, while other chemicals were guaranteed grade or higher. Deionized (DI) water (>18.2 MΩ) from a Milli-Q system (Millipore, USA) was used for all experiments.