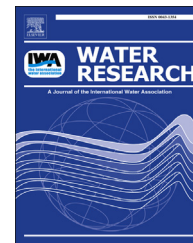




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# Sunlight-induced transformation of sulfadiazine and sulfamethoxazole in surface waters and wastewater effluents

Sabrina Bahnmüller<sup>a,b</sup>, Urs von Gunten<sup>a,b,c</sup>, Silvio Canonica<sup>a,\*</sup>

<sup>a</sup>Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-8600 Dübendorf, Switzerland

<sup>b</sup>Institute of Biogeochemistry and Pollutant Dynamics, ETH Zürich, CH-8092 Zürich, Switzerland

<sup>c</sup>School of Architecture, Civil and Environmental Engineering (ENAC), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

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## ABSTRACT

Sulfadiazine (SD) and sulfamethoxazole (SMX) are widely used sulfonamide antibiotics, which are present as contaminants in surface waters and are known to undergo phototransformation. This kinetic study was conducted to identify the processes responsible for their phototransformation in sunlit surface waters. Water samples from the Thur River (Switzerland) and from a pilot wastewater treatment plant, as well as aqueous solutions of two well-characterized natural dissolved organic matter (DOM) extracts, namely Suwannee River and Pony Lake fulvic acids (SRFA, PLFA), were examined. Both sulfonamides were found to undergo direct and indirect phototransformation, with contributions of excited triplet states of DOM and of effluent organic matter (EfOM) and possibly of hydroxyl radical and other unidentified reactive species. Under simulated sunlight, SMX mainly reacted through direct phototransformation, with a certain contribution of indirect phototransformation occurring for a wastewater effluent. The behavior of SD was found to be more diverse. For river waters, wastewater effluents and PLFA solutions, indirect phototransformation was predominant, while for SRFA solutions direct phototransformation prevailed. The rates of phototransformation of SD were interpreted as the result of a complex interplay between the photosensitizing and the inhibitory effect of DOM/EfOM, with an additional component related to the nitrite ion as a source of photoproduct hydroxyl radical. For typical conditions found in surface waters comparable to the Thur River, phototransformation half-lives on the order of 3–13 d were estimated for the two studied sulfonamides.

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## 1. Introduction

Pharmaceuticals and personal care products have been identified as contaminants of concern owing to their ubiquitous

occurrence and the risk that they might cause to the aquatic environment (Boxall et al., 2003; Daughton and Ternes, 1999; Kolpin et al., 2002). Among the pharmaceuticals, sulfonamide antibiotics are antibacterial compounds widely used in human and veterinary medicine (Hirsch et al., 1999).

\* Corresponding author. Tel.: +41 58 765 5453; fax: +41 58 765 5210.  
E-mail address: [silvio.canonica@eawag.ch](mailto:silvio.canonica@eawag.ch) (S. Canonica).

Depending on their application, they may enter the aquatic environment through wastewater effluents (Götz et al., 2010), leaching from manure (Sukul et al., 2008), or direct use in aquaculture ponds (Guerard et al., 2009a). Sulfonamide antibiotics, including the two title compounds, are frequently encountered at concentrations of 0.01–2 µg/L in surface waters (Hirsch et al., 1999; Hollender et al., 2009; Kolpin et al., 2002). Besides the possible risks connected to the presence of a low-concentration cocktail of pharmaceuticals (Pomati et al., 2006), the main concern is that bacteria in the environment might develop resistance against these antibiotics in spite of the low exposure levels (Dodd et al., 2009; Dodd, 2012; Gilliver et al., 1999; Witte, 1998).

The fate of sulfonamide antibiotics in the aquatic environment has been the subject of various studies in recent years. Although the capability of certain bacterial strains to degrade sulfonamide antibiotics has been newly demonstrated (Bouju et al., 2012; Zhang et al., 2012), investigations in an aquatic outdoor field microcosm lead to the conclusion that biodegradation was not an important loss process for sulfamethoxazole (SMX) and suggested photodegradation as the main depletion pathway (Lam et al., 2004). Boreen and coworkers characterized the phototransformation of ten sulfonamides containing five-membered (Boreen et al., 2004) and six-membered (Boreen et al., 2005) heterocyclic groups. While compounds of the first class were shown to undergo uniquely direct phototransformation under sunlight, the sulfonamides with the six-membered substituents were subject to both direct and indirect phototransformation, the latter apparently initiated by excited triplet states of dissolved organic matter (DOM), denoted hereafter as  $^3\text{DOM}^*$ . The photochemical kinetic behavior of sulfonamide antibiotics is complicated by the acid–base speciation of these compounds, which exhibit two  $\text{pK}_{\text{a}}$ s, typically in the range of  $\approx 1.5$ –3 and  $\approx 5$ –8, respectively (Boreen et al., 2004, 2005). The direct phototransformation kinetics could be described satisfactorily by considering the distinct species involved (protonated, neutral, anionic) and assigning them a constant quantum yield (Boreen et al., 2004, 2005), a method which was also applied to describe UVC-induced phototransformation of SMX (Canonica et al., 2008). At neutral pH, direct phototransformation half-lives (for mid-latitude, mid-summer, surface of water body conditions) were on the order of  $\approx 3$ –30 h, which should translate into half-lives of a few days to weeks if one considers the attenuation of light in a water body, daily and seasonal cycles, and meteorological variability of solar irradiance (Zepp and Cline, 1977). For SMX, an average half-life of 19 d was found in the mentioned microcosm study (Lam et al., 2004), compatible with the just mentioned rough estimation. The indirect phototransformation was studied in more detail for SMX (Lam and Mabury, 2005), sulfadimethoxine (Guerard et al., 2009a, 2009b) and sulfadiazine (SD) (Sukul et al., 2008). The transformation of sulfadimethoxine induced by simulated sunlight was found to be accelerated in the presence of autochthonous (phytoplankton-derived) DOM, while allochthonous (from soil runoff) DOM did not enhance the transformation (Guerard et al., 2009a, 2009b). The study on SD also showed an accelerating effect on the phototransformation rate induced by fulvic and humic acid. By contrast, the phototransformation of SMX was slowed down

by DOM, which was attributed to the light screening effect. A recent study (Ryan et al., 2011) showed that SMX may indeed undergo indirect phototransformation in wastewater effluent, and excited triplet states of effluent organic matter (EfOM), denoted hereafter as  $^3\text{EfOM}^*$ , as well as the hydroxyl radical were proposed to be the key species involved.

Besides the just mentioned investigations, the inhibiting effects of DOM on triplet-induced phototransformation of aquatic contaminants have to be considered as well (Canonica and Laubscher, 2008; Wenk et al., 2011; Wenk and Canonica, 2012). Along with several other contaminants and model aromatic compounds, sulfonamides were shown to be importantly affected by such an inhibition. Allochthonous DOM was found to be a better inhibitor than autochthonous DOM, meaning that indirect phototransformation rates were lower in the presence of allochthonous DOM, in striking coincidence with the results by Guerard and coworkers on sulfadimethoxine (Guerard et al., 2009a, 2009b). To date such an inhibiting effect of DOM on the indirect phototransformation of sulfonamides, induced by the chromophoric components of DOM itself, has only been studied under laboratory conditions using the UV-A and visible emission of a medium-pressure mercury lamp (Wenk and Canonica, 2012). An important result of the latter study was that phenolic antioxidants were successfully used to mimic the inhibiting effect caused by DOM, and phenol was able to inhibit the transformation of SMX and SD initiated by  $^3\text{DOM}^*$ . However, the validity of such a method still has to be demonstrated for the case of irradiation using (simulated) sunlight.

The present study was conceived to identify the various factors that affect the rates of sunlight-induced transformation of sulfonamide antibiotics in surface freshwaters, with a particular focus on DOM and EfOM. SMX and SD were selected as representative compounds of the mentioned two categories of sulfonamides identified by Boreen et al. (2004, 2005). In the pH range investigated in this study (7.9–8.7), no influence of pH on transformation rates of both sulfonamide antibiotics is expected, since both compounds are present almost exclusively (>96%) in their anionic form ( $\text{pK}_{\text{a},2} = 5.7$  for SMX and 6.4 for SD (Boreen et al., 2004, 2005)). The photochemical transformation kinetics of SMX and SD was investigated under simulated sunlight for solutions of two well-characterized fulvic acids, in surface waters and wastewaters, and in a number of water samples taken along the course of the Thur River (North-East Switzerland). Additional mechanistic tests were performed by adding, to the irradiation experiments, isopropanol and phenol to scavenge hydroxyl radical and oxidation intermediates of the sulfonamides, respectively.

## 2. Experimental section

### 2.1. Chemicals

The organic compounds sulfadiazine (SD, Sigma–Aldrich, >99%), sulfamethoxazole (SMX, Sigma–Aldrich >99%), 2,4,6-trimethylphenol (TMP, EGA-Chemie, 99%), isopropanol (Sigma–Aldrich, >99%) and phenol (Fluka,  $\geq 99.5\%$ ) were used without further purification. All inorganic chemicals were

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