



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_{As} kg_{soil}⁻¹ (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⁻¹ 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⁻¹ [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⁻¹ and 0.4 mg kg⁻¹ (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].

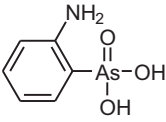
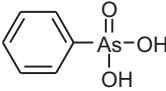
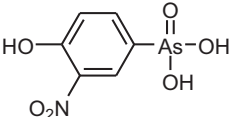
Upon arsenic, the adsorption characteristics of forest, arid zone, clay, silt loam and Ultisol soils have been examined [10]. Sorption of

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Table 1
Studied organoarsenic compounds and their properties.

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

^a pK_{a,1} corresponds to the deprotonation of the -NH₃⁺ substituent, pK_{a,2} and pK_{a,3} 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⁻¹ 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⁻¹ 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_a were performed with the Software pK_a DB from ACD Inc. taking the most probable tautomeric structure. The reported pK_a 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 nm² 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 Li₂B₄O₇ (Merck, Darmstadt, Germany) (1 g dried sample + 7 g Li₂B₄O₇) 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

certified values lie between 0.5 and 5.2% for the main components.

2.4. Sorption experiments

The adsorption isotherm measurements of AA, PA and RO were carried out in two trials: (i) soils were used with moisture at field capacity in order to preserve the organic fraction and to avoid irreversible changes of the soil surface and (ii) using oven-dried soil attempting to enhance the interaction of the soil minerals with arsenic leading to transformation products. Field capacity moisture was achieved during 24 h by the use of a hygostat [20]. The arsenic concentrations in (i) were in the $\mu\text{g L}^{-1}$ range and in (ii) at mg L^{-1} levels.

The soil samples were not sterilized to avoid modification of their properties and to represent natural field conditions. In the kinetic trials, 3 mL of a solution containing 50 mg L^{-1} of PA were added to each soil (707 μm sieved fraction) without pH adjustment. For (i) the concentration range for total arsenic was 25–500 $\mu\text{g L}^{-1}$. For (ii), the arsenic concentrations varied within 10–170 for AA, 10–190 for RO, and 10–570 mg L^{-1} for PA.

The soil/solution suspensions were shaken manually for 5 min. After that, the vessels were thermostated at 25°C under static conditions. Appropriated aliquots were taken at different time intervals for the kinetic experiments and after 24 h for the sorption isotherms. Afterwards, the samples were centrifuged for 30 min at 13,000 rpm and filtered with a Minisart RC 0.20 μm syringe filter (Sartorius, Germany). The liquid phase was stored at 5°C . Experiments for total arsenic retention were performed as follows: 100 mg of soil were equilibrated with 3 mL of a 0.01 M phenylarsonic acid solution for 24 h at 25°C . The liquid phase was collected as described before. The adsorbed amounts and the standard deviation of the adsorption parameters were calculated, respectively, according to the expressions: $a = V(C_0 - C_{\text{eq}})/m$ and $\text{SD} = \sqrt{\sum_{i=1}^N (y - y^{\text{calc}})^2 / (N - 1)}$; $y = (C_{\text{eq}}/a)$, where a is the amount of adsorbed As quantified in mg kg^{-1} expressed on a dry soil basis, V the volume in the adsorption cell, m the mass of adsorbent; and C_0 and C_{eq} are the initial and equilibrium concentrations, respectively.

2.5. Analytical methods

The solution that resulted from the sorption equilibrium was separated from the exhausted adsorbent and analyzed by UV-vis spectrophotometry using a Beckman DU 7500 spectrophotometer (Beckman Coulter, CA, USA) at 241 nm for AA, 262 nm for PA, and 340 nm for RO, respectively. The corresponding calibration graphs exhibited R^2 varying from 0.983 to 0.999, LOD (limit of determination) of $1\text{--}6 \text{ mg L}^{-1}$ (6σ). Solutions for the low range concentrations were analyzed by means of flow injection-ICPMS. For this purpose an HPLC instrument consisting of an LC series 1100 with degasser, binary pump, thermostated autosampler (Agilent Technologies, USA) coupled with ICPMS VG PQ Excell (Thermo Fisher Scientific, USA) was used. The ion intensity at m/z 75 was monitored. The corresponding calibration curves showed R^2 ranging from 0.984 to 0.999 within the working concentration range and LOD of $2 \mu\text{g L}^{-1}$ (6σ).

For arsenic speciation, the samples were analyzed using an HPLC-ICPMS system consisting of $\mu\text{-LC}$ Series 1100 (Degasser, binary pump, thermostated autosampler) coupled with ICP-MS 7500ce and ESI-qMS 6130 in parallel (Agilent Technologies, USA) by splitting the mobile phase by a T-piece. The injection volume was $8 \mu\text{L}$. For quantification of the phenylarsonic compounds, the ICP-MS peaks at m/z 75 (As) after chromatographic separation were considered. The column used was Atlantis[®] dC18 5 μm

Table 2

Percent chemical composition and physical properties of the studied soils.

| Oxides content and physical properties | Acrisol | Andosol | Tepetate |
|---|-------------|-------------|-------------|
| Na ₂ O | 0.180 | 0.772 | 2.913 |
| MgO | 0.318 | 1.149 | 1.427 |
| Al ₂ O ₃ | 26.87 | 26.84 | 18.93 |
| SiO ₂ | 46.53 | 45.611 | 59.24 |
| P ₂ O ₅ | 0.184 | 0.190 | 0.061 |
| K ₂ O | 0.356 | 0.626 | 0.989 |
| CaO | 0.262 | 1.603 | 4.064 |
| TiO ₂ | 2.087 | 1.192 | 1.117 |
| MnO | 0.168 | 0.056 | 0.058 |
| Fe ₂ O ₃ | 11.01 | 7.436 | 5.947 |
| C | 1.84 ± 0.12 | 3.82 ± 0.01 | 0.79 ± 0.05 |
| H | 2.68 ± 0.11 | 3.57 ± 0.20 | 2.25 ± 0.12 |
| Total nitrogen | 0.1 | 0.27 | 0.02 |
| Soil organic carbon (SOC), % | 1.2 | 3.1 | 0.3 |
| Leached carbonates, $\mu\text{g g}^{-1}$ | 0.7 | 0.3 | 1.7 |
| Theoretical exchange capacity, $\text{cmol}_c \text{ kg}^{-1}$ | 6.4 | 23.2 | 53.3 |
| Soil moisture (not sieved, oven dry), % | 2.1 | 22.4 | 2.5 |
| Soil moisture (500 μm , oven dry), % | 2.9 | 6.2 | 2.9 |
| Water at field capacity (500 μm), % | 35.0 | 36.5 | 24.0 |
| Textural classification | Clay | Silty loam | Clay loam |
| Specific surface (500 μm), $\text{m}^2 \text{ g}^{-1}$ | 72 | 136 | 83 |
| Total pore volume (500 μm), $\text{cm}^3 \text{ g}^{-1}$ | 0.22 | 0.19 | 0.20 |
| Micropore volume, % | 9.8 | 26.1 | 13.7 |
| Conductivity in water, dS m^{-1} | 30 | 16 | 15 |
| pH in water (dosage 33 g L^{-1}) | 5.9 | 6.5 | 6.8 |
| pH _{pzc} | 3.7 | 6.0 | 5.2 |
| Adsorption equilibrium pH _{ads} (dosage 33 g L^{-1}) | 4.2–4.4 | 5.6–5.7 | 4.4–4.6 |

(150 × 4.6 mm); eluent A: 0.1% HCOOH, 0.1% CH₃OH; eluent B: 0.1% HCOOH, 20% CH₃OH) and the gradient was: 0–3 min 100% A; 3–20 min 25% A (linear); 20–30 min 25% A; 30–31 min 100% A; 31–35 min 100% A. Quantification of arsenite and arsenate was performed using HPLC-ICPMS with an anion exchange column IonPack AS7 from Dionex (USA) as in Ref. [25]. The error in the calculation of the species concentration and thus in the retention did not exceed 3%.

3. Results and discussion

3.1. Soil characteristics

Characteristics of the soils not reported in previous publications [19,21,22] are gathered in Table 2. For the Tepetate soil, the theoretical exchange capacity value is higher than the exchange capacity of the Acrisol and Andosol soil samples used in this work. As seen from the values presented in Table 2, the Andosol soil exhibits the highest moisture level and water at field capacity, which is congruent with a greater magnitude of the specific surface. The three soils exhibit micro and mesoporosity in a different extent and their texture is clay, silty loam and clay loam. They displayed acidic character, with acidity decreasing in the order: Acrisol > Tepetate > Andosol.

3.2. Sorption kinetics

The sorption of RO changed with time depending on the soil type [5]. We chose PA as a representative compound of phenylarsonicals to study the sorption kinetics on the three soil samples. PA, being the smallest and less polar molecule among the studied

Table 3
Kinetic adsorption parameters of phenylarsonic acid.

| Soil | $k_2, \text{kg g}^{-1} \text{h}^{-1}$ | R^2 | $k_i, \text{g kg}^{-1} \text{h}^{-0.5}$ | $D, \text{cm}^2 \text{h}^{-1}$ |
|----------|---------------------------------------|-------|---|--------------------------------|
| Acrisol | 0.2 | 0.993 | – | – |
| Andosol | 0.7 | 0.996 | 16.3 | 1.4×10^{-4} |
| Tepetate | 9.2 | 0.998 | – | – |

phenylarsenicals (see Table 1), should exhibit the lowest adsorption energy, since this magnitude is proportional to the adsorbate size [26]. The Acrisol and Andosol soils sorbed a higher amount of PA after 10 h, while equilibrium was reached readily on the Tepetate soil. Despite differences in the time necessary to reach equilibrium, the experimental setup for the following investigations consisted of an equilibrium time of 24 h.

For the calculation of the sorption rate of PA, two models were employed [27]. Using the pseudo-first order or Lagergren equation, we obtained low R^2 values and the predicted amount sorbed at equilibrium a_e did not agree with the experimental magnitude. Testing the Ho's second order equation, linear regression plots were obtained with values of the determination coefficient $R^2 > 0.993$. The magnitudes of the pseudo-second order kinetic constant k_2 are presented in Table 3. The Weber and Morris equation [28] was employed to determine the intraparticle diffusion rate constant k_i . The results were different for the three soils. The plot of the sorbed amounts vs. the square root of the contact time yielded a straight line passing through the origin ($R^2 = 0.951$) only for Andosol, the soil with the largest extent of microporosity. This indicates congruently that diffusion into the micropores was the rate limiting step. Assuming that the solid phase consisted of spherical particles with radius r , the diffusion coefficient ($D = 0.03r^2k_2a_e$) [29] calculated for PA in Andosol and given in Table 3, was comparable to that for arsenite and arsenate on laterite reported in Ref. [30]. For the other soils, Acrisol and Tepetate, sorption processes might be described by the external mass transfer since the diffusion equations did not describe the experimental values.

3.3. Retention by soils with moisture at field capacity

In the present work, the sorption of the phenylarsenicals on soils differing in iron content and chemical composition, as well as in surface charge and textural properties was studied. The Langmuir and Freundlich sorption equations are the most commonly used. The adsorption isotherms of the phenylarsenicals are depicted in Fig. 1. This type of isotherm has been reported for roxarsone sorbed on litter amended and control soils from VA, USA in the initial concentration range 100–1000 $\mu\text{g L}^{-1}$ [5]. The Henry equation described well the adsorption equilibrium at low concentrations, so it was used for the examination of the sorption of

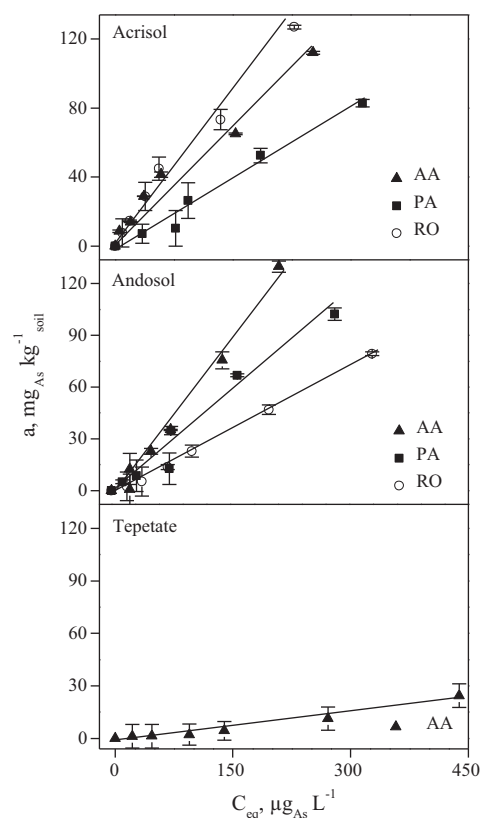


Fig. 1. Sorption isotherms at 25 °C of $\mu\text{g L}^{-1}$ concentrations of: o-arsanilic acid (AA), phenylarsonic acid (PA) and roxarsone (RO) by the Acrisol, Andosol and Tepetate soils (500 μm particles) at field moisture capacity and adsorbent dosage 3.3 g L^{-1} .

the phenylarsenicals in concentrations close to the environmental conditions.

The surface-normalized k_H -values presented in Table 4 are expressed per square meter of the 500 μm particles of soil at field water capacity. They show the following features: (i) the partitioning of AA acid and RO is similar on the Acrisol soil; (ii) partitioning of AA is the lowest on the Tepetate soil; and (iii) the Tepetate soil exhibits no adsorption of PA and RO. On the Ap and Bt1 soil horizons the partition coefficient of roxarsone was 5 and 260 L kg^{-1} , respectively, as reported in Ref. [5]. In comparison, our values are 540 and 231 L kg^{-1} on Acrisol and Andosol soils, respectively. The partition coefficient obtained in this study for o-arsanilic acid on Acrisol and Andosol soils are two orders of magnitude higher than those of the sorption investigation of p-arsanilic acid on iron (oxyhydro)oxides [31] calculated from Langmuir sorption constants in

Table 4
Adsorption equilibrium characteristics in the low and high concentration range.

| Organoarsenical | Henry adsorption constant by soils (500 μm) at field capacity $k_H \times 10^3, \text{L m}^{-2}$ $a = k_H C$ | | | Tóth equation and adsorption constants by the dried soil Acrisol (707 μm) $a = a_m C / (1/k_T + C^n)^{1/n}$ | | LF equation and adsorption constants by the dried soil Acrisol (707 μm) $a = a_m k C^n / (1/k_{LF} C^n)$ | |
|-------------------------|---|-------------------------------------|-------------------------------------|--|------------------------------------|---|-------------------------------------|
| | Acrisol | Andosol | Tepetate | $k_T, \mu\text{g As L}^{-1}$ | $a_m, \text{g As kg soil}^{-1}$ | $k_{LF}, \mu\text{g As L}^{-1}$ | $a_m, \text{g As kg soil}^{-1}$ |
| o-Arsanilic acid (AA) | 6.3 (R^2 0.97305) (SD 0.9) | 4.2 (R^2 0.98302) (SD 1.1) | 0.5 (R^2 0.95945) (SD 2.7) | 5.9 | 3.0 (R^2 0.9935) (SD 0.1) | 4.5 | 3.4 (R^2 0.9915) (SD 0.2) |
| Phenylarsonic acid (PA) | 3.7 (R^2 0.98276) (SD 1.7) | 2.7 (R^2 0.97631) (SD 1.5) | No adsorption | 0.7 | 8.9 (R^2 0.9714) (SD 0.6) | 0.7 | 10.9 (R^2 0.9678) (SD 1.2) |
| Roxarsone (RO) | 7.5 (R^2 0.98367) (SD 0.4) | 1.7 (R^2 0.99569) (SD 2.3) | No adsorption | 10.6 | 1.8 (R^2 0.9821) (SD 0.4) | 9.1 | 1.9 (R^2 0.9828) (SD 0.4) |

the submonolayer region. In contrast, the difference in regard to the Tepetate soil is only one order of magnitude higher.

3.4. Effect of moisture

The previous section described the results of the retention of phenylarsenicals in the $\mu\text{g L}^{-1}$ concentration range on soils with moisture at field capacity. Wishing to observe diverse transformation products of phenylarsenicals as a result of their interaction with the soil, we verified the retention on Andosol, dry and at field capacity. For this purpose, concentration was set up in the mg L^{-1} level. The soil (particle size $500 \mu\text{m}$) retained on a dry basis, $2.6 \pm 0.2 \text{ g}_{\text{As}} \text{ kg}^{-1}$ with moisture at field capacity and $3.0 \pm 0.3 \text{ g}_{\text{As}} \text{ kg}^{-1}$ when it was oven dry. It is not inconceivable that the organic matter content (the highest in Andosol) played a role, but the difference in retention may be also associated with the modification of the specific surface magnitude by drying. Larger, $707 \mu\text{m}$ particles of oven dry soil retained, similarly to the dry $500 \mu\text{m}$ particles, $2.9 \pm 0.3 \text{ g}_{\text{As}} \text{ kg}^{-1}$ from a 500 mg L^{-1} solution of roxarsone. The feasibility to form irreversibly agglomerates with a larger size during drying is known for the Andosol clay fraction [32]. Therefore, the similarity in the retention capacity cannot be explained by the differences in the original particle sizes, but depend on the agglomerates formed by drying. From these results, two factors were considered for the further work: (i) the lower retention by oven dry soils should be favorable to obtain detectable amounts of newly formed products and (ii) the larger $707 \mu\text{m}$ particles were an abundant fraction in the three soil samples.

3.5. Retention by oven dry soils

The Redlich–Peterson (RP), Tóth (T) and Langmuir–Freundlich (LF) equations describe sorption on heterogeneous surfaces and are well suited for heterogeneous surfaces as soils [33]. The RP approaches the linear isotherm (Henry's equation) at low concentrations and was already used to evaluate partition on the soils with moisture at field capacity in Section 3.3. The T equation gives a linear plot throughout the intermediate concentrations range and the LF curve approaches a maximum at high concentration. For this reason, we decided to evaluate the sorption of the phenylarsenicals in the mg L^{-1} concentration range on the oven-dried soil samples ($707 \mu\text{m}$) by the T and LF equations.

The results for the three soils were significantly different. Fig. 2 shows the sorption isotherms. The studied organoarsenicals exhibited asymptotic isotherms only on the Acrisol soil indicating its saturation capacity. The Andosol and Tepetate soils exhibited a high affinity as in the low concentration range (see Fig. 1). Table 4 presents the saturation capacity as evaluated by the T and LF equations, whereby the value of the heterogeneity coefficient n 0.95 yielded the best fit.

The different adsorption isotherms obtained with the Acrisol and Andosol soils can be explained firstly, on the basis of the different dry mass moisture since the differences in the specific surface are negligible (see Table 2). Moisture favors solvation and hydrogen bonding of the anionic phenylarsenicals retained in the Andosol soil. On the contrary, the Acrisol soil may involve coordination adsorption mechanisms due to its high iron content. Complementary, the manganese concentration is higher also in the Acrisol sample. This would explain the saturation capacity of the Acrisol soil. As known, adsorption of arsenic on soil depends partially on the adsorption capacity of the iron and manganese colloids [10]. The results presented in Table 4 for the Acrisol soil show a slightly better fit to the Tóth in comparison with the Langmuir–Freundlich equation. With the diminution of the molecular volume, the k_T values: $\text{RO} > \text{AA} > \text{PA}$ decrease, whereas the a_m magnitudes: $\text{RO} < \text{AA} < \text{PA}$ increase.

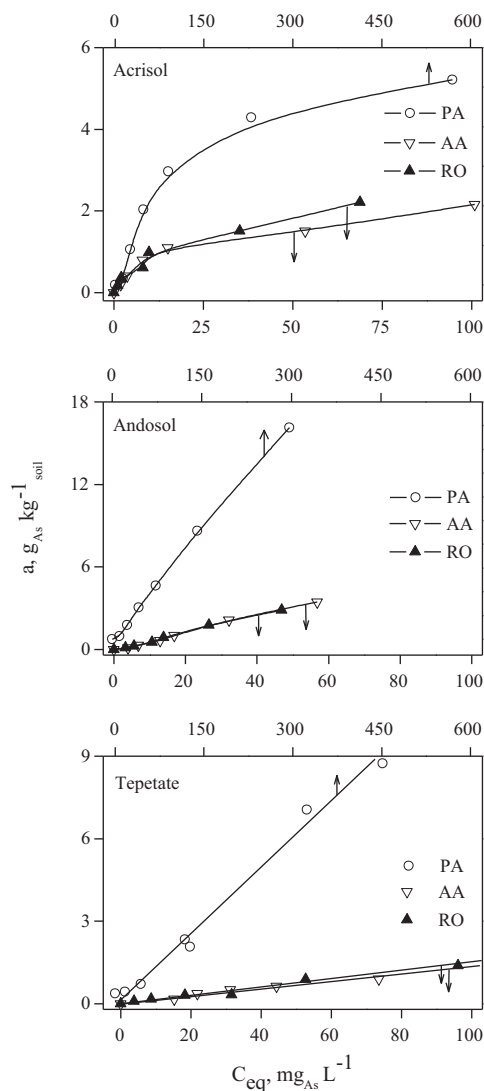


Fig. 2. Sorption isotherms at 25 °C of mg L^{-1} concentrations of: o-arsanilic acid (AA), phenylarsonic acid (PA) and roxarsone (RO) by the Acrisol, Andosol and Tepetate oven-dry soils ($707 \mu\text{m}$ particles) and adsorbent dosage 33.3 g L^{-1} .

The sorption of the three phenylarsenicals by the Andosol and Tepetate soils exhibits a less common C-type “constant partitioning” isotherm also in the mg L^{-1} concentration range (compare Figs. 1 and 2). According to Giles classification [34], the form suggests a constant partitioning of the organoarsenical between water and the adsorbing soil or/and penetration of the solute into the substrate micropores [35]. Here then, the form is related with the microporosity of the studied soils, since Andosol and Tepetate display a higher micropore volume in comparison with Acrisol.

The soils exhibited an acidic character (see pH_{pzc} in Table 2). We might expect that the surface was positively charged in the case of Andosol soil since $\text{pH}_{\text{pzc}} > \text{pH}_{\text{ads}}$ (see pH values in Table 2). Acrisol and Tepetate were negatively charged because ($\text{pH}_{\text{pzc}} < \text{pH}_{\text{ads}}$). On the other side, the three arsenic compounds are found with a net charge of -1 (see pK_a in Table 1 and pH_{ads} in Table 2) favoring the electrostatic interaction with Andosol. Electrostatic repulsion with the Acrisol soil could not explain the retention percentage by this soil in Table 5: $\text{Andosol} \geq \text{Acrisol} > \text{Tepetate}$. That means that not only electrostatic forces contributed to the sorption but also coordination mechanisms, whereby the retention percentage of the phenylarsenicals (Table 5) followed the series: $\text{RO} > \text{AA} > \text{PA}$ and correlated congruently with the solubility parameter (see Table 1).

Table 5

Amounts of the studied organoarsenicals retained by volcanic soils and detected amounts of arsenite and arsenate formed in the system. Initial organoarsenical concentration 743 mg L⁻¹ As. Contact time, 24 h.

| Soil | Retention of the organoarsenical, % | | | Arsenite/arsenate in the solution, mg L ⁻¹ | | |
|----------|-------------------------------------|--------------------|-----------|---|--------------------|-----------|
| | o-Arsanilic acid | Phenylarsonic acid | Roxarsone | o-Arsanilic acid | Phenylarsonic acid | Roxarsone |
| Acrisol | 63.4 | 33.8 | 70.1 | 2.9/8.7 | 0.02/n.d. | 0.2/0.01 |
| Andosol | 68.4 | 43.5 | 76.9 | 0.9/6.2 | 0.02/n.d. | 0.46/0.25 |
| Tepetate | 52.5 | 10.9 | 79.1 | 3.0/7.3 | 0.01/n.d. | 0.05/0.02 |

n.d. = not detectable because peaks overlapped.

A clear effect of the finite iron oxide content on the retention suggesting interaction with the As(V) oxyanion [5] and leading to saturation, would not be found without the measurement of the sorption isotherms on the Acrisol soil.

3.6. Arsenic retention and transformation of phenylarsenicals

The retention of roxarsone (743 mg_{As} L⁻¹), the most polar compound among the studied phenylarsenicals, was the highest (see Table 5). After 24 and 88 h contact, only some slight differences in the retained amounts could be observed. However, Brown et al. [5] have observed that approximately 5% of the roxarsone was transformed to As(V). Arsenate was also the dominant arsenic species recovered in the roxarsone-containing litter at the end of soil stockpiling [8]. There are few reports studying the behavior of phenylarsonic acid in soil. Shimamoto and Takahashi [36] found 7–10% of inorganic arsenic in the solution when phenylarsonic acid was sorbed onto ferrihydrite at pH = 12.

Roxarsone decomposed [6] after 3–4 weeks in composted poultry litter into arsenite/arsenate, dimethylarsinate and traces of other unknown arsenic compounds due to biotic processes. Three unknown compounds of *m/z* 278 have been detected as metabolism products of soil bacteria related to *Ensifer adhaerens* in salt medium supplemented with diphenylarsinic acid [37]. Table 5 presents the

results of the transformation of AA, PA and RO to arsenite and arsenate. Speciation analysis of the current sorption equilibrium solutions demonstrated that besides arsenate and arsenite, other arsenic-containing compounds were present in the solutions after short contact with the soils.

The use of high concentrations of the phenylarsenicals in our experiments evidences the presence of more than three arsenic containing compounds. Fig. 3 presents selected chromatograms, where the complex composition of the solution of roxarsone after 24 h in contact with the three soils under investigation can be appreciated. Considering the element-selective detection used here, the peaks marked as “M₁”–“M₆” are metabolism products consisting of arsenic-containing compounds. In the case of M₂–M₆, they show higher retention times, thus their polarity is lower than that of roxarsone. M₁ reveals higher polarity by eluting at a shorter retention time. The identification of three of the structures of the “M_i” arsenic-containing compounds has been published recently [38].

4. Conclusions

Phenylarsonic acid was retained and diffused into the micropores of the volcanic soil Andosol. Roxarsone sorbed on volcanic soils similarly as on Frederick series soils. The volcanic soil Tepetate did not retain phenylarsonic acid and roxarsone from solutions in the environmentally relevant concentrations range. The most polar compound roxarsone was retained in a higher extent by the studied volcanic soils. Besides arsenite and arsenate, new arsenic-containing compounds were detected.

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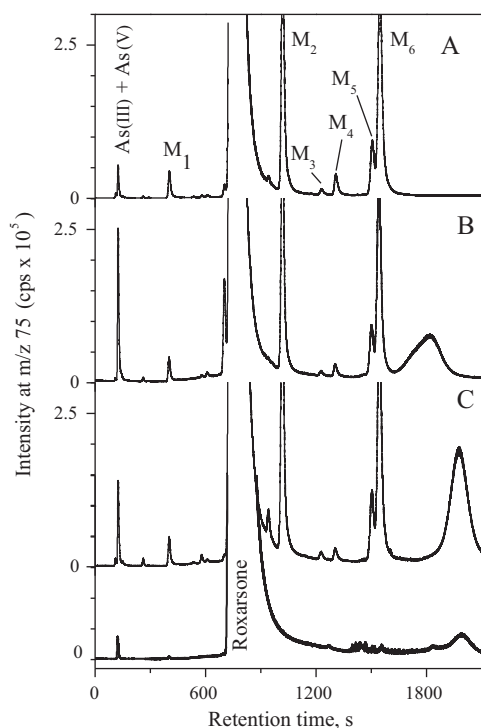


Fig. 3. Chromatograms of 743 mg L⁻¹ arsenic in roxarsone (thick line) and after 24 h contact with soils (A–C). A: Tepetate; B: Andosol; C: Acrisol. “M_i” are metabolism arsenic-containing compounds.

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