



Photodegradation of antibiotics under simulated solar radiation: Implications for their environmental fate



Sudha Rani Batchu^{a,b}, Venkata R. Panditi^{a,b}, Kevin E. O'Shea^a, Piero R. Gardinali^{a,b,*}

^a Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199, USA

^b Southeast Environmental Research Center, Florida International University, Miami, FL 33199, USA

HIGHLIGHTS

- Photolysis was studied using environmentally relevant conditions.
- Photolysis of antibiotics was studied in natural water matrices.
- Integrative effects of matrix composition on the rate of photolysis were reported.
- First report showing conversion of roxithromycin to erythromycin at UV 254 nm
- 15 photo transformation products were identified for the studied antibiotics.

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ABSTRACT

Roxithromycin, erythromycin, ciprofloxacin and sulfamethoxazole are frequently detected antibiotics in environmental waters. Direct and indirect photolysis of these problematic antibiotics were investigated in pure and natural waters (fresh and salt water) under irradiation of different light sources. Fundamental photolysis parameters such as molar absorption coefficient, quantum yield and first order rate constants are reported and discussed. The antibiotics are degraded fastest under ultraviolet 254 nm, followed by 350 nm and simulated solar radiation. The composition of the matrix (pH, dissolved organic content, chloride ion concentration) played a significant role in the observed photodegradation. Under simulated solar radiation, ciprofloxacin and sulfamethoxazole degrade relatively quickly with half-lives of 0.5 and 1.5 h, respectively. However, roxithromycin and erythromycin, macrolides are persistent (half-life: 2.4–10 days) under solar simulation. The transformation products (15) of the targeted antibiotics produced under irradiation experiments were identified using high resolution mass spectrometry and degradation pathways were proposed.

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1. Introduction

Antibiotics are chemotherapeutic agents used in human and veterinary medicine to prevent and treat microbial infections (Sarmah et al., 2006). Antibiotics enter the environment from many sources including household sewer systems, hospital effluents, agricultural runoff, manufacturing process, livestock, and disposal of unused and expired products (Kummerer, 2001). Hence, they have been routinely detected in environmental waters at concentrations up to 1.3 µg/L (Batt and Aga, 2005; Brown et al., 2006; Watanabe et al., 2008; Zuccato et al., 2010). The United States Food and Drug Administration (USFDA) reported that 3.28 million kilograms of antibiotics was sold for human medicinal

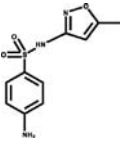
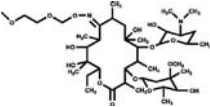
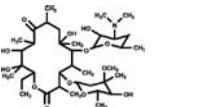
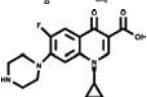
use in 2010 (Pham, 2012). Prevalence and persistence of antibiotics in the aqueous environments are of particular ecological concern because of their biological activity and potential to induce bacterial resistance in natural populations (Wright, 2010). Antibiotic resistance is a serious problem and widespread in wastewaters, environmental waters, marine sediments and in fish (Andersen and Sandaa, 1994; Costanzo et al., 2005; Miranda and Zemelman, 2001; Witte, 1998). Antibiotic resistance to widely used medical and veterinary medications is a serious problem and poses a significant threat to the health humans and livestock infected with the resistant bacterial strains. Particularly alarming is the fact that resistant genes can be mobilized between various environmental compartments and transferred into the food chain (Chee-Sanford et al., 2001).

Although the exposure periods required to induce bacterial resistance to antibiotics are largely unknown, the nature and environmental concentrations of antibiotics have a pronounced influence on the ability to induce such resistance. The environmental concentration and thus

* Corresponding author at: 3000 NE 151st ST, FIU Biscayne Bay Campus, MSB-350, North Miami, Florida 33181, USA. Tel.: +1 305 348 6354; fax: +1 305 348 3772.

E-mail addresses: sbatc001@fiu.edu (S.R. Batchu), vpand001@fiu.edu (V.R. Panditi), osheak@fiu.edu (K.E. O'Shea), gardinal@fiu.edu (P.R. Gardinali).

Table 1
Target antibiotics, structures, CAS and their classification.

Name	Structure	CAS	Classification
Sulfamethoxazole		723-46-6	Sulfonamide antibiotic
Roxithromycin		80214-83-1	Macrolide antibiotic
Erythromycin		114-07-8	Macrolide antibiotic
Ciprofloxacin		85721-33-1	Fluoroquinolone antibiotic

the ability to induce resistance are strongly correlated to antibiotic stability and natural attenuation through hydrolysis, sorption, biotransformation and photodegradation. Unfortunately, the common processes associated with sewage treatment, hydrolysis, biodegradation and sorption are ineffective for the removal of many antibiotics (Gartiser et al., 2007) and thus photodegradation may be the predominant transformation pathway for antibiotics in the environment.

In the recent years, the photodegradation of antibiotics was studied using different light sources including UV light (Pereira et al., 2007), solar simulation (Ge et al., 2010) and natural sunlight (Avisar et al., 2010) for a variety of water matrices including pure water, fresh water (from rivers and lakes) and salt water (Sirtori et al., 2010). The effectiveness of photodecomposition depends on the integrative effects of photon flux, the structure of the molecule and water-matrix composition. For example, the photodegradation of five membered sulfonamides in natural sunlight is solely due to pH dependent direct photolysis (faster) whereas in nitrate-enriched waters it is due to the combination of direct and indirect photolysis (slower) (Boreen et al., 2004). Sirtori et al. (2010) studied the photodegradation kinetics of trimethoprim in demineralized and simulated salt water in a solar simulator and reported that the degradation rate was hindered by the salt content of the water matrix. Moreover, they reported that the nature and abundance of photo-transformation products varied with water matrices (Sirtori et al., 2010). Avisar et al. (2010) reported that photodecomposition rates by UV photolysis decreased for sulfamethoxazole, but was enhanced for oxytetracycline and ciprofloxacin when the pH of the water was increased

Table 2
Characteristics of canal water and salt water used in the experiment.

Parameter	Canal water	Salt water
pH	8.1	7.9
Dissolved organic carbon (mg-C/L)	10.4	1.37
Electrical conductivity ($\mu\text{S}/\text{cm}$)	544	88,000
Salinity (ppt)	0.2	36.0

Table 3
Summary of the gradient program for the chromatographic separation.

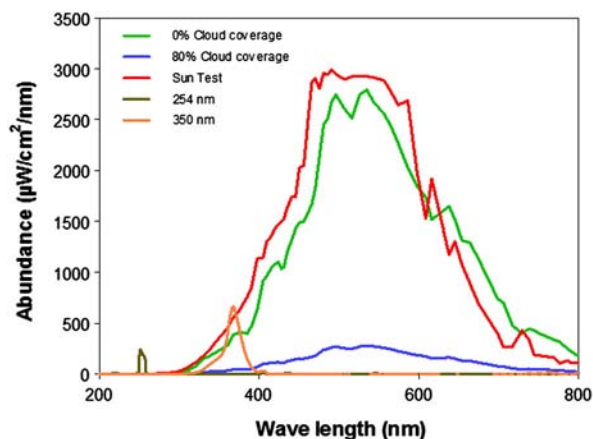
Time (min)	% solvent A (methanol)	% solvent B (0.3% formic acid in water)
0	20	80
13	90	10
16	20	80
25	20	80

Table 4
Optimized parameters for the detection of all analytes and internal standard in MS/MS SRM mode.

Analyte	ESI parameter					
	Precursor ion	m/z	SRM 1	SRM 2	Optimal collision energy	Rt (min)
Sulfamethoxazole	[M + H] ⁺	254	188	194	32	11.5
Roxithromycin	[M + H] ⁺	837	679	522	32	11.7
Erythromycin	[M + H] ⁺	734	558	576	30	10.4
Ciprofloxacin	[M + H] ⁺	332	314	288	55	5.87
Sulfathiazole	[M + H] ⁺	256	156	190	30	8.21

from 5 to 7. Stangroom et al. (1998) showed that dissolved organic matter in natural waters can inhibit or enhance the rate of photolysis of organic compounds. Clearly, past studies suggest that photochemical transformation of antibiotics is a complex process and not easily predicted. In fact, most of the photodegradation studies for antibiotics were performed in amended matrices enriched with humic acids, particulate organic matter, oxidants like titanium dioxide, metal ions like Fe^{3+} or in controlled pH solutions (Belden et al., 2007; Boreen et al., 2004; Paul et al., 2010; Vione et al., 2009; Yan et al., 2013). In contrast to previous studies, kinetic experiments were performed in natural water matrices here. The rate constants obtained in our studies are important for the fundamental understanding required to predict the environmental fate and concentration of these antibiotics in natural waters and drinking water sources. It is also important to understand the effects of water quality on the enhancement/attenuation of the degradation processes involved in the natural transformation of antibiotics. With this in mind, we studied the photolysis of four antibiotics frequently detected in surface waters. Sulfamethoxazole [SMX] is a sulfonamide antibiotic, commonly used in humans in synergistic combination with trimethoprim (under the trade name Bactrim) to treat urinary tract infections and in veterinary medicine as growth promoters (Crosby, 1991). Roxithromycin [ROX] and erythromycin [ERY] are macrolide antibiotics widely used to treat respiratory tract infections (Cals et al., 2008). Ciprofloxacin [CIP], is a fluoroquinolone antibiotic and is one of the most popular fluoroquinolone antibiotic used in human medicine (Giger et al., 2003). Detailed structural information on the selected antibiotics is shown in Table 1.

Photolyses were conducted on the selected antibiotics in matrices modeled to natural water bodies using specific light sources. Reported herein is the photolysis of four problematic antibiotics in pure and natural water matrices under 254 nm, 350 nm and solar simulated light. Our results provide a better fundamental understanding of the photochemical conversion of antibiotics in aqueous media and provide insight about the potential application of photochemical water treatment of problematic antibiotics.

**Fig. 1.** SRM chromatograms of canal water spiked with target antibiotics and internal standard at a concentration of 100 $\mu\text{g}/\text{L}$.

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