Science of the Total Environment 650 (2019) 173–183

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Retention-release of ciprofloxacin and azithromycin in biosolids and biosolids-amended soils

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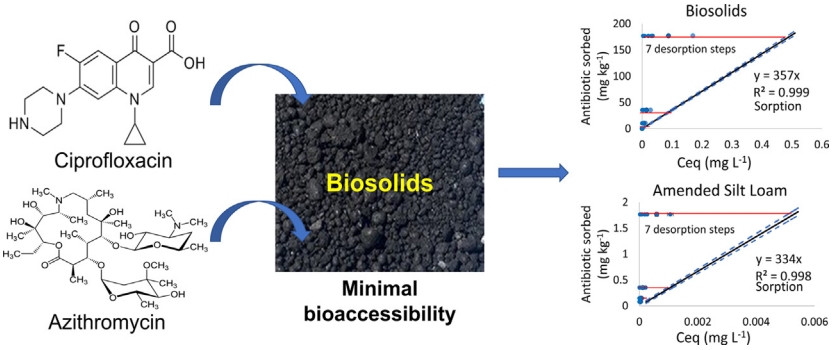
HIGHLIGHTS

- CIP and AZ extensively sorbed to biosolids and fine-textured soils.
- Desorption of biosolids-borne CIP and AZ was minimal.
- Biosolids control the retention-release behavior of biosolids-borne CIP and AZ.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 June 2018
Received in revised form 28 August 2018
Accepted 1 September 2018
Available online 03 September 2018

Editor: Jay Gan

Keywords:
Bioaccessibility
Biosolids
Antibiotics
Batch equilibration
DGT

ABSTRACT

Ciprofloxacin (CIP) and azithromycin (AZ) are commonly prescribed antibiotics, often found at elevated concentrations in treated sewage sludge (biosolids), and could pose human and ecological risks when land applied. Limited retention-release data preclude assessing potential risks from the target antibiotics in biosolids and biosolids-amended soils. The present work assessed sorption-desorption of CIP and AZ in biosolids and biosolids-amended soils using the "traditional" batch equilibration method. The batch equilibration method also included unamended soils for comparison. Release potentials of the biosolids-borne antibiotics were assessed via multiple desorption equilibrations in the presence of $CaCl_2$, soils, $PbCl_2$, or competing antibiotic (CIP versus AZ) solutions. Desorption kinetics of CIP from biosolids were also evaluated by the diffusive gradient in thin films technique (DGT), coupled with a diffusion transport-exchange model available in 2D-DIFs. Sorption of both antibiotics followed linear models with partitioning coefficient (K_d) values for CIP ranging between 40 and 334 L kg^{-1} in soils and 357 L kg^{-1} in biosolids, and values for AZ ranging between 11 and 202 L kg^{-1} in soils and 428 L kg^{-1} in biosolids. Antibiotic desorption from the biosolids was highly hysteretic (hysteresis coefficients < 0.003) and desorption of the biosolids-borne chemicals was extremely small (<3%) using any of the various desorption equilibration approaches. Desorption was hysteric in soils too; where desorption percentages were 4, 5, and 26% for CIP and 6, 32, and 50% for AZ in the silt loam soil, manured sand, and sand, respectively. CIP release from biosolids determined by DGT was also small (<1%), ascribed to low dissolved and labile concentrations in the solid phase and a small effective diffusion coefficient. Results obtained using equilibrium and dynamic approaches suggest that the target antibiotic bioaccessibilities from biosolids and finer-textured (typical agricultural) soils would be minimal and that biosolids (not soils) control desorption of the two biosolids-borne chemicals.

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https://doi.org/10.1016/j.scitotenv.2018.09.005
0048-9697/

1. Introduction

Ciprofloxacin (CIP) and azithromycin (AZ) are broad spectrum antibiotics that are often prescribed to treat bacterial infections in humans (Girardi et al., 2011; Parnham et al., 2014). Up to 60% of CIP (Girardi et al., 2011) and 75% of AZ (Zuckerman, 2000) is excreted from the human body as unchanged parent compound and can accumulate in treated sewage sludge (biosolids) at concentrations up to 5 mg AZ kg^{-1} (dw) and 41 mg CIP kg^{-1} (dw) (USEPA, 2009). The average (mean), median (50th percentile), and 95th percentile concentrations of CIP in US biosolids are 10.5 ± 17.7, 5.4, and 36.1 mg kg^{-1}, respectively (USEPA, 2009). Similarly, the average, median, and 95th percentile concentrations of AZ in US biosolids are 0.83 ± 2.3, 0.25, and 3.2 mg kg^{-1}, respectively. About half of biosolids produced in the USA are land applied to improve many soil characteristics (McLain et al., 2017). Based on the typical annual agronomic application rates of 1%(dw dw^{-1}), the nominal environmentally relevant CIP and AZ concentrations in biosolids-amended soils range between few μg to 0.36 (CIP) and 0.032 (AZ) mg kg^{-1} on dry weight basis. Persistence and numerous gaps in fate and toxicity data (USEPA, 2009; McClellan and Halden, 2010; Walters et al., 2010) raise concerns about the environmental fate, transport, and ecological effects of biosolids-borne target antibiotics. For example, hydroponic studies or studies utilizing unrealistic concentrations directly spiked to soils link CIP to plant uptake and phytotoxicity (Aristilde et al., 2010; Kipper et al., 2010; Lillenberg et al., 2010; Eggen et al., 2011) and adverse effects on soil microbes and microbially mediated nutrient cycling (Girardi et al., 2011; Cui et al., 2014). Potential antibiotic resistance development, spread, and associated risks are another cause for concern with land-applied antibiotics (Girardi et al., 2011; Munir and Xagoraraki, 2011; Bengtsson-Palme and Larsson, 2016).

Soil- and/or biosolids-specific bioavailability studies are critical for higher tier contaminant risk assessments, but such studies are resource and time intensive and are scarce for the target antibiotics. Bioaccessibility estimates (derived from desorption and partitioning data) can be useful first order approximations of antibiotic bioavailability in screening level risk assessments (Menz et al., 2018). One of the first steps needed to predict bioaccessibility of contaminants is to understand retention-release behavior when a chemical is deposited to the environment. Herein, bioaccessibility refers to the chemical concentration in solution phase, such as when the chemical is released from the solid to solution phase by desorption and diffusion in the solid matrix. Numerous studies have evaluated the retention behavior of the target antibiotics in soils and sorption equilibrium constants (K_d values) reportedly range between 100 and >45,000 L kg^{-1} for CIP (Nowara et al., 1997; Castela-Papin et al., 1999; Hari et al., 2005; Carmosini and Lee, 2009; Vasudevan et al., 2009; Aristilde and Sposito, 2013; Jiang et al., 2013; Goulas et al., 2016) and ~40 to 150 L kg^{-1} for AZ (Radović et al., 2016; Maier and Tjeerdema, 2018; Kaeseberg et al., 2018). However, relatively few studies have evaluated target antibiotic retention-release in biosolids and biosolids-amended soils, even though the residuals are common sources to the environment. In biosolids, K_d values of ~2500 to >19,000 L kg^{-1} for CIP (Wu et al., 2009; D'Angelo and Starnes, 2016) and ~250 to 380 L kg^{-1} for AZ (Göbel et al., 2005; Okuda et al., 2009) are reported. The wide spans in the reported K_d values likely reflect the numerous types of interactions that can occur between the various species/functional groups of the two antibiotics and those of the solid phases. Chemical structures (Fig. 1) and speciation (Fig. 2) reveal that both CIP and AZ possess cationic moieties throughout environmentally relevant pH range of 4 to 9. Both CIP and AZ cationic moieties can interact with negatively charged soil surfaces via a host of interactions involving non-specific columbic interactions and/or specific binding. These interactions are influenced by solid phase composition as well as target antibiotic pKa values (Fig. 1), which dictates antibiotic speciation (Fig. 2) in the environment at a particular pH. Interactions such as cation exchange and cation bridging with negatively-charged surface sites, H-bonding with electronegative F—, O—, COO—, and N groups, and pi-pi bonding between aromatic moieties are reported (Nowara et al., 1997; Hari et al., 2005; Carmosini and Lee, 2009; Vasudevan et al., 2009; Gong et al., 2012; Aristilde and Sposito, 2013; Jiang et al., 2013; Wu et al., 2013; de Sousa et al., 2018; Zhang et al., 2018). Additionally, CIP also has a negatively charged moiety (COO— function group; Fig. 1) through most of the environmentally relevant pH (5–9; Fig. 2) and anion exchange, cation bridging, and surface metal complexation can also contribute to CIP retention at pH values >6. Consequently, biosolids properties (e.g. pH, cation exchange capacity, metal oxides, organic matter, etc.) likely govern release/release behavior of the two biosolids-borne antibiotics. In addition to the aforementioned properties, soluble organic matter can competitively bind compounds such as CIP; decreasing sorption onto solid matrices and increasing bioaccessibility (Cheng et al., 2018). Hydrophobic interactions likely play a smaller role in sorption of cationic trace organic chemicals (TOrCs) such as CIP and AZ due to low octanol-water distribution ratios (D_{ow}) of the two antibiotics (Ericson, 2007; Carmosini and Lee, 2009; Gong et al., 2012; Aristilde and Sposito, 2013; Goulas et al., 2016). Hydrophobic interactions can contribute to AZ sorption at pH values greater than ~8.5 as neutral (AZ 0) species becomes important (Fig. 2), but pH values ≥8.5 are rare in the environment.

Assessing potential release is at least as important as sorption because it determines bioaccessibility (and ultimate bioavailability) of the biosolids-borne antibiotics over time. However, very few studies have evaluated desorption potential of antibiotics from soils, and studies pertaining to desorption of the target antibiotics in biosolids and biosolids-amended soils are scarce (CIP) or absent (AZ). To our knowledge, only one study focused on desorption kinetics of CIP from biosolids (D'Angelo and Starnes, 2016). The CIP desorption kinetics was shown to be slow (<4% in 10 d) due to slow diffusion and desorption kinetics. In that study, desorption kinetics were determined using

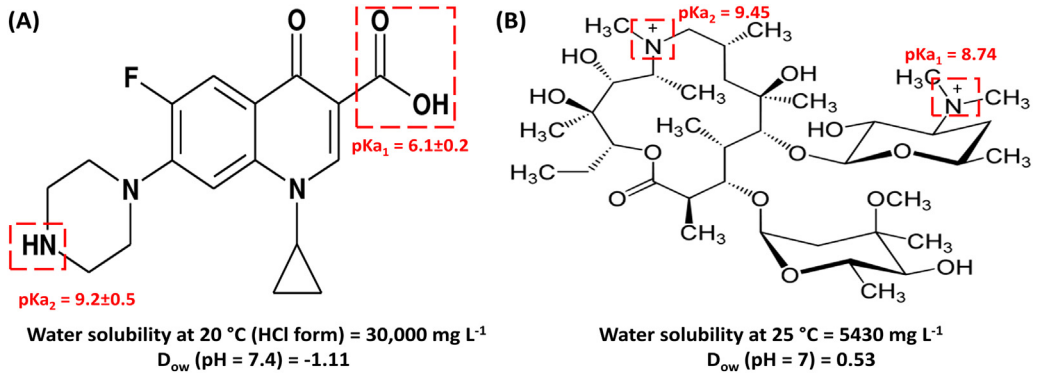

Fig. 1. Structures, pKa values (McFarland et al., 1997; Aristilde and Sposito, 2013), water solubilities (Varanda et al., 2006; Ericson, 2007), and octanol-water distribution ratios (Takacs-Novak et al., 1992; Ericson, 2007) of ciprofloxacin (CIP) and azithromycin (AZ).