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Deriving sulfamethoxazole dissipation endpoints in pasture soils using first order and biphasic kinetic models

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HIGHLIGHTS

- Single first-order model resulted in poor goodness of fit parameters.
- Non-linear biphasic models improved statistical measures of goodness of fit.
- Two compartment model provides a mechanistic explanation for antibiotic dissipation.

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ABSTRACT

Single first-order (SFO) kinetic model is often used to derive the dissipation endpoints of an organic chemical in soil. This model is used due to its simplicity and requirement by regulatory agencies. However, using the SFO model for all types of decay pattern could lead to under- or overestimation of dissipation endpoints when the deviation from first-order is significant. In this study the performance of three biphasic kinetic models — bi-exponential decay (BEXP), first-order double exponential decay (FODED), and first-order two-compartment (FOTC) models was evaluated using dissipation datasets of sulfamethoxazole (SMO) antibiotic in three different soils under varying concentration, depth, temperature, and sterile conditions. Corresponding 50% (DT_{50}) and 90% (DT_{90}) dissipation times for the antibiotics were numerically obtained and compared against those obtained using the SFO model. The fit of each model to the measured values was evaluated based on an array of statistical measures such as coefficient of determination (R^2_{adj}), root mean square error (RMSE), chi-square (χ^2) test at 1% significance, Bayesian Information Criteria (BIC) and % model error. Box–whisker residual plots were also used to compare the performance of each model to the measured datasets. The antibiotic dissipation was successfully predicted by all four models. However, the nonlinear biphasic models improved the goodness-of-fit parameters for all datasets. Deviations from datasets were also often less evident with the biphasic models. The fits of FOTC and FODED models for SMO dissipation datasets were identical in most cases, and were found to be superior to the BEXP model. Among the biphasic models, the FOTC model was found to be the most suitable for obtaining the endpoints and could provide a mechanistic explanation for SMO dissipation in the soils.

1. Introduction

The fate of veterinary antibiotics in soils has received significant attention during the last few decades because of their potential effects on surface and groundwater quality as well the risk that may arise due to the development of antibiotic resistance genes. Occurrences of commonly used veterinary antibiotics such as sulfonamides are widespread in many parts of the world with trace levels of a variety of compounds within this group being detected in environmental media such as soils, surface water, and ground water (Bartelt-Hunt et al., 2011; Garcia-Galan et al., 2010; Kim et al., 2011; Pereira et al., 2012). Among processes that govern the ultimate fate of antibiotics in the environment, dissipation in soils is vital and complex due to multitude factors which underpin the complex kinetics of compound sorption and dissipation (Sarmah et al., 2006). Laboratory incubation studies are common and often carried under controlled conditions to simulate the field environment for the compound and to investigate the pattern of antibiotic dissipation in soil (Herman and Scherer, 2006).

Most mathematical models used to determine the dissipation endpoints are empirical in nature. These models are typically used to fit the observed compound dissipation and facilitate in the interpretation of the results, and allow appropriate predictions concerning the environmental fate of chemicals in soils. Models are generally selected

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based on simplicity, mechanistic hypotheses or empirical fit to a dataset (Herman and Scherer, 2006). Common models include single first order (Liu et al., 2010), apparent zero-order (Yang et al., 2012), pseudo-first-order (Hammesfahr et al., 2011) and availability adjusted first order (Wang et al., 2006a; Wang et al., 2006b) equations. Available literatures on sulfonamide dissipation have shown that dissipation parameters and associated dissipation endpoints for veterinary antibiotics are often evaluated using single first order (SFO) kinetic or its modified form, however, this leads to the difficulties in comparing the endpoints obtained in separate studies (Table 1). However, the kinetics of dissipation may also exhibit biphasic, triphasic, and even a logistics pattern, depending on the soil type, or the combination of a multitude of factors (Sarmah and Rohan, 2011). Using SFO model for all types of decay pattern could lead to under- or overestimation and thus bias the dissipation endpoints derived (Herman and Scherer, 2006). Proper selection and utilization of appropriate mathematical models capable of describing the entire degradation kinetics in water and soil media should be considered in order to predict appropriate dissipation endpoints. This was also highlighted by the FOCUS (FOrum for Co-ordination of pesticide fate models and their Use) group who developed guidelines for estimating dissipation endpoints for pesticides in both soil and surface water scenarios for the European Union (FOCUS, 2006). Given many fate and transport or simulation models often require datasets on degradation or dissipation rate constant (k day^{-1}) as input parameter, determining true dissipation endpoints for an organic chemical would not only provide the proper prediction by the models, but would also validate its utility as input parameters often required for risk assessment purposes and in many regulatory modeling exercises.

To avoid an underestimation of dissipation endpoints the use of more complex non-linear kinetic models has been recommended to describe laboratory degradation data and to obtain appropriate degradation endpoints (Lucas and Jones, 2006; Sarmah et al., 2008). Various biphasic models have been successfully applied in the past to model aerobic degradation of 4-*n*-nonylphenol and bisphenol-A in groundwater–aquifer material slurry (Sarmah and Rohan, 2011), degradation kinetics of estrone-3-sulfate (Scherr et al., 2008), and a number of pesticides in New Zealand (Sarmah et al., 2009) and US soils (Herman and Scherer, 2006). Similarly these models could also be applied to the newly classed emerging contaminants like pharmaceuticals and personal care products (PPCPs).

Earlier, we reported dissipation of sulfamethoxazole (SMO) antibiotic under controlled laboratory conditions in freshly collected top and subsoils from three dairy farming regions of New Zealand, where deviation from first-order kinetic of the observed datasets was found (Srinivasan and Sarmah, 2014). Although the coefficient of determination (R^2) values were acceptable (0.80–1.00) for most soils and under varied treatment conditions, some evidence of a biphasic degradation pattern was found for a few particular datasets in which the R^2 values were low. An example of such problem has been presented in SI Fig. 1, which shows the kinetics of dissipation for SMO in Hamilton topsoil (0.5 mg kg^{-1}, 25 °C and non-sterile) and Hamilton (sterile subsoil) to be a biphasic behavior than first order kinetic.

The purpose of this work was to apply three non-linear biphasic models, namely bi-exponential decay (BEXP), first-order double exponential decay (FODED), and first-order two-compartment (FOTC) decay models, to fit the laboratory measured dissipation data for SMO in three soils under varied treatment conditions. Corresponding dissipation endpoints: DT_{50} and DT_{90} values for SMO were numerically obtained and compared against those estimated by the SFO model. Model selection and evaluation of performance were based on an array of statistical measures such as coefficient of determination (R^2_{adj}), root mean square error (RMSE) and chi-square (χ^2) test at 1% significance, Bayesian Information Criteria (BIC), and % model error. Additionally, we also performed ANOVA on the model predicted dissipation endpoints (DT_{50}) to judge the significance of each model prediction against one another. Model predicted dissipation endpoints were discussed in relation to available literature data for SMO and limitations of each model are highlighted.

2. Materials and methods

2.1. Dissipation datasets

Laboratory incubation experiments were conducted to investigate the dissipation kinetics of SMO antibiotic in three different pastoral soils (Te Kowhai, Hamilton and Horotiu). The conditions for soil incubation studies with SMO involved maintaining the water content at 60% maximum water holding capacity (MWHC) and with varying initial antibiotic spiked concentrations, with different depth profiles, with different temperature regimes (7.5 °C and 25 °C) and with sterilization at 60%

Table 1
Available literature data on sulfonamide dissipation in soils, and other matrices along with the models used to calculate their endpoints.

Sulfonamides	Concentration	Matrix	Conditions	Degradation	Time	Reference
		pH/OC%		%	DT_{50}, DT_{90} (day)	
Sulfachloropyridazine	35.4 mg L^{-1}	Sandy loam soil	Field condition	50, 90 (SFO)	3.5, 18.9	Blackwell et al. (2007)
12 sulfonamides	250–1000 μg L^{-1}	Activated sludge	6 °C, 20 °C	50 (LDM)	0.4–4.1 (HL)	Ingerslev and Halling-Sørensen (2000)
Sulfadimethoxine	18–270 μmol g^{-1}	Manure/8.37/14	25 °C, 83% MC	50% (AAFO)	1.4 to 10.2 (HL)	Wang et al. (2006a)
Sulfadimethoxine	10–100 μmol g^{-1}	Manure amended soils	25 °C, 20% MC	50% (AAFO)	3 to 11	Wang et al. (2006b)
Sulfadiazine	1, 10, 25 mg kg^{-1}	3 soils/4.3 to 8.5/0.35 to 2.57	25 °C, 50% MWHC,	50% (SFO)	2–265	Yang et al. (2009)
Sulfamethoxazole	10 mg kg^{-1}	Soil/4.9/13.5 g kg^{-1}	Aerobic, 25 °C	50% (SFO)	2,4 days	Liu et al. (2010)
Sulfamethoxazole	0.5/5 mg kg^{-1}	6 soils	Non-sterile/sterile 25 °C & 7.5 °C	50, 90% (SFO)	4.5–13 days	Srinivasan and Sarmah (2014)
Sulfachloropyridazine	1, 10, 100 mg kg^{-1}	Silt loam/7.5/1.8 Sand/7.2/0.94	Non-sterile/sterile	50% (SFO)	18.6, 21.3 18.6, 21.3	Accinelli et al. (2007)
Sulfamethazine	10 mg kg^{-1}	Swine slurry/7.8/20	25 °C, MC at −33 kPa	50% (SFO)	NR, >10	Accinelli et al. (2007)
Sulfamethoxazole	2000 mg kg^{-1}	Sewage sludge/6.5/73	20 °C, 10 h light/14 h dark	50, 90 (SFO)	1,18	Holtge and Kreuzig (2007)
Acetyl sulfamethoxazole	3000 mg kg^{-1}	Soil/6.9/1.6	20 °C, 10 h light/14 h dark	50, 90 (SFO)	1,9	Holtge and Kreuzig (2007)
Sulfamethoxazole, sulfadimethoxine, sulfamonomethoxine	100 μg L^{-1}	Activated sludge (MLSS of 2.56 g L^{-1})/pH 7.0	25 °C, DO of 3.0 mg L^{-1}	100% (AZK)	12–14 (HL)	Yang et al. (2012)
Sulfadiazine	1, 10, 100 mg kg^{-1}	Soil/4.8/1.0% Manure/7.5	Manure amendment 10 °C in dark	50% (PFO)	1–2 (graph)	Hammesfahr et al. (2011)
Sulfapyridine	10 to 1000 mg kg^{-1}	Sandy topsoil	25 °C & 50% MWHC,	50% (SFO)	1–3 (graph)	Thiele-Bruhn and Aust (2004)
Sulfamethoxazole & 2 metabolites	20 μg L^{-1}	Sediment/7.0/9.4%	25 °C, with sterile controls	50% (SFO)	3.3–25.6 (h)	Radke et al. (2009)

Single first order (SFO); availability adjusted first order (AAFO); apparent zero order kinetic (AZK); pseudo first order (PFO); logistic degradation model (LDM). DT_{50} and DT_{90}, are the dissipation endpoints for 50, and 90% antibiotic dissipation. HL = half-life, h = hour and NR = not reported.