



Environmental availability of sulfamethoxazole and its acetylated metabolite added to soils via sludge compost or bovine manure

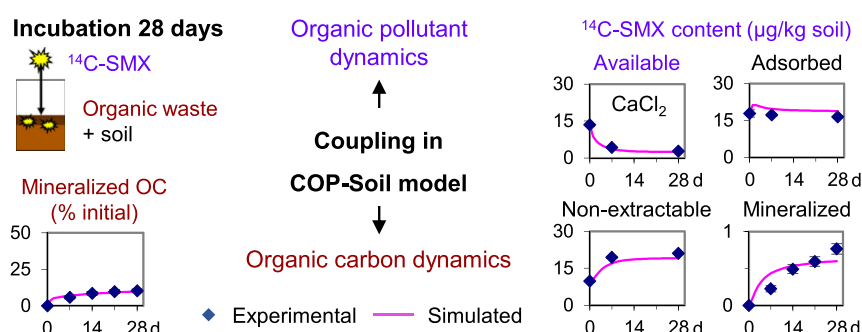
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HIGHLIGHTS

- The decomposition of the added organic matter influenced the fate of SMX and AcSMX in soil.
- SMX and AcSMX were initially more available in soil/manure than in soil/compost mixtures.
- The dynamics of SMX and its acetylated metabolite in amended soils were similar.
- Co-metabolism could originate the formation of non-extractable residues.
- CaCl₂ extraction could be the best method to assess the sulfonamide availability, resulting in best simulations.

GRAPHICAL ABSTRACT



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ABSTRACT

The fate of antibiotics and their metabolites in soils after application of organic waste depends on their environmental availability, which depends on the quality and biodegradability of the added exogenous organic matter (EOM). This study aimed at better understanding the fate of sulfamethoxazole (SMX) and *N*-acetyl-sulfamethoxazole (AcSMX) metabolite added to soils via sludge compost or cow manure application, during a 28-day incubation. Experimental results obtained for mineralized, extractable, and non-extractable fractions as well as EOM mineralization were used to couple SMX and AcSMX dynamics to the EOM evolution using the COP-Soil model. According to various mechanisms of extraction, CaCl₂, EDTA and cyclodextrin solutions extracted contrasted available fractions (31–96% on day 0), resulting in different sets of parameter values in the model. CaCl₂ extraction was the best method to assess the sulfonamide availability, leading to low relative root mean squared errors and best simulations of SMX and AcSMX dynamics. The decrease of SMX and AcSMX availability over time went with the formation of non-extractable residues, mostly of physicochemical origin. Using the COP-Soil model, the co-metabolism was assumed to be responsible for the formation of biogenic non-extractable residues and the low mineralization of SMX and AcSMX.

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1. Introduction

Antibacterial agents such as sulfonamides are often used for humans and animals and are partly excreted by organisms. Consequently, antibiotic residues, i.e., parent compounds, metabolites and other transformation products, can be found in exogenous organic matter (EOM)

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like sewage sludge or livestock effluents (Du and Liu, 2012). For example, sulfamethoxazole (SMX) concentrations in sludge may vary from <1 to 178 $\mu\text{g kg}^{-1}$ dry matter (Nieto et al., 2010). There are few data for the main SMX metabolite, the acetylated form *N*⁴-acetylsulfamethoxazole (AcSMX; Baran et al., 2011), e.g., <1.5 $\mu\text{g kg}^{-1}$ (Le Minh et al., 2012). Then, sulfonamide residues can be transferred into agricultural soils when EOM is spread as organic fertilizer or amendment. The SMX concentration may vary from 6.2 to 100 $\mu\text{g kg}^{-1}$ dry matter in manure-amended soils (Karcı and Balcıođlu, 2009; Watanabe et al., 2010; DeVries and Zhang, 2016).

Sulfonamide compounds can adsorb both on inorganic (Gao and Pedersen, 2005) and organic compounds (Schwarz et al., 2012) in the soil or EOM matrix, with the major role of organic matter (Kahle and Stamm, 2007a, b), not only for the quantity of organic carbon but also for its quality (Thiele-Bruhn et al., 2004). Sorption depends on pH, the ionic strength of solution, the type of exchangeable cations on surfaces, and time (Gao and Pedersen, 2005; Ter Laak et al., 2006; Chen et al., 2017). The pH determines the sulfonamide speciation which is compound specific, and directly influences the interactions that can occur: e.g., ionic interaction for cationic/anionic species, covalent bonding with humic materials for neutral species (Bialk and Pedersen, 2008), Van der Waals and H bonding (Thiele-Bruhn et al., 2004). Sulfonamides can undergo transformations primarily biologically driven (Höltge and Kreuzig, 2007; Sittig et al., 2012). Mineralization is often low even under aerobic conditions, e.g., <2% for SMX in soil amended with sludge and compost in 84 days (Li et al., 2015). More than 75% of SMX residues became non-extractable in soils amended with liquid sludge in the first week (Höltge and Kreuzig, 2007). Sulfonamide non-extractable residues in manure-amended soil were poorly bioavailable for soil organisms and plants (Heise et al., 2006).

Using radiolabeled molecules and chemical extractions can help to follow the distribution of the radioactivity among fractions of decreasing accessibility in EOM-amended soils: potentially available and easily-extractable, solvent-extractable, non-extractable fractions. The targeted ¹⁴C-molecules in fractions can be parent molecules, degradation products, free molecules and also those associated to organic matter. Förster et al. (2009) and Müller et al. (2013) successively used calcium chloride (CaCl₂) and methanol to extract the most available ¹⁴C-sulfadiazine residues before a solvent extraction. Schmidt et al. (2008) performed a CaCl₂ extraction and a Soxhlet extraction with ethanol-water mixture, while Kreuzig and Holtge (2005) only used ethyl-acetate as a mild solvent before the quantification of non-extractable residues. Less studies have dealt with ¹⁴C-sulfamethoxazole (SMX). Höltge and Kreuzig (2007) and Li et al. (2015) only quantified the ethylacetate-extractable residues for ¹⁴C-SMX and ¹⁴C-AcSMX in different EOM-amended soils. It is crucial to assess the environmental availability of sulfonamides to understand the contaminant behavior in terms of transport in soil, bioavailability for soil microorganisms to be degraded, and further potential impacts such as the development and transfer of antibiotic resistance. The environmental availability of contaminants can be assessed by soft extractions with aqueous solutions (Lanno et al., 2004) while the use of organic solvents should be avoided (Alexander, 2000). Moreover, the environmental availability assessment by using different soft extractants, involving different mechanisms of extraction, can highlight different binding strengths of compounds with soil or EOM components and their evolution in time. In a previous study, the SMX availability decreased with regard to the concentrations of free molecules quantified by UHPLC-MS/MS and the types of co-extracted organic matter in the aqueous extracts (Goulas et al., 2017).

In a complementary way to experiments, models can help to understand the contribution of physical, chemical and microbiological processes to the contaminant behavior and the evolution of its environmental availability. Zarfl et al. (2009) simulated the fate of sulfadiazine and two of its metabolites in manure-amended soils. The decomposition of the EOM bringing the pollutants into the soil is usually not

considered while it could influence the distribution of the sulfonamide residues between the different fractions in soil/EOM mixtures (e.g., between the easily-extractable and residual fractions). Moreover, the added organic matter could be used by microorganisms to transform organic pollutants by co-metabolism, as previously shown for pesticides and other families of compounds brought to soil with compost (Haudin et al., 2013). Geng et al. (2015) developed the COP-Soil model coupling the organic pollutant (OP) fate, like PAHs, surfactants and herbicide (glyphosate), to the organic carbon (OC) evolution in time after the addition of EOM (compost) into soils. Brimo et al. (2018) added a new module to simulate the availability of PAHs in soil during compost decomposition. Even if the PAHs simulated in Geng et al. (2015) and Brimo et al. (2018) were more hydrophobic than compounds such as antibiotics, we hypothesized that the model could be used for sulfonamides, considering their possible sorption to organic matter (Wegst-Uhrich et al., 2014; Goulas et al., 2017).

Through an experimental and a modelling approaches, the objective of this study was to investigate the fate of SMX and AcSMX in soils amended with sludge compost or cow manure over a 28-day incubation, in parallel to the EOM transformation. The first approach aimed at following the evolution of available, adsorbed, non-extractable and mineralized SMX and AcSMX fractions by using ¹⁴C-labeled molecules. Aqueous solutions of CaCl₂, EDTA and cyclodextrin were used to assess the environmental availability of compounds. In the second approach, the COP-Soil model was used to simulate the experimental results, in order to: i) understand the evolution of the available fraction coupled to that of organic matter and, ii) identify a soft extractant for which the best simulations of SMX and AcSMX availability would be obtained.

2. Materials and methods

2.1. Exogenous organic matters and soils

A cow manure and a compost of sewage sludge and green waste (20:80% v/v, respectively) were sampled in September 2013 before their spreading on respective plots of a long-term field experiment located in Feucherolles (Yvelines, France). Compost and manure differed according to pH: 7.7 and 8.8, dry mass: 67 and 34% (fresh mass), organic carbon content: 257 and 355 g kg^{-1} dry mass, and biochemical composition (Table S1 in Appendice A - Supplementary Data), respectively. The compost was sieved to 5 mm and the manure was ground. Both EOMs were stored at $-20\text{ }^{\circ}\text{C}$.

The soil of Feucherolles is a silt loam Glossic Luvisol (IUSS Working Group WRB, 2015). The topsoil (0–28 cm), receiving each EOM at 4 t carbon/ha/application every two years since 1998 (Cambier et al., 2014), was sampled in 2013 and 2015, two months after the EOM application. Soil samples were sieved to 4 mm, dried to 20% (0.2 g water/g dry soil) and stored at 4 $^{\circ}\text{C}$. The main characteristics were similar between the soils amended with compost and manure: 15% clay, 79% silt, 6% sand; 15.2 g organic carbon kg^{-1} dry soil; pH 7 and cationic exchange capacity (CEC) 9.8 $\text{cmol}_+ \text{kg}^{-1}$. The initial microbial biomass was 287 and 278 mg C kg^{-1} in manure-amended soil and compost-amended soil, respectively (Chalhoub et al., 2013).

2.2. Experimental study

2.2.1. Chemicals and reagents

Stock solutions of [phenyl-¹⁴C] sulfamethoxazole (SMX) and *N*-acetylsulfamethoxazole (AcSMX) in ethanol (radiochemical purity, 99%; specific activity, 2.85 GBq mmol^{-1}) were purchased from the American Radiolabeled Chemicals Incorporation (Saint Louis, MO, USA). Diluted solutions at 1.1 mg L^{-1} for ¹⁴C-AcSMX (12 MBq L^{-1}) and 2.2 mg L^{-1} for ¹⁴C-SMX (24 MBq L^{-1}) were prepared in Milli-Q water (Millipore, Saint-Quentin-en-Yvelines, France).

Calcium chloride (CaCl₂, purity >98%; Carlo Erba Reagents, Val-de-Reuil, France), sodium ethylenediaminetetraacetic acid (EDTA, >99%;

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