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Abiotic, biotic and photolytic degradation affinity of 14 antibiotics and one metabolite – batch experiments and a model framework☆

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ABSTRACT

In this study, degradation affinities of 14 antibiotics and one metabolite were determined in batch experiments. A modelling framework was applied to decrypt potential ranges of abiotic, biotic and photolytic degradation coefficients. In detail, we performed batch experiments with three different sewages in the dark at 7 °C and 22 °C. Additionally, we conducted further batch experiments with artificial irradiation and different dilutions of the sewage at 30 °C – de novo three different sewages were used. The batch experiments were initially spiked with a stock solution with 14 antibiotics and one metabolite to increase background concentrations by 1 μg L^{-1} for each compound. The final antibiotic concentrations were sub-inhibitory with regard to sewage bacteria. The here presented modelling framework based on the Activated Sludge Model No. 3 in combination with adsorption and desorption processes. The model was calibrated with monitored standard sewage compounds before antibiotic degradation rates were quantified. The model decrypted ranges of abiotic, biotic and photolytic degradation coefficients. In detail, six antibiotics were not abiotic degradable at 7 °C, five antibiotics not at 22 °C and only 2 antibiotics at 30 °C. Finally, nine antibiotics were not significantly biodegradable at 7 °C and 22 °C. The model determined the link between adsorption characteristics and biodegradation rates. In detail, the rate was significantly affected by the bio-solid partition coefficient and the duration until adsorption was balanced. All antibiotics and the metabolite were photolytic degradable. In general, photolytic degradation was the most efficient elimination pathway of presented antibiotics except for the given metabolite and penicillin antibiotics.

1. Introduction

Antibiotics are widely used in the treatment and prevention of bacterial infections during a viral disease (Goossens et al., 2005; Van Boeckel et al., 2014). They have been massively administered and persist in the environment (Carvalho and Santos, 2016). The major public concern of the massively consumed antibiotics is their potential to promote antibiotic resistance genes (ARGs) and bacteria (ARB) especially at low concentration levels (Berendonk et al., 2015). Antibiotics and ARGs have been continuously detected in the aquatic environment (Gao et al., 2018; Kümmerer, 2009a; b; Xu et al., 2016). In urban systems, the main anthropogenic source of antibiotics is human excretion. In particular, antibiotics prescribed for humans are partly metabolized in the human body and enter the sewage system via excreted urine and faeces. In Germany, 70% of the antibiotics consumed is excreted unchanged (Kümmerer, 2009a). Sewers have been regarded as one of the most important sinks for antibiotics, ARGs and ARB (Auguet et al., 2017; Wunder et al., 2011). Although most wastewater is drained into wastewater treatment plants (WWTPs), conventional WWTPs are not sufficient to prevent the release of antibiotics into adjacent surface waters (Menz et al., 2017; Michael et al., 2013; Wang et al., 2017b). In addition, the discharge of wastewater, a composite of sewage and stormwater, through combined sewer overflow (CSO) structures into receiving waters is inevitable due to the capacity limitations of urban drainage systems. Consequently, antibiotics enter the

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Nomenclature

Fractions

S_O	Dissolved oxygen [M L^{-3}]
S_S	Readily biodegradable substrate [M L^{-3}]
S_{NH}	NH_4^+ and NH_3 nitrogen [M L^{-3}]
S_{NO}	Nitrate and nitrite nitrogen [M L^{-3}]
X_{BH}	Heterotrophic biomass [M L^{-3}]
X_{BA}	Autotrophic biomass [M L^{-3}]
X_S	Slowly biodegradable substrate [M L^{-3}]
X_I	Particulate inert organic matter [M L^{-3}]
CIP	Ciprofloxacin [M L^{-3}]
LEV	Levofloxacin [M L^{-3}]
AZI	Azithromycin [M L^{-3}]
CLA	Clarithromycin [M L^{-3}]
ROX	Roxithromycin [M L^{-3}]
SMX	Sulfamethoxazole [M L^{-3}]
TRI	Trimethoprim [M L^{-3}]
CER	Cefuroxim [M L^{-3}]
CET	Cefotaxim [M L^{-3}]
AMO	Amoxicillin [M L^{-3}]
PEN	Phenoxymethyl-penicillin [M L^{-3}]
PIP	Piperacillin [M L^{-3}]
DOX	Doxycycline [M L^{-3}]
CLI	Clindamycin [M L^{-3}]
CLS	Clindamycin-sulfoxide [M L^{-3}]
S_{AB}	Dissolved antibiotic of interest [M L^{-3}]
X_{AB}	Adsorbed antibiotic of interest [M L^{-3}]

Sub-, superscripts and others

COD_{tot}	Chemical oxygen demand in total [M L^{-3}]
COD_{mf}	Chemical oxygen demand membrane filtrated (0.45 μm) [M L^{-3}]
TSS	Total suspended solids [M L^{-3}]
NH_4-*N*	Ammonia nitrogen [M L^{-3}]
NO_3-*N*	Nitrate nitrogen [M L^{-3}]
NO_2-*N*	Nitrite nitrogen [M L^{-3}]

Parameter

$i_{N,SS}$	N content of readily biodegradable substrate [$M_N M_{SS}^{-1}$]
$i_{N,XS}$	N content of slowly biodegradable substrate [$M_N M_{XS}^{-1}$]
$i_{N,BM}$	N content of biomass [$M_N M_{XBH}^{-1}$ or $M_N M_{XBA}^{-1}$]
$Y_{H,NO}$	Yield coefficient for heterotrophs in anoxic growth [$M_{XBH} M_{SS}^{-1}$]
Y_H	Yield coefficient for heterotrophs in aerobic growth [$M_{XBH} M_{SS}^{-1}$]
Y_A	Yield coefficient for autotrophs in aerobic growth [$M_{XBA} M_{SNO}^{-1}$]
f_{XS}	Production of X_S in endogenous respiration [$M_{XS} M_{XBA}^{-1}$ or $M_{XS} M_{XBH}^{-1}$]
α_{NO}	Oxygen equivalent of nitrate nitrogen [$M_{SO} M_{SNO}^{-1}$]
k_H	Hydrolysis rate constant [$M_{XS} M_{XBH}^{-1}$ d^{-1}]
μ_H	Heterotrophic max. growth rate [T^{-1}]
b_H	Aerobic endogenous respiration rate of X_{BH} [T^{-1}]
$b_{H,NO}$	Anoxic endogenous respiration rate of X_{BH} [T^{-1}]
η_{NO}	Anoxic reduction factor for growth of X_{BH} [-]
μ_A	Autotrophic max. growth rate [T^{-1}]
b_A	Aerobic endogenous respiration rate of X_{BA} [T^{-1}]
$K_{NH,H}$	Saturation constant of S_{NH} for X_{BH} [M L^{-3}]
$K_{NH,A}$	Saturation constant of S_{NH} for X_{BA} [M L^{-3}]
$K_{NO,H}$	Saturation constant of S_{NO} for X_{BH} [M L^{-3}]
$K_{O,H}$	Saturation constant of S_o for X_{BH} [M L^{-3}]
$K_{O,A}$	Saturation constant of S_o for X_{BA} [M L^{-3}]
K_S	Saturation constant of S_S for X_{BH} [M L^{-3}]
K_X	Saturation constant of X_S for X_{BH} [M L^{-3}]
k_la	Reaeration coefficient [T^{-1}]
T	Temperature [°C]
$S_{O,sat}$	Oxygen saturation concentration [M L^{-3}]
β	Ratio of solubility of oxygen under practical conditions to that in clean water [-]
p	Atmospheric pressure [M L^{-2}]
k_{ads}	Adsorption coefficient [T^{-1}]
k_{des}	Desorption coefficient [T^{-1}]
K_{TOM}	Bio-solid liquid partition coefficient [L^3 M^{-1}]
AB	Antibiotic of interest
$k_{abiotic,T}$	Temperature-specific abiotic degradation coefficient of AB [T^{-1}]
$k_{bio,T}$	Temperature-specific biological degradation coefficient of AB [$L^3 M_{XBH+XBA}^{-1} T^{-1}$]
k_{UV}	photolytic degradation coefficient of AB [$M_{AB} L^{-3} T^{-1}$]
DIL	Mathematical dilution term [-]

environment dissolved and some as well particulate-bound. Although several studies have reported adsorption (Guo et al., 2017; Hou et al., 2010; Maier and Tjeerdema, 2018; Pan et al., 2012; Wang et al., 2017c) and desorption behaviour of antibiotics in soil sciences (D'Angelo and Starnes, 2016; Fernandez-Calvino et al., 2015; Li and Zhang, 2016, 2017; Li et al., 2015; Wu et al., 2013), or adsorption in sludge sediments at WWTPs (Marx et al., 2015a; Polesel et al., 2016; Polesel et al., 2015; Wang et al., 2017a), reports about the adsorption/desorption kinetics of sewer sediment-bound antibiotics are scarce (Kaeseberg et al., 2018). In addition, biodegradation of several antibiotics was studied in laboratory tests such as the OECD test series (301–303, 308). Their affinity to biodegrade was assessed of minor importance, even for some of the ß-lactams (Alexy et al., 2004). Nonetheless, degradation processes during transport in the sewer system as well as in the WWTP were determined (Marx et al., 2015a; Marx et al., 2015b), but quantified antibiotic removal efficiencies vary in the review published by Tiwari et al. (2017) and particularly reports about degradation rates of several antibiotics are scarce.

Furthermore, mathematical models are a useful tool to comprehend complex nexuses. Modelling of antibiotics removal in WWTPs is currently state of the art (Plósz et al., 2013; Polesel et al., 2016; Ramin et al., 2016). Although Box and Draper (1987) concluded that all mathematical models are wrong, they stated that some are useful. Nonetheless, the compromise between the precision of the model and the accessibility of the model parameters remains a challenge (Pomies et al., 2013).

Accordingly, 14 antibiotics and one metabolite were monitored in batch experiments. A modelling framework, based on the Activated Sludge Model No. 3 with adsorption and desorption processes, with secondary metabolic processes, which consider abiotic, biotic and photolytic degradation, was applied. Finally, a literature review was done. We identified and quantified (i) abiotic degradation due to thermal instabilities and chemical hydrolysis, (ii) biodegradation due to bacteria, which are ubiquitous in sewers, WWTPs and in adjacent surface waters due to overflow events, (iii) the effect of adsorption affinity on biodegradation rates, in detail bio-solid partition coefficients and adsorption rates and (iv)