Sorption of roxarsone onto soils with different physicochemical properties

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Qing-Long Fu [a, b], Jian-Zhou He [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, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Department of Chemical, Biochemical and Environmental Engineering, University of Maryland Baltimore County, 1000 Hilltop Circle, Baltimore, MD 21250, USA

HIGHLIGHTS

- ROX sorption to soils was rate-limited by both film and intra-particle diffusion.
- Adsorption and partitioning were involved in the sorption of ROX to soils.
- ROX sorption parameters were influenced by soil Fe_{DCB}, TOC, and DOC.
- Acidic carboxylic and alkaline amide groups are responsible for ROX sorption.
- ROX mobility in soils is profoundly facilitated by soil DOM, P(V), As(III), As(V).

GRAPHICAL ABSTRACT
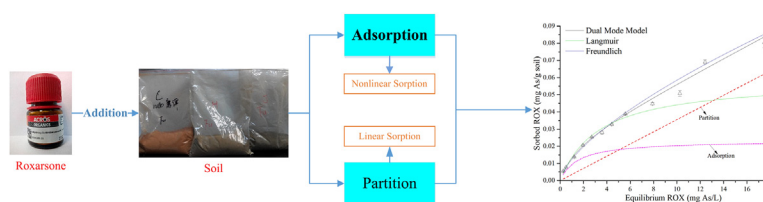
ABSTRACT

Elevated roxarsone (ROX) concentrations in soils, caused by land application of ROX-bearing poultry litter, mandate investigation of ROX sorption onto soils. Equilibrium and kinetic studies of ROX sorption onto five soils were carried out to explore the relationship between sorption parameters and soil properties, and to reveal the effects of coexisting humic acid (HA), P(V), As(V), and As(III) on ROX transport. Experimental results indicated that ROX sorption reached equilibrium within 24 h, with pseudo-second order rate constants of $5.74–5.26 \times 10^2$ g/(mg h); film and intra-particle diffusion were the rate-limiting processes. ROX sorption to soils involved partitioning and adsorption phenomena; however, their relative contributions varied for different soils. The maximum ROX sorption varied with soil type, ranging from 0.59 to 4.12 mg/g. Results from correlation analysis and multiple linear regressions revealed that the maximum sorption capacities, partition coefficients, and desorption percentages were correlated with soil properties, especially iron content, total organic carbon, and dissolved organic carbon. ROX sorption to soils was affected more by soil pH than the initial pH of ROX-containing solutions. Carboxylic and amide functional groups were determined to be responsible for ROX sorption to soils. ROX sorption capacities decreased in the presence of HA, P(V), As(V), and As(III), indicating that ROX mobility in soils was facilitated by dissolved organic matter (DOM) and competing anions.

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* Corresponding author.
  E-mail address: dmzhou@issas.ac.cn (D.-M. Zhou).

1. Introduction

Roxarsone (4-hydroxy-3-nitrophenylarsonic acid; ROX) is an organoarsenic feed additive used in the poultry industry to control intestinal parasites, promote animal growth, and improve feed efficiency. It was reported that 88% of US chickens raised for human consumption were fed ROX in 2010 (Nachman et al., 2013). In China, 1200 tons of ROX was used in the animal production industry in 2003 (Zhu, 2013). Moreover, a survey revealed that organoarsenicals were detected in 25.4% of animal feed supplies in China, with an average content of 7.0 mg As/kg (Yao et al., 2013). Organoarsenic additives are minimally metabolized within animals and are primarily excreted unchanged to manure (Garbarino et al., 2003). Therefore, land application of ROX-bearing poultry manure as fertilizer results in elevated ROX levels in agricultural soils.

Sorption is a critical process controlling the environmental fate and transport of toxic contaminants in soils. However, limited information is available for the sorption of ROX to soils. Sorption of polar organic pollutants to soils is comprised of two simultaneous processes: partitioning into soil organic matter (SOM) (Xing et al., 1996), and adsorption to soil minerals (Shimizu et al., 2011; Guo et al., 2013; Kang and Jeong, 2015). The adsorption of ROX to Bt soil horizons of Frederick soils was governed by adsorption of its arsenate (As(V)) functionality on soil iron oxides (Brown et al., 2005). Because of the intrinsic presence of both As(V) and phenyl moieties, it is reasonable to expect that ROX will partition into SOM and selectively adsorb to soil minerals. However, quantification of ROX partitioning and adsorption components in a variety of soils has not been reported.

The sorption of toxic pollutants is significantly affected by soil physicochemical properties. As(V) sorption has been positively correlated to soil Fe content (Jiang et al., 2005; Dias et al., 2009) and crystalline Fe and Al content (D'Angelo et al., 2012). For aromatic arsenicals, it was reported that Acrisol soil exhibited a higher adsorption capacity for diphenylarsinic acid (DPAA) than Phaeozem soil (Wang et al., 2013). Compared with Bt soil, Ap soil showed a weaker sorption affinity for ROX due to its lower clay and Fe oxide content (Brown et al., 2005). Similarly, total As content in long term poultry waste-amended soils was strongly correlated with Fe oxide (Han et al., 2004). Partitioning of ROX into SOM is related to soil types (Arroyo-Abad et al., 2011). However, the relationship between ROX sorption capacities and soil physicochemical properties has not yet been elucidated.

ROX has been frequently detected with its inorganic metabolites and phosphate (P(V)) (Garbarino et al., 2003; Jackson et al., 2006; Huang et al., 2014). Arsenic mobility in poultry litter-amended soils was increased by the elevated P(V) levels (Han et al., 2004; D'Angelo et al., 2012). Greater than 70% inhibition of ROX and *p*-arsanilic acid (*p*-ASA) sorption to Fe and Al oxides was observed due to the presence of P(V) (Chen and Huang, 2012). Soil-derived dissolved organic matter (DOM) is another important parameter affecting the transport of arsenicals in soils. Several studies have indicated that arsenical mobility in soils was increased in the presence of DOM (Han et al., 2004; Brown et al., 2005; Jackson et al., 2006; D'Angelo et al., 2012). Inorganic arsenic oxyanions, including arsenite (As(III)) and As(V), are important organoarsenical metabolites commonly found in soils. Since ROX retention in soils is controlled by its As(V) functional group (Mangalgiri et al., 2015), the potential effects of As(III) and As(V) on ROX sorption to soils require study.

The objectives of this study were to (1) investigate the sorption kinetics and isotherms of ROX on five soils with different physicochemical properties; (2) quantify the relative contribution of partitioning and adsorption to overall ROX sorption; (3) explore the relationship between ROX sorption parameters and soil physicochemical properties; (4) study ROX sorption capacity on soils as a function of humic acid (HA), initial solution pH, P(V), As(III), and As(V).

2. Materials and methods

2.1. Chemicals

ROX was purchased from Acros Organics (98%, USA). The molecular structure, pK_a values, and speciation of ROX in solution are shown in Fig. S1 (in the Supplemental Data) as a function of pH. ROX stock solutions were prepared by dissolving ROX in deionized water, which were stored in the dark at 4 °C. HA-sodium salt was obtained from Sigma-Aldrich. Other chemicals were of analytical grade or higher. Deionized water (18.2 MΩ cm^{-1}) was used throughout experimentation.

2.2. Soil sampling

Surface soils (0–20 cm) with different physicochemical properties were collected from agricultural land in the Heilongjiang (A-Soil), Sichuan (B-Soil), Jiangxi (C-Soil), Jiangsu (H-Soil), and Guizhou (J-Soil) provinces, China. Soil samples were air dried, homogenized, and ground to pass through a 60-mesh sieve before use.

2.3. Sorption kinetics experiments

According to previous reports (Shimizu et al., 2011), sorption kinetics studies were investigated at room temperature using beakers containing soil suspensions and 8 mg/L ROX-As (always expressed as As concentration, below) with a background composition of 100 mg/L NaN$_3$, 10 mmol/L NaNO$_3$, and 1 mmol/L 2-(N-morpholino)ethanesulfonic acid (MES) buffer at pH 6.0 ± 0.1. Aliquots (0.5 mL) were collected at predetermined times, and suspensions were filtered (0.22 μm) before analysis. The soil dose in this study was 50.0 g/L, with an exception of 13.3 g/L for C-Soil due to its high sorption capacity to ROX.

2.4. Sorption-desorption experiments

Sorption and desorption experiments were conducted using batch reactors at room temperature in polypropylene centrifuge tubes. Soil suspensions containing the background solution with various concentrations of ROX were shaken at 200 rpm for 24 h. The initial ROX concentrations ranged from 0.5 to 22 mg/L. Suspensions were passed through 0.22 μm filters before ROX analysis. Control experiments without soils were conducted to evaluate the possible loss of ROX by the interaction with tubes/filters, microbial degradation, and/or photodegradation. All of those mechanisms were found to be negligible.

Desorption tests were conducted following the completion of sorption experiments. After centrifuging, the supernatant was decanted, replaced by 10 mL of background solution, and shaken at 200 rpm for an additional 24 h. ROX concentrations in the filtrate (0.22 μm) were determined, and the desorbed ROX levels were calculated (Wang et al., 2013).

2.5. Effects of environmental factors on the sorption of ROX to soils

Effects of initial solution pH on ROX sorption were assessed at various pH, ranging from 3.0 to 9.0, with soil suspensions containing 8.5 mg/L ROX, 100 mg/L NaN$_3$, and 10 mmol/L NaNO$_3$. In accordance with previous work (Wang et al., 2013), different concentrations of NaH$_2$PO$_4$ (0-10 mg-P/L; always expressed as P, below) were prepared in the background solution with 8.5 mg/L