



## Retention of phenylarsenicals in soils derived from volcanic materials

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### ABSTRACT

Sorption of phenylarsenicals including 4-hydroxy-3-nitrophenylarsonic acid (roxarsone), an animal feed additive widely used for growth stimulation, on soils was investigated in batch systems. Phenylarsonic acid, o-arsanilic acid and roxarsone were retained differently by unpolluted, non-sterilized soils. Sorption isotherms were analyzed by the Henry, Tóth and Langmuir–Freundlich equations. The saturation capacity of the Acrisol soil was 3.4 for o-arsanilic acid, 10.9 for phenylarsonic acid and 1.9 g<sub>As</sub> kg<sub>soil</sub><sup>-1</sup> (dry mass) for roxarsone. The iron content in the soil was not the only factor determining retention of the studied phenylarsenicals. The order of retention on the three soils after 24 h was: roxarsone > o-arsanilic acid > phenylarsonic acid. Besides arsenite and arsenate, new arsenic-containing compounds were detected.

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### 1. Introduction

The use of some organoarsenicals as anticoccidial and antiparasitic drugs has become important to the growing animal food industry. For example, in the United States the phenylarsenicals: 4-hydroxy-3-nitrophenylarsonic acid (roxarsone), 4-aminophenylarsonic acid (p-arsanilic acid) and [4-(carbamoylamino)phenyl]arsonic acid (carbarsone) are used as antibiotics for swine, chicken, turkey, quail and pheasant production [1]. Arsanilic acid and roxarsone have been widely used as feed additive for intensive poultry and swine farming in China [2], Canada and Australia [1]. In the European Union, 3500 t of veterinary pharmaceuticals are used for therapeutic (antibiotic together with parasiticide) purposes, annually [1].

Roxarsone is excreted unchanged in the manure of poultry and accumulates in the litter, which is a combination of wood chip bedding, feathers and manure. This makes poultry litter containing nitrogen, phosphorous and roxarsone, an eventual fertilizer for agricultural fields and a potential source for arsenic contamina-

tion. Roxarsone has been found in concentrations up to 2 µg L<sup>-1</sup> in water of a drinking water treatment plant [3] and its mineralization to As(V) has been shown to occur during composting and stockpiling [4–8]. The total arsenic concentrations found in fresh litter are 27 mg/kg and in composted manure less than 2 mg/kg [5]. While for drinking water, the WHO allowed arsenic concentration is 10 µg L<sup>-1</sup> [9], no limits have been established for soil. The reported maximum arsenic concentrations in contaminated soils range from 57.8 to 363.8 mg/kg in the upper 40 cm of soil [10]. The German ordinance of soil protection established a threshold value of total arsenic in soil depending on cultivation of 200 mg kg<sup>-1</sup> and 0.4 mg kg<sup>-1</sup> (dry mass) for grassland and cropping soil, respectively, in 1999 [11].

Roxarsone has displayed sorption–desorption from an Ultisol soil [4] and the solubility of arsenic enhanced after litter application due to competitive sorption of the litter organic constituents. Sorption studies of organoarsenicals have been mainly focused on roxarsone on soil minerals [12,13] and less, on unpolluted soils [14].

There are few reports studying the behavior of phenylarsonic acid in soil, where it has been degraded by bacteria [15]. Research on the biotransformation of roxarsone has been conducted under anaerobic conditions [16,17], while the transformations of o-arsanilic acid and phenylarsonic acid have been investigated by the metabolism of the terrestrial plant *Tropaeolum majus* [18].

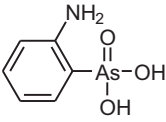
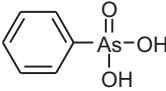
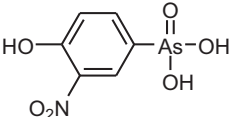
Upon arsenic, the adsorption characteristics of forest, arid zone, clay, silt loam and Ultisol soils have been examined [10]. Sorption of

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**Table 1**  
Studied organoarsenic compounds and their properties.

Organoarsenic and code	Formula	Molecular properties			pH in water	pK <sub>a,i</sub> <sup>a</sup>	
		Volume, cm <sup>3</sup> mol <sup>-1</sup>	Polarity, MPa <sup>0.5</sup>	Hansen solubility, MPa <sup>0.5</sup>		Reported	Calculated
o-Arsanilic acid (AA)		86.1	7.8	29.7	3.9	pK <sub>a,1</sub> 2 pK <sub>a,2</sub> 3.77 pK <sub>a,3</sub> 8.66	pK <sub>a,1</sub> 1.99 ± 0.10 pK <sub>a,2</sub> 4.21 ± 0.10 pK <sub>a,3</sub> 8.56 ± 0.12
Phenylarsonic acid (PA)		79.0	6.4	27.2	3.9	pK <sub>a,2</sub> 3.47 pK <sub>a,3</sub> 8.48	pK <sub>a,2</sub> 3.61 ± 0.10 pK <sub>a,3</sub> 8.71 ± 0.18
Roxarsone (RO)		98.0	10.8	30.4	4.0	pK <sub>a,2</sub> 3.41	pK <sub>a,2</sub> 3.51 ± 0.10 pK <sub>a,3</sub> 8.96 ± 0.30

<sup>a</sup> pK<sub>a,1</sub> corresponds to the deprotonation of the -NH<sub>3</sub><sup>+</sup> substituent, pK<sub>a,2</sub> and pK<sub>a,3</sub> to the As-OH groups.

roxarsone has been studied on unpolluted Ultisol [4] and dolomitic limestone Frederick soil [5], but not on unpolluted and not fertilized volcanic soils. Mineral rich soils derived from volcanic loams and altered volcanic ashes are particularly good for pasture growth, horticulture and maize. The majority of these soils occurs in the region of the circum-Pacific seismic belt and shows unique physical properties different from other soils; they have high cation exchange capacity, variable charge characteristics and water-soluble aluminium.

The main goal of this work was to study the sorption of three phenylarsenicals with environmentally relevant concentrations (µg L<sup>-1</sup> range), on selected clay-rich soils derived from volcanic materials and utilized in agriculture. At one site for example, the land use was 46% forest and 37% agriculture (maize and wheat) [19]. Aim was to determine the different retention behavior, in terms of sorption models, of different soils upon roxarsone (RO), o-arsanilic acid (AA) and phenylarsonic acid (PA). The interaction between soils and these phenylarsenicals with concentrations in the mg L<sup>-1</sup> range was aimed at detecting diverse transformation products as result of the interaction of the phenylarsenicals with the minerals contained in the soil.

## 2. Materials and methods

### 2.1. Phenylarsenicals

The molecular formula of the studied organoarsenicals: o-arsanilic acid (Sigma, purity 98%), phenylarsonic acid (TCI Europe, purity 99%) and roxarsone (Fluka, purity 98%) are shown in Table 1. Their molecular parameters were calculated by means of the software Molecular Modeling Pro from Chem SW after conformational minimization. The calculations of the pK<sub>a</sub> were performed with the Software pK<sub>a</sub> DB from ACD Inc. taking the most probable tautomeric structure. The reported pK<sub>a</sub> values were taken from Dean [20].

### 2.2. Soil samples

The soils selected for this study were: an Acrisol resulting from old volcanic ashes, and a Tepetate [21], corresponding to

a volcanic tuff. The term Tepetate derives from the Nahuatl *tepetlatl* and means “stone mat”. The third soil was an Andosol, a product of redistributed volcanic ashes. The <2 µm fractions of Acrisol and Tepetate were made up of kaolinite and halloysite, respectively. Akaganeite was the principal Fe-mineral component in the Acrisol, but less quantities of goethite and hematite were also present [22]. The main minerals in the Andosol <500 µm fraction were α-cristobalite, halloysite-10A and quartz with traces of aluminum silicate hydroxide, hematite and Akaganeite-Q.

### 2.3. Characterization of the soils

The determination of the point of zero charge was carried out at 21 °C according to the procedure described by Fiol and Villaescusa [23] using 200 mg of soil. The moisture of each soil (1 g) was determined by drying at 105 °C until constant weight was achieved, then it was cooled to room temperature and weighed (oven dry soil). Water at field capacity was determined for each soil by the graduated cylinder method [24]. Texture was determined at room temperature by sedimentation with correction of the settling time applying the Stokes law [24].

Soil organic carbon (SOC) was analyzed by dry combustion with a TOC-5050A apparatus (Shimadzu Scientific Instruments, MD, USA). Elemental analysis of the soils was performed with a CHN 1000 elemental analyzer (Leco Corporation, Mönchengladbach, Germany). The specific surface area was determined by the BET method at -196 °C considering a nitrogen molecular area of 0.162 nm<sup>2</sup> and using an Autosorb-1 apparatus (Quantachrome Corporation, FL, USA). Calculation was performed on an oven dry basis (110 °C) of the sample mass. The extent of microporosity was calculated from the nitrogen adsorption isotherms. The amount of oxides in the samples was determined by wavelength dispersive X-ray fluorescence spectroscopy (WDXRF) in pellets prepared by fusion of the samples with Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (Merck, Darmstadt, Germany) (1 g dried sample + 7 g Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) using a S4 Pioneer spectrometer (Bruker axs, Karlsruhe, Germany) working with a Rh tube (60 kV). Additionally, two Chinese stream sediments GBW 07309 and GBW 07310 were analyzed as reference materials. The deviation between the measured and the

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