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Tetracycline desorption kinetics in municipal biosolids and poultry litter amendments determined by diffusive gradients in thin films (DGT)

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HIGHLIGHTS

- Dissolved organic carbon strongly inhibited TET sorption by amendments.
- <5% of total TET in amendments was readily released to the solution phase.
- TET release from amendments was short-lived and diffusion-limited.

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ABSTRACT

Tetracycline (TET) is commonly used to treat bacterial diseases in humans and chickens (*Gallus gallus domesticus*), is largely excreted, and is often found at elevated concentrations in treated sewage sludge (biosolids) and poultry litter (excrement plus bedding materials). Land spreading of these materials is practiced worldwide to improve soil fertility, but the practice raises questions about whether TET could be released to the environment and cause adverse effects. Hazard risks largely depend on the concentration in the solid phase that can be released to the solution phase (labile TET), it's desorption rate constant, and diffusion rate of dissolved TET in amendments. In this study, these quantities were evaluated in biosolids and three types of litter amendments by combinations of equilibrium sorption-desorption isotherm and desorption kinetic studies using diffusive gradient in thin films (DGT) samplers. Results from isotherm experiments showed that TET partitioning was inhibited at the high dissolved organic carbon (DOC) concentrations in amendments (6–15% of dry mass). Despite low partition coefficients determined at high particle/DOC concentrations of amendments ($K_d = 9–46\ mL\ g^{-1}$), results from DGT experiments revealed that TET release by desorption and diffusion would be slow and short-lived (<3 d) due to small effective diffusion coefficients ($<8 \times 10^{-8}\ cm^2\ s^{-1}$) and low concentrations of labile TET in amendments (<5% of total TET). Despite this, evaluations of antibiotic uptake during microbial colonization and plant root interception of amendment surfaces are highly warranted.

1. Introduction

Worldwide, tetracycline (TET) is commonly used to treat bacterial diseases in humans and chickens (*Gallus gallus domesticus*) (FDA, 2015; Sarmah et al., 2006; Sims and Wolf, 1994; WHO, 2001), is largely excreted (>50% by humans; Agwuh and MacGowan, 2006), and is often found at elevated concentrations in treated sewage sludge (biosolids) and poultry litter (excrement plus bedding materials) (up to $2\ \mu g\ g^{-1}$; Furtula et al., 2010; Karci and Balcioğlu, 2009; Kim et al., 2005; Lindberg et al., 2005; Liu et al., 2009; Martínez-Carballo et al., 2007). These materials are considered valuable soil amendments for improving fertility and other characteristics in many regions of the world (Brown et al., 2011; Lu et al., 2012; Moore et al., 1995), but this practice raises questions about potential release of antibiotics from amendments and detrimental ecological and health effects (Popowska et al., 2012; Thiele-Bruhn, 2005).

Hazard risks of applying amendments with antibiotics to soils depend largely on antibiotic interactions with the solid phase.

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Equilibrium partitioning studies (e.g. batch isotherms) have revealed a great deal about the mechanisms and factors that govern antibiotic interactions (D'Angelo, 2017; Li et al., 2013; Loke et al., 2002; MacKay and Canterbury, 2005). Unfortunately, equilibrium partition coefficients determined using such approaches may not be as useful at predicting environmental fate and transport processes because they are determined under highly artificial conditions (e.g. low particle concentrations, small particle size, agitation, etc) (D'Angelo and Starnes, 2016; EPA, 1999; Yazgan et al., 2005). Moreover, equilibrium relationships do not account for kinetic controls of exchange between the solution and solid phases and transport processes that can strongly influence contaminant mobility and bioavailability including sorption-desorption rates and diffusion rates through intra-particle nanopores (Pignatello and Xing, 1995).

The "Diffusive Gradient in Thin Films" (DGT) technique has been applied to quantify exchange kinetics of labile metals and antibiotics (i.e. fraction of total solute possessing rapid dissociation kinetics) in soils (Wang et al., 2016; Chen et al., 2014; Ernstberger et al., 2005), sediments (Davison et al., 1997), and biosolids (D'Angelo and Starnes, 2016). A key feature of DGT samplers is the solute binding layer that induces desorption and diffusion in the sample under *in situ* conditions such as would occur during solute uptake by plant roots or microbial biofilms. For this reason, solute concentrations determined by the DGT approach are often more highly correlated to bioavailability than those determined by conventional extraction methods (e.g. desorption with water, salt, and solvent solutions) (Wang et al., 2016).

The main objectives of this research were to determine (i) desorption/diffusion exchange rates of TET in four types of common soil organic amendments, and (ii) effects of particle and dissolved organic carbon (DOC) concentrations on TET partitioning in the amendments. The first objective was accomplished by quantifying TET release kinetics from amendments using DGT samplers and estimating sorption-desorption exchange parameters by fitting DGT data to diffusion transport and exchange equations available in the software program "2D DGT Induced Fluxes in Sediments and Soils" (2D DIFS) (D'Angelo and Starnes, 2016; Chen et al., 2014; Sochaczewski et al., 2005). The second objective was achieved by comparing sorption-desorption equilibrium constants determined in batch isotherm experiments with increasing particle and DOC concentrations in the four organic amendments.

2. Methods and materials

2.1. Chemicals and reagents

Tetracycline (TET) used in experiments and calibration standards was obtained from Sigma-Aldrich (St. Louis, MO, USA) and Ultra Scientific (Kingston, RI, USA). All other chemicals were reagent-grade and obtained from Thermo-Fisher Scientific (Waltham, MA, USA). Reagent grade water was prepared using a Thermo-Fisher Scientific Barnstead Nanopure water purification system.

2.2. Organic amendments

Organic amendments included Louisville Green municipal biosolid (LG), poultry manure (PM), wood chips litter (WC), and rice hull litter (RH). LG was a commercially available Class A Exceptional Quality Biosolids produced by anaerobic digestion, centrifuge dewatering, and thermal drying of primary sludge at the Morris Forman Water Quality Treatment Center (Louisville, KY, USA). PM and WC were obtained from the Poultry Research Facility located at the University of Kentucky Coldstream Research Station in Lexington, KY, USA. PM consisted of excrement that accumulated underneath layer cages, and WC consisted of litter (wood chips and manure) produced by cage-free layers in a poultry house. RH consisted of litter (rice hulls and manure) produced by broilers in houses that was composted for several months in Princeton, KY, USA. No TET was used at the poultry facilities. Chemical properties of amendments (pH, total C and N, cation exchange capacity, exchangeable cations) were described previously (D'Angelo, 2017).

2.3. DGT sampler preparation

DGT samplers without binding discs or diffusive layers were purchased from DGT Research (Model Number R-SLU; Lancashire, UK). Binding gels were prepared by mixing an appropriate amount of washed XAD18 resin beads (according to manufacturer instructions) with heated 1.5% agarose solution to give 20% XAD18 adsorbent (wet mass:volume). The heated mixture was poured onto a pre-heated glass plate (12 cm × 20 cm) with 0.05 cm spacers, covered with a matching glass plate, and clamped in place with gel cast clamps. Diffusion gels were prepared by dissolving an appropriate amount of agarose in boiling water to give a 1.5% agarose solution. The heated mixture was transferred with a needle and syringe to a pre-heated gel casting system (12 cm × 20 cm) with 0.08 cm spacers.

After cooling to room temperature, binding and diffusive gels were removed from glass plates and cut into 25-mm diameter discs with a circular gel cutting tool. The binding disc, diffusion gel, and a 25-mm diameter 0.45-μm nylon filter membrane were layered on the bottom piston and secured in place by the upper sealing ring of the DGT sampler. Samplers were stored by submerging in water in sealed plastic containers at 4 °C until used in experiments (<1 week). Preliminary experiments showed binding discs rapidly removed 10 μg TET from solution, and the diffusive gel and nylon filter did not sorb an appreciable amount of the antibiotic.

2.4. Preparation of amendments and incubations on DGT samplers

All experiments were conducted in subdued light in Teflon and plastic containers to minimize photo-degradation and sorption of TET to container surfaces. Before applying amendments to DGT samplers, amendments (70 g air-dried and sieved with 4 mm mesh) were aged for two weeks with 100–130 mL of 27 mg L^{-1} TET solution prepared in 0.01 M $CaCl_2$/0.01 M NaN_3 (as microbial inhibitor) in plastic bags. The initial dissolved TET concentration in amendments ranged between 23 and 25 μg mL^{-1}, which corresponded to between 44 and 77 μg g^{-1} on a dry weight basis (Table 1). TET concentrations were about 20 x higher than those typically measured in biosolids and poultry litter, but were evaluated so that measurable concentrations could be detected by HPLC-UV. After the aging period, 6 g wet amendment was transferred to Teflon centrifuge tubes, centrifuged at 10,000 g for 15 min, and supernatants were analyzed for dissolved TET. These concentrations were used as C_d values to calculate R ratios as shown in section 2.5.

Amendments aged for two weeks with TET (6 g) were applied to ten DGT samplers and incubated in tightly-sealed plastic incubation containers lined with water-saturated paper towels (to minimize evaporation) at 23 °C for 24, 48, 72, 120, and 168 h. After each time period, two DGT samplers were removed from incubation containers, and amendment particles were removed by gently rinsing with water. Using a scalpel, the diffusive layer and binding disc were cut along the circumference of the sampler window. The binding disc was transferred to a Teflon centrifuge tube and gently rinsed with water. TET in the binding discs was extracted by macerating with a Teflon spatula and sonicating with 2 mL