Journal of Contaminant Hydrology 177–178 (2015) 30–42

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

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

Fate of the antibiotic sulfadiazine in natural soils: Experimental and numerical investigations

Irina Engelhardt [a,*], Stephan Sittig [a,b], Jirka Šimůnek [c], Joost Groeneweg [a], Thomas Pütz [a], Harry Vereecken [a]

[a] Forschungszentrum Jülich, Institute of Bio- and Geosciences, 52425 Jülich, Germany
[b] Knoell Consult GmbH, Marie-Curie-Straße 8, 51377 Leverkusen, Germany
[c] University of California Riverside, Department of Environmental Sciences, Riverside, CA, USA

ARTICLE INFO

Article history:
Received 1 October 2014
Received in revised form 12 February 2015
Accepted 25 February 2015
Available online 14 March 2015

Keywords:
Sulfonamides
Sulfadiazine
Manure
Hydrus
Lysimeter
Dual-permeability model

ABSTRACT

Based on small-scale laboratory and field-scale lysimeter experiments, the sorption and biodegradation of sulfonamide sulfadiazine (SDZ) were investigated in unsaturated sandy and silty-clay soils. Sorption and biodegradation were low in the laboratory, while the highest leaching rates were observed when SDZ was mixed with manure. The leaching rate decreased when SDZ was mixed with pure water, and was smallest with the highest SDZ concentrations. In the laboratory, three transformation products (TPs) developed after an initial lag phase. However, the amount of TPs was different for different mixing-scenarios. The TP 2-aminopyrimidine was not observed in the laboratory, but was the most prevalent TP at the field scale. Sorption was within the same range at the laboratory and field scales. However, distinctive differences occurred with respect to biodegradation, which was higher in the field lysimeters than at the laboratory scale. While the silty-clay soil favored sorption of SDZ, the sandy, and thus highly permeable, soil was characterized by short half-lives and thus a quick biodegradation of SDZ. For 2-aminopyrimidine, half-lives of only a few days were observed. Increased field-scale biodegradation in the sandy soil resulted from a higher water and air permeability that enhanced oxygen transport and limited oxygen depletion. Furthermore, low pH was more important than the organic matter and clay content for increasing the biodegradation of SDZ. A numerical analysis of breakthrough curves of bromide, SDZ, and its TPs showed that preferential flow pathways strongly affected the solute transport within shallow parts of the soil profile at the field scale. However, this effect was reduced in deeper parts of the soil profile. Due to high field-scale biodegradation in several layers of both soils, neither SDZ nor 2-aminopyrimidine was detected in the discharge of the lysimeter at a depth of 1 m. Synthetic 50 year long simulations, which considered the application of manure with SDZ for general agricultural practices in Germany and humid climate conditions, showed that the concentration of SDZ decreased below 0.1 μg/L in both soils below the depth of 50 cm.

1. Introduction

Veterinary antibiotics are used all over the world for preventive and therapeutic treatments and growth promotion in industrial livestock farming, as well as in aquaculture (Boxall et al., 2003; Chee-Sanford et al., 2009; Du and Liu, 2011; Halling-Sørensen et al., 1998; Sarmah et al., 2006). The German Pharmaceutical Law follows EU legislation and restricts the usage of pharmaceuticals for therapeutic use only (EAEM, 1997), while the application as a growth promoter has been prohibited in the EU since 2006 (Council of the European Union, 2001). The use of pharmaceuticals in livestock results in residues reaching the environment via human fertilization

* Corresponding author at: Forschungszentrum Jülich, Institute of Bio- and Geosciences, IBG-3 — Agrosphere, Wilhelm-Johnen-Strasse, 52425 Jülich, Germany.
E-mail address: i.engelhardt@fz-juelich.de (I. Engelhardt).

http://dx.doi.org/10.1016/j.jconhyd.2015.02.006
0169-7722/

practices with their manure, or directly via animal grazing (Sukul and Spiteller, 2006). During passage through the animal body parent compounds are partly transformed into products (transformation products) that may have even higher water solubility, lower sorption, or limited degradation properties than the parent substance.

As a result of wide applications of manure to the environment, sulfonamides were detected in Germany in surface waters at concentration levels between 7 and 100 ng/L (Christian et al., 2003). Under specific circumstances, such as highly permeable soils, high infiltration rates, or high temperatures, sulfonamides may be able to migrate through the soil and reach the groundwater (Boxall, 2008). This hypothesis is underpinned by a screening conducted in Germany, where sulfonamides were found in 2012 in 12% of groundwater wells above the limit of quantification (LOQ) and in 2013 in 15% of groundwater wells above LOQ, with concentrations of 11 ng/L to 950 ng/L for sulfadiazine (SDZ) and sulfamethoxazole, respectively (Hannappel et al., 2014).

The effects of veterinary antibiotics range from acute toxicity to *Daphnia magna* (Halling-Sørensen, 2000), development of resistant genes (Chee-Sanford et al., 2009; Gullberg et al., 2011), inhibition of soil bacteria growth, and changes in the composition of the soil microbial population. Veterinary antibiotics can thus also reduce the soil degradation properties for other organic substances (Thiele-Bruhn, 2003). Gullberg et al. (2011) showed that resistant bacteria develop even in conditions with concentrations below the minimum inhibitory concentrations for tetracyclines and other antibiotics. Heuer and Smalla (2007) investigated the persistent effects of SDZ on soil bacterial communities, and showed that the numbers of culturable resistant bacteria and sulfonamide resistance genes increased. However, the investigations of Halling-Sørensen (2000) indicated that the transformation products of SDZ showed no significant impact on the bacterial population in sewage and sludge habitats.

In this research, we focus on one of the widely used veterinary antibiotics: SDZ (IUPAC: 4-amino-N-(2-pyrimidinyl)benzene sulfonamide; SDZ). SDZ is a slightly hydrophilic compound with a low sorption affinity that forms non-extractable residues in soils (e.g., Müller et al., 2013; Rosendahl et al., 2011; Sittig et al., 2012). SDZ undergoes several transformation processes, in which the parent compound can be inactivated (acetylation), transformed into a less toxic state (hydroxylation), or to a more polar metabolite with a lower molecular mass (Sittig et al., 2014). Concentrations of SDZ measured in pig manure range between 0.3 and 198 mg of SDZ per kg dry matter, depending on medication, dilution, and age of the manure (Grote et al., 2004; Hamscher et al., 2005; Höper et al., 2002). When SDZ is fed to pigs, a mixture of the parent compound and two main metabolites is excreted (Lamshöft et al., 2007). When SDZ is applied together with manure to soils, current investigations by Hammesfahr et al. (2011) and Fang et al. (2014) indicate that manure can affect the microbial biomass by changing the biomass' structural composition and thus its functional processes.

Distinctive differences exist in the observed leaching potential of sulfonamides. In laboratory column experiments, Kwon (2011) observed increased leaching of three sulfonamides when they were applied together with manure. This was the consequence of elevated pH that resulted from the manure application. Kreuzig and Höltge (2005) detected not only higher leaching, but also increased degradation rates when SDZ was applied together with manure. In contrast, Unold et al. (2009) observed a low mobility and accumulation of SDZ in the presence of manure in laboratory column experiments on disturbed soil samples. Different leaching, sorption, and degradation may have been due to different types of manure that were used in the three experimental set-ups.

Wehrhan et al. (2007) observed that kinetic sorption was the most relevant process for the removal of SDZ at the laboratory scale. Within a larger scale of lysimeter studies, Aust et al. (2010) observed an increased leaching potential of sulfonamides after their application with manure. However, Aust et al. (2010) did not investigate the transformation processes of SDZ, nor did they use numerical models to analyze or predict the long-term and large-scale fate of sulfonamides. Currently, long-term and large-scale field studies that investigate the leaching potential and biodegradation of sulfonamides, such as SDZ, using undisturbed natural soils and under variable hydrological conditions, are still not available. Currently, research results are usually based on small-scale laboratory experiments, while research is still needed with respect to i) transformation pathways in native soils, and the impact of ii) manure, and iii) natural climate conditions on the leaching potential of the sulfonamides (Sukul and Spiteller, 2006).

Therefore, the objective of this study was to investigate the migration, retardation, and biodegradation of SDZ and its transformation products (TPs) over three years and at the field scale. Lysimeter experiments were employed to analyze the migration of ^{14}C-labeled SDZ and manure using i) a highly permeable homogeneous sandy soil and ii) a heterogeneous clayey silt soil containing a less permeable soil matrix and preferential flow pathways. Results of the lysimeter experiments were compared with small-scale laboratory experiments. The lysimeter experiments were analyzed using a joint inversion of measured saturation, discharge, and breakthrough curves of the tracer bromide, the parent SDZ, and its transformation products. The experimental and numerical investigations accounted for the natural heterogeneity of soils, variable hydrological conditions, and reactive transport processes under variably-saturated conditions. The calibrated numerical model was then used to carry out predictive scenario simulations to estimate the long-term leaching risk of SDZ and its accumulation in soil.

2. Materials and methods

2.1. Soil types and climate

Laboratory small-scale soil column and field-scale lysimeter experiments were conducted with two types of soil: an orthic luvisol and a cambisol. The luvisol was located near Merzenhausen (MER) and the cambisol near Kaldenkirchen (KAL), both in a region of North Rhine-Westphalia, Germany, that is intensively used for agricultural production. The luvisol (MER) is dominated by silt (83%) and clay (13%). It contains 0.97% (mass-based) of organic carbon and has a CEC of 11.4 cmol kg^{-1}. The cambisol (KAL) is a loamy sand (70% sand and 26% silt) with 0.88% of organic carbon and a CEC of