



Transport of gadolinium- and arsenic-based pharmaceuticals in saturated soil under various redox conditions



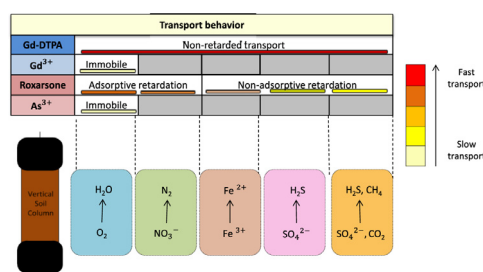
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HIGHLIGHTS

- Transport of Gd-DTPA, ROX, and respective metals in soil columns were studied.
- The respective metal salts showed reduced mobility.
- Gd-DTPA behaved as a conservative tracer.
- ROX showed delayed transport under stronger biologically-reduced conditions.
- A mechanism for ROX delayed behavior is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

The release of pharmaceuticals and personal care products (PPCPs) to the soil–water environment necessitates understanding of PPCP transport behavior under conditions that account for dynamic flow and varying redox states. This study investigates the transport of two organometallic PPCPs, Gd-DTPA and roxarsone (arsenic compound) and their metal salts (Gd(NO₃)₃, AsNaO₂); Gd-DTPA is used widely as a contrasting agent for MRI, while roxarsone is applied extensively as a food additive in the broiler poultry industry. Here, we present column experiments using sand and Mediterranean red sandy clay soil, performed under several redox conditions. The metal salts were almost completely immobile. In contrast, transport of Gd-DTPA and roxarsone was affected by the soil type. Roxarsone was also affected by the different redox conditions, showing delayed breakthrough curves as the redox potential became more negative due to biological activity (chemically-strong reducing conditions did not affect the transport). Mechanisms that include adsorptive retardation for aerobic and nitrate-reducing conditions, and non-adsorptive retardation for iron-reducing, sulfate-reducing and biologically-strong reducing conditions, are suggested to explain the roxarsone behavior. Gd-DTPA is found to be a stable complex, with potential for high mobility in groundwater systems, whereas roxarsone transport through groundwater systems is affected by redox environments, demonstrating high mobility under aerobic and nitrate-reducing conditions and delayed transport under iron-reducing, sulfate-reducing and biologically-strong reducing conditions.

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1. Introduction

Pharmaceuticals and personal care products (PPCPs) encompass a wide range of chemicals, and are found in almost every facet of

modern human life. The PPCP industry is developing continuously and PPCP output is increasing exponentially, adding to the already large array of chemical classes in the environment (Daughton and Ternes, 1999). PPCP presence in the soil–water environment results from continuous disposal by different sources, via domestic and industrial sewage systems, wet-weather runoff, landfill leachate (Christensen et al., 1993; Andreozzi et al., 2003; Yaron et al., 2012),

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and use of raw and treated wastewater for irrigation (Ternes et al., 2004), as well as by application of animal manure and sewage sludge as fertilizer in agricultural soils (Jones et al., 2001; Carballa et al., 2004).

In soil-subsurface systems, redox reactions are ubiquitous. The sequence of redox processes depends on the difference in energy released by microorganisms that utilize carbon sources (e.g., Barbieri et al., 2011). While it is known that redox conditions in the soil-subsurface regime affect the fate of PPCPs (Mompelat et al., 2009; Barbieri et al., 2011; Banzhaf et al., 2012), few studies have actually investigated PPCP behavior in groundwater as a function of redox environments. Barbieri et al. (2012) examined two pharmaceuticals in a series of batch experiments with natural aquifer material, under nitrate-reducing conditions. They found that the aromatic amines of diclofenac and sulfamethoxazole could be temporarily and reversibly affected by denitrifying conditions. Banzhaf et al. (2012) investigated the influence of specific redox conditions on transport of four pharmaceuticals in a laboratory column experiment at varying nitrate concentrations, and demonstrated that changes in nitrate concentration might have a strong influence on the degradation of these pharmaceuticals.

We focus here on Gd-DTPA and roxarsone, two representative PPCPs used extensively in medical applications and animal husbandry, respectively, and detected in the aquatic environment (as parent compound or metabolites) at concentrations of $\text{ng-}\mu\text{g L}^{-1}$ (Kulaksiz and Bau, 2011; Yaron et al., 2012).

Gd-DTPA is a complex of gadolinium with a chelating agent, diethylenetriamine penta-acetic acid (Supplementary material, S1). Gd-DTPA is a common MRI contrasting agent used in more than 5 million applications annually, in 101 countries (Knopp et al., 2006), and between 22 and 66 tons of Gd for contrast agent applications are used each year worldwide (Kulaksiz and Bau, 2011). Due to high Gd-DTPA stability, it is almost chemically inert within the human body, and together with its high hydrophilicity, it is excreted unchanged from the body in urine within a few hours (Weinmann et al., 1983; Bau and Dulski, 1996). After Gd-DTPA excretion from the body, it is discharged into public sewage systems mostly via hospital wastewater (Kümmerer, 2001).

As Gd-DTPA readily passes through wastewater treatment plants, it contaminates surface water (Howard, 2007), and may reach groundwater by irrigation with raw and treated wastewater or by landfill leachate from improper disposal. Gd-DTPA is highly mobile in the soil-subsurface due to its high stability, polarity and water solubility, which prevents it from being adsorbed by particulate matter or undergoing ion exchange with clay minerals (Howard, 2007; Möller et al., 2011). In contrast, the free ion Gd^{3+} has a high affinity to aquifer material, and in the soil-subsurface it is adsorbed immediately onto colloids, clay minerals and suspended material. Gd-DTPA is reported to have a half-life of >100 days and it may dissociate in the aquatic environment by transmetallation, photodegradation, and biodegradation. These processes depend on redox states and other environmental conditions (Holzbecher et al., 2005; Möller et al., 2011).

Roxarsone (ROX; 4-hydroxy-3-nitrobenzenearsonic acid) is an aromatic organoarsenic compound (Supplementary material, S1). ROX is used extensively in the broiler poultry industry as a feed additive to promote growth, to improve meat pigmentation, and to prevent coccidiosis, which is a common parasitic disease in poultry chickens. ROX was first used in the 1940s, and became so widespread that approximately 70% of broiler chickens produced in the United States were fed ROX (Cortinas et al., 2006; Nachman et al., 2013). This led to use of almost one million kg per year in the USA (Chen and Huang, 2012). Since 2011, ROX was banned for use in the USA, but it is still used extensively in other countries (D'Angelo et al., 2012). Literature mentions that between 36 and 88% of the total arsenic in the litter of chickens fed with ROX is un-

altered ROX. The remaining As is mostly inorganic arsenate (As(V)), with minor traces of dimethylarsenic acid (DMA(V)) and unidentified As species originating from metabolism of ROX (Covey et al., 2010).

ROX may undergo biotic and abiotic transformation, resulting in toxic and mobile arsenic species. ROX is degraded rapidly during composting of litter, during storage and land application of litter, and in leachates from fields. Degradation products include inorganic As(V) and As(III) , known to be the most toxic arsenic compounds, as well as a variety of organic arsenicals (O'Connor et al., 2005; Komorowicz and Baralkiewicz, 2011), depending on pH, redox conditions (Covey et al., 2010), interaction with minerals, and organic matter in soils and aquifer sediments (Brown et al., 2005). There are three main biotransformation processes of arsenic in the environment: redox transformation between As(V) and As(III) , reduction and methylation of arsenic, and biosynthesis of organo-arsenic compounds (Yaron et al., 2012). Complexation of As(V) and As(III) with dissolved organic matter in natural environments prevents sorption and co-precipitation with the solid phase, resulting in high mobility; see Supplementary material (S1) for structure and details on arsenic compound mobility.

The present study focuses on the transport of Gd-DTPA and ROX under different redox conditions pertinent to natural soil-subsurface systems. The transport is characterized by column experiments, under saturated steady-state flow, as a function of different redox conditions. The effects of porous medium type (natural soil vs. sand) and of the particular species (compound vs. corresponding salt) on the transport are examined systematically.

2. Materials and methods

2.1. Materials

Gd-DTPA, (0.5 M) was obtained from Soreq Radiopharmaceuticals and roxarsone from Sigma. Bet Dagan soil, a Mediterranean red sandy clay soil, was sieved (0.250 mm) and used throughout the study. A list of all other chemicals and soil properties is given in Supplementary material (S2, S3).

2.2. Column experiments

Vertical column experiments were performed to study the transport behavior of Gd-DTPA, Gd salt ($\text{Gd(NO}_3)_3$), ROX, and As salt (AsNaO_2) under saturated flow and different environmental conditions. Plexiglas columns (19 cm high, 3.2 cm inner diameter, with total volume of 152.8 cm^3) were packed with sand or Bet-Dagan soil and placed vertically in the experimental system, as shown in Fig. S1. Sand columns were used as a control, employing two redox conditions, (1) aerobic conditions, and (2) strong chemically-induced reducing (SCIR) conditions, achieved by addition of a NaBH_4 solution. Bet Dagan soil columns were prepared with each of the following redox conditions by modifying a protocol of Barbieri et al. (2011), as described in the Supplementary material (S3): aerobic, nitrate-reducing, Fe(III) -reducing, sulfate-reducing, strong biologically-induced reducing (SBIR), and SCIR. Each redox condition was obtained by flowing a corresponding solution through packed columns with a peristaltic pump.

A (conservative) tracer test with 300 ppb NaBr was run to account for interactions between the analyte and the porous medium. The tracer test was run together with 1000 ppb As, supplied as ROX or the corresponding salt (AsNaO_2), or 500 ppb Gd, supplied as Gd-DTPA or 5000 ppb Gd from the corresponding salt ($\text{Gd(NO}_3)_3$). The tracer and the respective analyte were added to a solution that was prepared for each redox state, and the resulting solution was introduced to the column by a long pulse of 1–5 pore volumes (PV) for Gd-DTPA, and 1–24 PV for ROX and

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