Desorption Kinetics of Ciprofloxacin in Municipal Biosolids Determined by Diffusion Gradients in Thin Films

Elisa D'Angelo (edangelo@uky.edu) and Daniel Starnes

Department of Plant and Soil Sciences, University of Kentucky, Lexington KY 40546, USA

Introduction and Objectives

- Ciprofloxacin (CIP) is one of the most commonly prescribed antibiotics in the world, is mostly excreted by the body, and is found at elevated levels in municipal biosolids at many wastewater treatment plants (up to about 12 mg kg^{-1})[1].
- CIP-laden biosolids are widely applied to agricultural soils, which could pose hazard risks to soil and aquatic biota[2].
- The primary aims of this study were to assess risks by
  (i) determining the concentration of readily desorbed CIP from biosolids to solution phase
  (ii) determining the sorption/desorption rate constants in biosolids.

Theory of DGT Approach

The DGT sampler used to address the research aims consisted of a filter holder with stacked layers of XAD18 binding disc, diffusion layer, and nylon membrane (Fig. 1).

As shown in Fig. 2, when biosolids are placed on the DGT membrane, dissolved CIP in the biosolids (C_D) diffuses through the diffusion layer (with thickness of Δg and CIP diffusion coefficient of D_d), and accumulates in the binding disc, in accordance to Fick's first law of diffusion.

$$\text{CIP flux to binding disc} = D_d \times C_{DGT} \times \Delta g^{-1} \qquad \text{eq 1}$$

A decrease in dissolved CIP in biosolids at the sampler interface (C_{DGT}) by the sampler induces desorption from the solid phase at a rate that depends on the desorption rate constant (k_b) and CIP concentration in biosolids that can be readily released to solution (C_s).

Thus, determination of C_{DGT} with time, determined by rearranging eq 1, can be used to derive values of C_s and k_b, by fitting the data to a sorption-desorption exchange and diffusion transport model, such as that available in software tool 2D-DIFS[3].

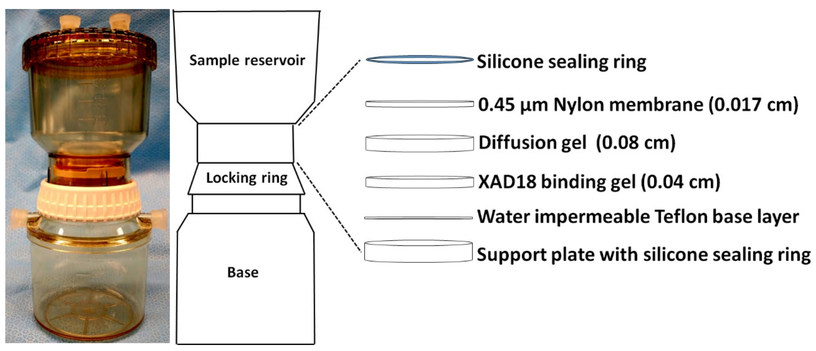

Fig. 1. Photograph and schematic of DGT sampler used to determine CIP desorption kinetics in biosolids

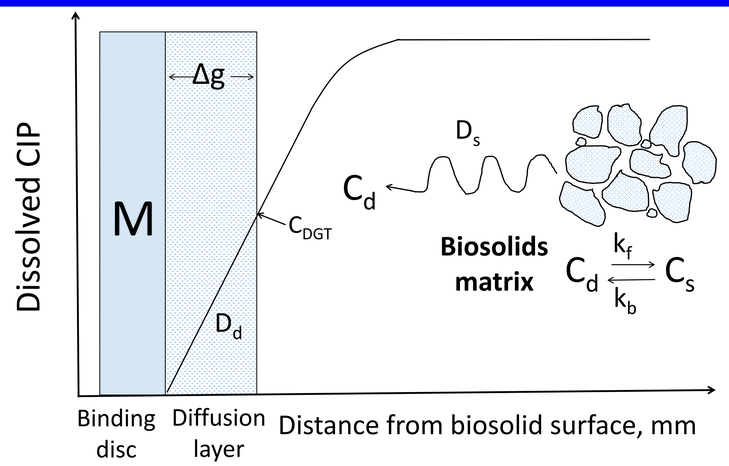

Fig 2. Kinetic exchange parameters measured with the DGT sampler and numerical modeling of measured data using 2D DIFS.

Methods

Biosolids

- CIP desorption kinetics were determined in an anaerobically-digested, thermally-dried organic-based biosolids pellet fertilizer called 'Louisville Green'
- Biosolids had 3.85 µg CIP g^{-1}, pH 5.8, 42% organic carbon, 6.1% total N, 1.6% total P.

DGT Deployment

- Biosolid pastes were incubated on DGT samplers for 24, 48, 72, 144, and 240 h in a darkened incubator set at 23 °C.
- After each deployment period, DGT samplers were dismantled, and binding discs were extracted by sonication with acidified acetonitrile, which were immediately analyzed for CIP by HPLC-UV.
- CIP in the binding disc was used to determine C_{DGT} with time, which was used to derive C_s , k_f and k_b (Fig 2) by numerical fitting of data to the transport and exchange model available in 2D-DIFS[3].

Results and Discussion

- As seen in Fig 3, dissolved CIP at the DGT sampler interface (C_{DGT}) rapidly decreased with time, which indicated that the sampler removed CIP faster than it was replenished from biosolids.

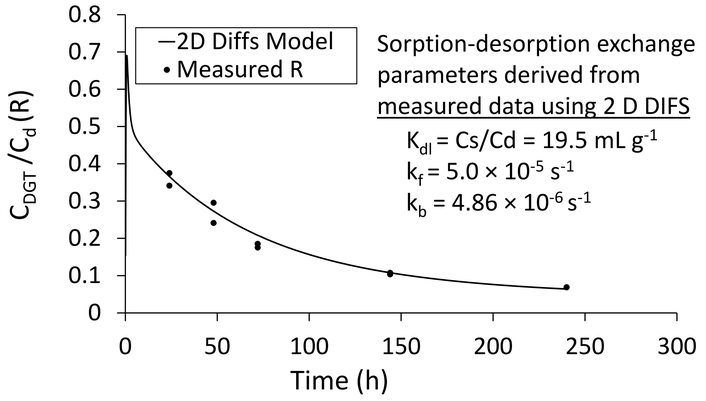

Fig 3. Change in CIP concentration at the interface of DGT samplers deployed with biosolids for 240 h.

Results and Discussion

- The partition coefficient of labile CIP in biosolids (Cs/Cd) was 19.5 mL g^{-1}, which equated to 25% of total CIP that could be readily released to solution when concentrations were depleted by the DGT sampler.
- Although labile CIP in biosolids was considerable, release rates to solution were slow (<1 ng cm^{-2} h^{-1}) due to the small desorption rate constant (4.9 × 10^{-6} s^{-1}) and small effective diffusion coefficient (5.8 × 10^{-9} cm^2 s^{-1}; ≈1000× smaller than diffusion in water).
- CIP release from other types of biosolids could be different depending on physical and chemical properties that influence C_s, k_b and D_s, which was evident from simulations using 2D-DIFS (Fig 4).

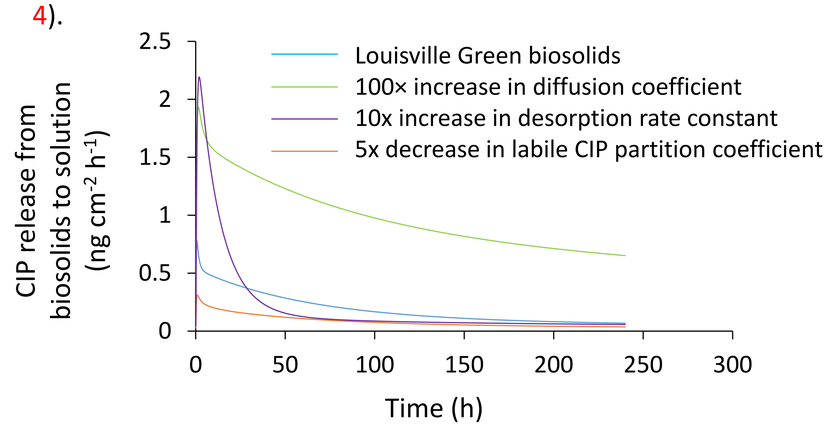

Fig 4. Effects of labile CIP partition coefficient, diffusion coefficient, and desorption rate constant on CIP release from biosolids to solution.

Environmental Implications

- CIP release from biosolids induced by the DGT sampler revealed that more CIP could be released to the solution phase than predicted by traditional equilibrium partitioning.
- Although the concentration of CIP in biosolids that can be released to solution was considerable (25% of total CIP), release rates were greatly constrained by slow desorption kinetics and diffusion.
- CIP release from other organic amendments could be much different, depending on physicochemical properties that influence diffusion and desorption rate constants.

References

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2. Langdon, K., Warne, Ms. & Kookana, R. Aquatic hazard assessment for pharmaceuticals, personal care products, and endocrine-disrupting compounds from biosolids-amended land. *Integr. Environ. Assess. Manag.* **6,** 663–676 (2010).
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