



Transport of oxaliplatin species in water-saturated natural soil

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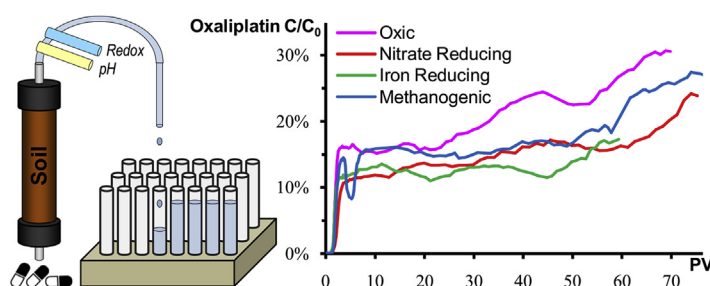
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HIGHLIGHTS

- Oxaliplatin transport is studied in fully saturated sand/soil-water columns.
- Sand exhibits low retention that is largely unaffected by added chelators.
- In soil, sorption is strongest under Fe-reducing regime, weakest under oxic regime.
- Increased concentrations of K^+ and Na^+ in the inlet solution weaken sorption.

GRAPHICAL ABSTRACT



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ABSTRACT

This study reports the transport characteristics of the organometallic anticancer compound oxaliplatin and its derivatives in natural soil-water environments. Although pharmaceuticals and their derivatives have for many years been detected in water resources, and linked to toxicological impacts on ecological systems, their transport in soil and groundwater is not fully understood. Specifically, studies that describe transport of organometallic pharmaceuticals in porous media are rare, and the transport characteristics of platinum complexes have received little attention. Oxaliplatin transport was studied in sand, as a function of two added natural chelators (citrate and humic acid), and in soil, under four continuously monitored, environmentally-relevant redox conditions: oxic, nitrate reducing, iron reducing and methanogenic. In sand, oxaliplatin species retention was about 7%, and affected only mildly by added citrate, and by humic acid under buffered pH. Transport with unbuffered humic acid was affected significantly by pH variations, and exhibited strong retention at $pH < 8$. In soil, unexpectedly similar breakthrough patterns of oxaliplatin species were found for all redox conditions, exhibiting linear, reversible retention of 79–87%. The strongest retention was observed under iron reducing conditions, whereas the weakest retention was under oxic conditions. Increased cation activity appears to promote weaker sorption. The results indicate that soil composition is the leading factor affecting oxaliplatin species mobility and fate in the soil-water environment, followed by the weaker factors of redox conditions and cation activities.

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1. Introduction

Over the last decades, many pharmaceuticals have become recognized as widespread, potential emerging pollutants (Monteiro

and Boxall, 2010; Li, 2014; Ebele et al., 2017). However, the chemical processes affecting pharmaceutical transport and transformation in natural environments, as well as the associated health risks, are not well understood to date (Arnold et al., 2014; Vasquez et al., 2014; Ebele et al., 2017).

Many of the pharmaceutical compounds that reach wastewater treatment plants are unaffected (partially or completely) by

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wastewater treatment processes (Monteiro and Boxall, 2010; Jelic et al., 2011), and pharmaceuticals ultimately reach surface water and groundwater (Monteiro and Boxall, 2010; Li, 2014; Ebele et al., 2017). Many of the pharmaceutical pathways to water resources include infiltration through soil and interaction with it. Soil and soil solution properties, such as particle size distribution, mineral composition, organic matter, pH, cation exchange capacity (CEC) and redox, have a significant impact on the transport properties and fate of the introduced pharmaceutical pollutants (Monteiro and Boxall, 2010; Burke et al., 2014; Kodesova et al., 2015; Menahem et al., 2016). Generally, soil pH has been found to affect significantly the sorption of ionizable compounds (Kodesova et al., 2015). Redox conditions in soil were also shown to have a significant effect on the transport and fate of a variety of pharmaceuticals. It is further noted that soil and groundwater systems are rich in microbial activity that uses electron transfer processes to sustain life functions and reproduction (Essington, 2003).

Redox regimes affect both soil structure (Brookins, 1988) and contaminant transformation (Heberer et al., 2008; Massmann et al., 2008). A column experiment of Banzhaf et al. (2012) under water saturated conditions, with a nitrate gradient along the column, demonstrated the sensitivity of the examined pharmaceuticals to different nitrate concentrations, and indicated that the wide variation in behavior of the compound sulfamethoxazole in the literature may originate from the different redox conditions in each experiment; therefore a complete investigation and interpretation of pharmaceutical fate must address the redox conditions in aquatic environments. Burke et al. (2017) studied the transport of 20 wastewater-derived organic pollutants (most of which are pharmaceutical compounds) through saturated columns under four simulated environmental redox conditions; the degradation of ten pharmaceutical compounds was found to be redox-dependent. Menahem et al. (2016) explored the transport behavior of Gd and As organometallic pharmaceutical compounds in soil and sand under five simulated environmental redox conditions; the results demonstrated that As complexes are sensitive to different redox conditions, whereas the very stable Gd complex transport is unaffected by redox conditions. However, to the best of our knowledge, there are no transport studies of other organometallic pharmaceuticals.

Pharmaceuticals may also be biodegraded by soil biota; biodegradation is promoted or impeded by functional groups of a compound (Loonen et al., 1999; Bertelkamp et al., 2014). Most recently, de Wilt et al. (2018) demonstrated the influence of four different soil redox regimes on the sorption and biodegradation of six pharmaceutical compounds; sorption was found strongest under sulfate reducing and methanogenic anaerobic conditions. Optimal biodegradation rates, on the other hand, were either under aerobic or strongly anaerobic conditions. Moreover, the study showed that compound hydrophobicity and solution ionic strength did not affect sorption.

A prevalent class of organometallic pharmaceuticals involves platinum complexes used in anticancer therapy, such as cisplatin, carboplatin and oxaliplatin (Clarke and Sadler, 2013). In recent years, there has been growing concern regarding the occurrence and fate of these compounds, as they have been detected continuously in hospital effluents, surface water and groundwater at concentrations ranging from several pg/mL to >600 ng/mL (Kümmerer and Helmers, 1997; Di Francesco et al., 2002; Lenz et al., 2005, 2007; Vyas et al., 2014; Franquet-Griell et al., 2015; Ghafuria et al., 2017), while their removal by wastewater treatment processes is limited (Lenz et al., 2007; Ghafuria et al., 2017). Anticancer compounds and their transformation products are cytotoxic, and their indirect consumption (e.g., by drinking water or irrigated vegetables) may represent a potential health risk (Supalkova et al.,

2008; Easton et al., 2011; Fonseca et al., 2017).

This study reports the transport of oxaliplatin and oxaliplatin derivatives in saturated sand and soil columns. Oxaliplatin is a widely used, third-generation, anticancer compound that is typically used to treat colorectal cancer, and is on the 19th WHO Model List of Essential Medicines (WHO, 2015). Oxaliplatin features a square planar Pt(II) center, a bidentate ligand 1,2-diaminocyclohexane (dach), and a bidentate labile oxalate group (ox) (see Fig. S3.A in the Supplementary Data (SD)).

Several studies have addressed the reactivity and sorption of organometallic platinum pharmaceuticals in soil-water environments and wastewaters, e.g. (Lenz et al., 2005, 2007; Curtis et al., 2010; Turner and Mascorda, 2015; Vidmar et al., 2015). To date, however, it appears that there are no studies of Pt-based pharmaceuticals transport in aquifer systems, despite the potential risk of groundwater contamination by the cytostatic compounds (Ghafuria et al., 2017). Transport experiments mimic environmentally relevant, non-equilibrium (or quasi-equilibrium) conditions and reflect the mutual influence between the pharmaceutical transport mechanisms, i.e., advection, dispersion, diffusion, together with pharmaceutical interactions with soil, e.g., sorption, precipitation, biodegradation (Banzhaf and Hebig, 2016). Therefore, understanding contaminant transport characteristics in aquifer-like systems is important for ensuring safe groundwater consumption and improving water quality regulations and remediation solutions.

Complexation studies of oxaliplatin and similarly structured Pt derivatives indicate that oxaliplatin is a reactive substance, mostly through the removal of the labile oxalate moiety (Lustig et al., 1996, 1998; Luo et al., 1999; Sures and Zimmermann, 2007). Recently, Turner and Mascorda (2015) studied the sorption of oxaliplatin, cisplatin and carboplatin to sediments in two types of natural waters, with different salinity (<0.1 vs. 3.20 g/kg), showing that the adsorption isotherms were linear for all three pharmaceuticals, under all conditions. In both types of water, oxaliplatin exhibited only a small difference in adsorption (following 24 h equilibration).

The goal of the present study was to determine the previously uninvestigated transport behavior of oxaliplatin in natural sand and soil, by conducting flow-through experiments in water-saturated columns, and examining the effect of pH, soil type, chelators and four environmentally relevant redox conditions (oxic, nitrate reducing, iron reducing, and methanogenic conditions).

2. Materials and methods

2.1. Materials

Oxaliplatin ($C_8H_{12}N_2O_4Pt$, pharmaceutical secondary standard), humic acid sodium salt (tech.), $Na_3C_6H_5O_7 \cdot 2H_2O$, KNO_3 , HCl 37% (ACS), $HNO_3 \geq 69.0\%$ (TraceSELECT), $NaCH_3COO$ anhydrous ($\geq 99\%$) were obtained from Sigma Aldrich, Israel. $MgSO_4 \cdot 7H_2O$ (purum p.a. $\geq 99\%$) was obtained from Fluka. KBr ($\geq 99.5\%$), $NaHCO_3$ ($\geq 99.5\%$), K_2HPO_4 anhydrous ($\geq 99\%$) were obtained from Merck. MeOH (HPLC Grade) and $CaCl_2$ anhydrous ($\geq 96\%$) were obtained from J.T. Baker. NH_4Cl ($\geq 99.5\%$) was obtained from Mallinckrodt Chemicals. NaOH was obtained from Bio-Lab LTD. Goethite synthesis and humic acid salt purification are described in Section 3 in the SD. All aqueous solutions were prepared with double deionized water (DDW, 18.2 M Ω cm).

2.2. Experimental setup

Soil was collected and sieved (250 μ m) from the upper 5 cm layer at the Weizmann Institute campus. The soil was characterized as loamy sand; detailed properties can be found in Tables 1 and S1.

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