

Fate of sulfamethoxazole in groundwater: Conceptualizing and modeling metabolite formation under different redox conditions



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ABSTRACT

Degradation of emerging organic compounds in saturated porous media is usually postulated as following simple low-order models. This is a strongly oversimplified, and in some cases plainly incorrect model, that does not consider the fate of the different metabolites. Furthermore, it does not account for the reversibility in the reaction observed in a few emerging organic compounds, where the parent is recovered from the metabolite. One such compound is the antibiotic sulfamethoxazole (SMX). In this paper, we first compile existing experimental data to formulate a complete model for the degradation of SMX in aquifers subject to varying redox conditions, ranging from aerobic to iron reducing. SMX degrades reversibly or irreversibly to a number of metabolites that are specific of the redox state. Reactions are in all cases biologically mediated. We then propose a mathematical model that reproduces the full fate of dissolved SMX subject to anaerobic conditions and that can be used as a first step in emerging compound degradation modeling efforts. The model presented is tested against the results of the batch experiments of Barbieri et al. (2012) and Nödler et al. (2012) displaying a non-monotonic concentration of SMX as a function of time under denitrification conditions, as well as those of Mohatt et al. (2011), under iron reducing conditions.

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1. Introduction

The presence of pharmaceutical compounds in aquatic environments has been frequently addressed in recent years, and it is the topic of numerous review articles (Gavrilescu et al., 2015; Schwarzenbach et al., 2006). The discharge of antibiotics into the environment has become a major concern, as this group of pharmaceuticals is not only prone to directly influencing microbial communities (Fent et al., 2006; Yan et al., 2013), but also because of the risk of worldwide dispersal of antibiotic-resistant bacterial genes (Szczepanowski et al., 2009). Antibiotics may enter the environmental system via wastewater or else as wastewater treatment plant (WWTP) effluents, diffusive agricultural input (Jjemba, 2002), or landfill discharge (Heberer, 2002), and they can be found in different environmental compartments such as surface and subsurface water bodies, sediments, and soils.

Sulfamethoxazole (SMX) is a polar sulfonamide antibiotic, and the most widely detected antibiotic in aquatic environments (Gao

et al., 2014). SMX mainly enters wastewater via human excretion either unmodified or as its human-metabolized transformation products, N-acetyl-SMX or N-SMX-glucuronide (Göbel et al., 2005). Both transformation products are easily cleaved back to the SMX parent compound (Göbel et al., 2005). Since SMX is not completely degraded in wastewater treatment plants, it is found in minute concentrations in the WWTP water effluents, eventually reaching soils and surface or subsurface water bodies. Actually, it has been found in concentrations up to 0.47 µg/L in aquifers and 0.48 µg/L in surface waters (Hirsch et al., 1999). SMX has a very low adsorptivity to most soils (Henzler et al., 2014; Schaffer et al., 2015). Thus, it is postulated that sorption into aquifer sediments is usually negligible, so that the observed reduction of concentrations of SMX in the environmental compartments is mainly due to degradation.

In general, the literature on SMX degradation in both WWTPs and natural aqueous environments is marked by inconsistent results. This is supposedly because elimination amounts and rates depend on various environmental factors such as *in situ* redox potential, available nutrients, soil characteristics, seasonal temperature, microbial adaptation, and light variations (Müller et al., 2013), all such factors being site-dependent and temporally

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variable.

Based on field observations and laboratory experiments, it is postulated that degradation of SMX is biologically mediated and occurs preferentially under strictly anaerobic conditions (Banzhaf et al., 2012; Grünheid et al., 2005; Heberer et al., 2008; Schaffer et al., 2015; Valhondo et al., 2015). Some lab experiments reported the fate of SMX for particular redox conditions such as denitrification (e.g., Barbieri et al., 2012; Nödler et al., 2012) or iron reducing conditions (e.g., Mohatt et al., 2011). Nevertheless, aerobic degradation of SMX has also been observed in aerobic environments such as activated sludge (Baumgarten et al., 2011; Drillia et al., 2005; Gauthier et al., 2010; Reis et al., 2014).

Besides biological processes, abiotic SMX elimination has also been reported. For example, chemical oxidation was found to be an effective degradation process by using persulfate in the presence of ferrous iron oxidizing to ferric iron (Ji et al., 2014). The complementary mechanism was described in Mohatt et al. (2011), where abiotic degradation was enhanced by the biological reduction of ferric iron into ferrous iron.

Only in experiments performed under either aerobic conditions sustained for large times (Müller et al., 2013; Reis et al., 2014) or in anaerobic iron reducing conditions (Mohatt et al., 2011), the irreversible breakage of the SMX molecule was observed. Contrarily, the metabolites observed during denitrification conditions resulted from the substitution of the primary amine of SMX, forming either 4-nitro-SMX or else desamino-SMX (Barbieri et al., 2012; Nödler et al., 2012). In these last two papers, the authors reported that metabolites were not stable, meaning that when the denitrification process was over they were retransformed into the parent compound (see also Banzhaf et al., 2012).

Despite all the existing literature dealing with the fate of SMX under different redox conditions, there is little work postulating the processes taking place at the molecular scale, proposing closed-form expression for reaction rates, and reproducing the experimental observations of SMX fate through mathematical modeling. According to Henzler et al. (2014), this assertion is also valid for a large number of emerging organic compounds (EOCs). Most of the published works assume that degradation can be explained by (apparent) first-order degradation rates for all EOCs in a given cocktail (Henzler et al., 2014; Nham et al., 2015; Schaffer et al., 2015). Only few studies have investigated quantitatively the actual processes driven by varying redox conditions over degradation rates of EOCs (Greskowiak et al., 2006; Liu et al., 2013). Moreover, this simplified approach, based on first-order reactions, accounts only for the presence of irreversible reactions, contradicting a number of experiments where reversibility of the transformation processes has been observed (Barbieri et al., 2012; Stadler et al., 2015). While it is obvious that each antibiotic displays an individual, non-generalizable degradation behavior, it is also true that understanding one of them will open the door to analyze in the future the fate of a cocktail of antibiotics (and their metabolites), including also potential synergies.

Considering all of this, the objective of this work was to develop a conceptualization of the molecular mechanisms of degradation of the sulfamethoxazole molecule under different redox conditions ranging from aerobic to iron-reducing conditions, and a mathematical model capable of reproducing these mechanisms, with the overall aim of tracing the metabolite formation from different degradation pathways. To our knowledge, this is the first work which integrates all known processes on the degradation pathways of sulfamethoxazole as well as its metabolites in groundwater and under different redox conditions in a consistent mathematical framework that is able to describe various experimental data sets. To illustrate the conceptual and mathematical work, we model and interpret three published experiments, two of them performed

under nitrate reducing conditions (Barbieri et al., 2012; Nödler et al., 2012), and one under iron reducing ones (Mohatt et al., 2011).

2. Methods

2.1. Observations and conceptualization of the molecular mechanisms

The literature provides information regarding degradation of SMX only under aerobic and partially under anaerobic (nitrate and iron reduction) conditions. Although in Mohatt et al. (2011) SMX degradation under sulfate reduction condition was observed, to our knowledge, no experimental information is available describing such process, and thus no metabolites have been observed. So, in this work we conceptualize the SMX degradation for aerobic conditions, denitrification, and iron reducing conditions.

2.1.1. SMX behavior under aerobic conditions

Aerobic degradation of SMX has been mostly studied in the context of WWTPs and surface water bodies, and it is not expected to be a significant process in groundwater bodies due to their generally low oxygen concentrations. Degradation has mostly been observed for large SMX concentrations (Drillia et al., 2005) and with acclimated biomass in active sludge systems (Müller et al., 2013; Reis et al., 2014). SMX degradation was observed either via direct metabolism or else via co-metabolism (Gauthier et al., 2010; Reis et al., 2014; Drillia et al., 2005); in the latter case, degradation rates were generally comparably larger. Additionally, one study reported aerobic degradation of SMX in a column experiment supplied with surface water (Baumgarten et al., 2011). The degradation was linked to large adaptation times, around 1 year for the degradation at the lowest concentration of SMX (0.25 µg/L) and 3–12 months for the highest reported one (1.4 µg/L).

The most frequent metabolite produced under aerobic conditions was 3-amino-5-methylisoxazole (Müller et al., 2013; Reis et al., 2014). This metabolite represents an irreversible breakage of the SMX molecule, more precisely of the sulfonamide radical, in concordance with the aerobic degradation pathway first predicted by Gao et al. (2010) (Fig. 1). This pathway would facilitate the complete mineralization of 4-aminobenzolsulfonate (a by-product of the reaction), as this compound could also be degraded under aerobic conditions (Gao et al., 2010).

According to different authors (Baumgarten et al., 2011; Gauthier et al., 2010; Reis et al., 2014), aerobic degradation can be modelled as first-order kinetics. Table 1 shows a review of the apparent half-lives for SMX degradation compiled from experiments available in the literature. It is noticeable that all half-live

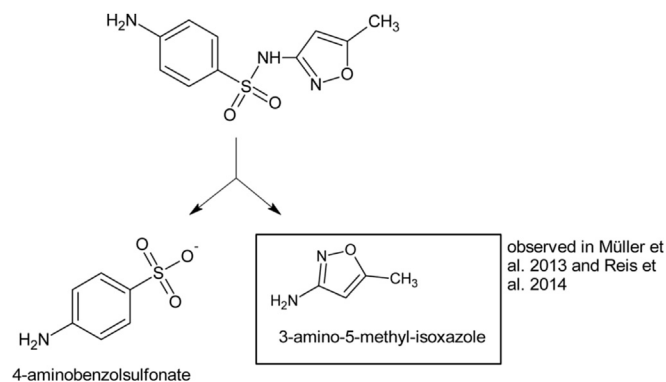


Fig. 1. Pathway of aerobic degradation of SMX proposed by Gao et al. (2010) and later confirmed experimentally by Müller et al. (2013) and Reis et al. (2014).

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