NERC Open Research Archive

sharing our research

Centre for Ecology & Hydrology

NATURAL ENVIRONMENT RESEARCH COUNCIL

Article (refereed) - postprint

Liu, Xiaowei; Lv, Kai; Deng, Chengxun; Yu, Zhimin; Shi, Jianghong; Johnson, Andrew C. 2019. **Persistence and migration of tetracycline, sulfonamide, fluoroquinolone, and macrolide antibiotics in streams using a simulated hydrodynamic system**.

Contact CEH NORA team at
noraceh@ceh.ac.uk
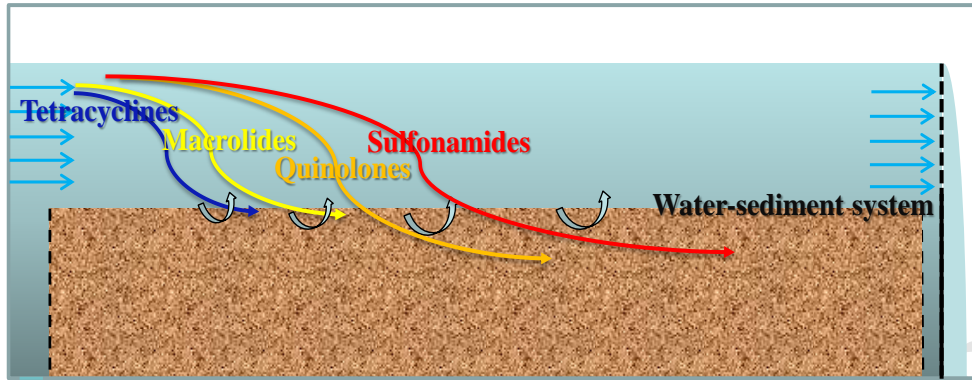
1 Persistence and migration of tetracycline, sulfonamide, fluoroquinolone, and

2 macrolide antibiotics in streams using a simulated hydrodynamic system

3 Xiaowei Liu [a,*], Kai Lv [a], Chengxun Deng [b], Zhimin Yu [b], Jianghong Shi [c], Andrew C.

4 Johnson [d]

5 [a] *School of Resources and Environmental Engineering, Hefei University of Technology, Hefei 230009,*

6 *China*

7 [b] *Department of Biological and Environmental Engineering, Hefei University, Hefei 230022, China*

8 [c] *Guangdong Provincial Key Laboratory of Soil and Groundwater Pollution Control, School of*

9 *Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen*

10 *518055, China*

11 [d] *Centre for Ecology and Hydrology, Wallingford, Oxfordshire OX10 8BB, UK*

12 * Corresponding author.

13 E-mail address: liuxw@hfut.edu.cn (X. Liu).

14 Full postal address: School of Resources and Environmental Engineering, Hefei University of Technology,

15 No. 193 Tunxi Road, Hefei City 230009, China

16 MS Number: ENVPOL_2018_5055

17

18   Abstract: The potential persistence and migration of 14 antibiotics comprising sulfonamides,

19   fluoroquinolones, macrolides and tetracyclines were conducted using a 50-d recirculating

20   flume study supported by batch attenuation experiments with spiked concentrations. The

21   study demonstrated that photodegradation was the dominant attenuation process for these

22   antibiotics in the water environment. The half-lives of 2 to 26 d were in order of

23   sulfadiazine > sulfadimethoxine > sulfamerazine > sulfamethoxazole > sulfamethazine >

24   sulfathiazole > ofloxacin > enrofloxacin > norfloxacin > ciprofloxacin > erythromycin >

25   tetracycline > roxithromycin > oxytetracycline. These modest half-lives meant that the

26   antibiotics were predicted to travel 30-400 km down a typical river before half the

27   concentration would be lost. All antibiotics were detected on the surface sediment in the

28   flume study. Under hyporheic exchange, some of them continually migrated into the deeper

29   sediment and also the sediment pore water. All fluoroquinolones were detected in the

30   sediments. The sulfonamides were detected in the pore water with relatively high

31   concentrations and frequencies. Sulfadiazine, sulfamethazine and sulfathiazole in the upper

32   layer pore water were found to be approaching equilibrium with the surface water. The high

33   presence of sulfonamides in the pore water indicated that their high mobility and persistence

34   potentially pose a risk to hyporheic zone.

35   Keywords: attenuation; hyporheic exchange; conservative tracer; water-sediment system;

36   flume experiment

37   Capsule: Natural attenuation of antibiotics in streams.

38   1. Introduction

39   Antibiotics are now widely used to treat human and animal infections and to promote animal

40   growth in China. The current usage of antibiotics in China recently was estimated at 162 000

41   tons. The usage with daily doses per 1000 inhabitants per day (DID) is almost six times

42   greater than each of those in European countries and America (Ying et al., 2017). Around half

43   of the un-metabolized human-sourced antibiotics enter waterways following partially

44   effective removal in municipal sewage treatment plants (Kümmerer, 2009a; Qiao et al., 2018).

45   Animal-sourced antibiotics move to waterways via surface runoff from manure applied to

46   land (Zhang et al., 2015). Therefore, rivers can become a major sink for antibiotics, and

47   antibiotics have been widely detected in surface waters across the world (Kümmerer, 2009b;

48   Qiao et al., 2018). Although antibiotics in the water environment rarely pose an acute toxicity

49   risk to aquatic organisms (Johnson et al., 2015), the levels may still induce transfer and

50   selection of antibiotic resistance genes (Lopatkin et al., 2016; Wang et al., 2016). Spread of

51   antibiotic resistance genes via the food chain could have consequences for the safety and

52   health of humans (Verraes et al., 2013).

53   In order to assess the risk caused by water borne antibiotics, the determination of the

54   dominant attenuation processes and overall attenuation rates including biodegradation,

55   photodegradation, adsorption and hydrolysis are needed. Currently, most research on the fate

56   of antibiotics in water and sediment have mostly focused on individual attenuation processes

57   based on batch experiments (Baena-Nogueras et al., 2017; Conde-Cid et al., 2018; Li et al.,

58   2018; Kaeseberg et al., 2018). However, in the real-world water environment, multiple

59   processes are occurring simultaneously and the key challenges are to assess which one

60 dominates and to obtain an overall attenuation rate from the multiple processes. Although

61 Luo et al. (2011) provided information on the occurrence and overall attenuation rates of 12

62 antibiotics in rivers, this still did not distinguish which were the dominant mechanisms.

63 Additionally, the exchange of shallow groundwater and surface water (hyporheic exchange)

64 might cause antibiotics to move into groundwater. Li et al. (2015) has studied

65 sulfamethoxazole fate in the hyporheic zone. Little is known about the transport of other

66 antibiotics in the hyporheic zone.

67 This study used a recirculating flume to provide hydrodynamic simulation system to mimic

68 material and energy transfer in streams. To complement the flume work, a series of batch

69 experiments were conducted to investigate the major loss mechanism. Fourteen antibiotics

70 which are frequently detected in Chinese rivers including the sulfonamides sulfadiazine

71 (SDZ), sulfamerazine (SMR), sulfamethazine (SMZ), sulfadimethoxine (SDM),

72 sulfamethoxazole (SMX), sulfathiazole (STZ), the fluoroquinolones enrofloxacin (EFC),

73 ofloxacin (OFC), norfloxacin (NFC), ciprofloxacin (CFC), the tetracyclines oxytetracycline

74 (OTC), tetracycline (TC), and the macrolides erythromycin (ETM) and roxithromycin (RTM)

75 (Table S1) (Bu et al, 2013; Li et al., 2018) were selected for this study. It is believed EFC is

76 only used in animal husbandry; the other antibiotics are used both in human health and

77 animal welfare in China (Zhang et al., 2015). The objectives of this study were:

78 • Assess overall attenuation rates using a flume with local Chinese river water and

79   sediment.

80 • Use the same flume set-up to study migration in the water-pore-sediments

81   • Through batch studies, to identify the dominant attenuation mechanism causing these

82   antibiotics to be lost from the water column.

83   • Assess the consequences of these processes in likely transport of these antibiotics in

84   Chinese rivers

85 2. Materials and methods

86 2.1. Chemicals and reagents

87 Target standards Sulfadiazine (SDZ), Sulfamerazine (SMR), Sulfamethazine (SMZ),

88 Sulfadimethoxine (SDM), Sulfamethoxazole (SMX), Sulfathiazole (STZ) and Enrofloxacin

89 (EFC) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Target standards

90 Ofloxacin (OFC), Norfloxacin (NFC), Ciprofloxacin (CFC) hydrochloride, Oxytetracycline

91 (OTC) hydrochloride, Tetracycline (TC) hydrochloride, Erythromycin (ETM) and

92 Roxithromycin (RTM) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

93 Internal standards Sulfamethazine-$^{13}C_6$ (SMZ-$^{13}C_6$) and Enrofloxacin-D_5 (EFC-D_5)

94 hydrochloride were purchased from Witrga Laboratorien Berlin-Adlershof GmbH (Berlin,

95 Germany); Sulfamethoxazole-D_4 (SMX-D_4) was obtained from Dr. Ehrenstorfer GmbH

96 (Augsburg, Germany); Erythromycin-^{13}C, D_3 (ETM-^{13}C, D_3) and Tetracycline-D_6 (TC-D_6)

97 were obtained from Toronto Research Chemicals (North York, ON, Canada). Each antibiotic

98 standard was dissolved in methanol as standard stock solutions (100 mg L^{-1}). The standard

99 stock solutions were stored at -18°C and were used within three months of purchase to reduce

100 error caused by antibiotic degradation. Working standard mixtures (5, 10, 20, 50, 100 µg L^{-1})

101   were freshly prepared by serial dilution of the stock solutions with acetonitrile and Milli-Q

102   water with 0.1% formic acid (5/95, v/v) at each batch analysis. A mixture of internal

103   standards including SMZ-$^{13}C_6$, EFC-D_5 hydrochloride, SMX-D_4, ETM-^{13}C, D_3 and TC-D_6

104   were prepared in methanol (2 mg L^{-1}).

105   HPLC-grade methyl alcohol and acetone were purchased from Tedia Company (Fairfield, OH,

106   USA). HPLC-grade acetonitrile was obtained from Merck (Darmstadt, Germany).

107   HPLC-grade formic acid (purity of 99%) was purchased from Anaqua Chemicals Supply

108   (Wilmington, USA). The other analytical reagents were obtained from Sinopharm Chemical

109   Reagent Co. Ltd (Shanghai, China).

110   2.2. Water and sediment collection and characterization

111   Water and sediment used in the experiment were taken from the upstream tributary of

112   Tong-yang River in October 2rd 2017 (31°43'14"N; 117°35'29"E; Fig. S1). The Tong-yang

113   River, connecting to the Chaohu Lake in eastern China, was less influenced by human and

114   farming activities. No background antibiotics were found in these samples using sample

115   pre-treatment and instrumental analysis described in detail in Section 2.5 and 2.6. Water was

116   collected in amber containers. Physico-chemical parameters of water (pH, dissolved oxygen,

117   temperature, conductivity, and Oxidation-reduction potential (ORP)) were measured using

118   handheld water quality monitor (Ultrameter II™ 6P, Myronl, US) in situ and in the lab-scale

119   test. Sediment was collected from the top sediment (20-30 mm), and wet sieved (2-mm mesh)

120   in situ. The particle sizes of the sieved sediment were analyzed by a Laser Particle Sizer

121 (Mastersizer 2000, Malvern, UK). The total organic carbon contents (TOC) in water and

122 sediment samples were determined with the TOC Analyser (Multi N/C 3100, Analytikjena,

123 Gemany). The cooled water and sediment samples (4 °C) were transported to the lab located

124 in Hefei City within 8 hours for use in the flume and batch experiments.

125 2.3. Hydrodynamic simulation system using flumes

126 The migration and occurrence of antibiotics in natural water environment was simulated in a

127 recirculating flume with a 5-m long, 30-cm wide and 50-cm deep rectangular channel (Fig.

128 S2). A water pump with 0.75 kw was used to derive water flow. The structure and parameters

129 of the flume were based on descriptions by Elliott and Brooks (1997) and Jin et al. (2010),

130 which are described in the SI and Fig. S3. The sediment was put into the rectangular channel

131 with an approximately 18-cm thickness and 0.3-m^3 sediment. Approximate 0.9-m^3 water was

132 poured into the tank of the flume system with 17-cm water depth in the rectangular channel.

133 Flow velocity was controlled by a valve at 0.2 m s^{-1}, and was monitored by a flow meter

134 (Flowatch, Switzerland). The system was settled beside a window to allow natural sunlight to

135 shine on the apparatus. The system was equilibrated for a week and then run from October

136 3rd to November 21st 2017. The amount of water lost from the system by evaporation was

137 quantified by using a water gauge every two days. The same amount of the evaporated water

138 was added into the system to maintain water balance. A one hundred-milliliter liter standard

139 solution containing the 14 target antibiotics (9 mg L^{-1} of each compound) was added into

140 water column to obtain an initial concentration of approximately 10 μg L^{-1} for each

141 compound to simulate a high exposure level for a natural water environment level (der Beek

7

142   et al., 2016).

143   2.4. Batch experiments

144   In parallel to the flume experiment, batch experiments were carried out to explore the

145   dominant attenuation process of each compound. These used water and sediment freshly

146   collected from the Tong-yang River. The experiments were divided into four groups: 1) the

147   sterile water-only group to quantify photodegradation and hydrolysis; 2) sterile water-only

148   group in the dark for hydrolysis only; 3) non-sterile water-sediment group in the dark for

149   biotransformation, adsorption and hydrolysis); 4) sterile water-sediment group in the dark for

150   adsorption and hydrolysis. Each group was set up in duplicate. A one-liter quantity of water

151   was transferred into each glass bottle for the water-only experiments. In the water-sediment

152   groups, 400g (wet) of sediment was put into each glass bottle and then 950-mL water was

153   added (similar to OECD 308). The steady-state photo-degradation test was conducted in an

154   illuminated incubator with sunlight simulators (SPX-250B-G, Boxun, China). The

155   illumination intensity and wavelength were set as 140 W m^{-2} and 300–800 nm, repectively;

156   the photoperiod was eight hours per day. The annual average values of the intensity and

157   photoperiod for Hefei region during October to December were from the NASA Atmospheric

158   Science Data Center (https://eosweb.larc.nasa.gov/). In the sterile test, water was autoclaved

159   at 121 °C for 20 min, and sodium azide (NaN$_3$, final concentration 0.1%) was added into

160   water-sediment system of groups 1, 2, 4 for inhibiting microbial activity. The initial

161   concentration 50 μg L^{-1} of target compounds was spiked with the antibiotic standards

162   solution. All the systems were incubated at 25 °C over a 30 d period. The percentages of

163   methanol spiked in the batch and flume experiments were approximate 0.05% and 0.011%,

164   respectively, thus there was negligible impact on microbial growth (Ramil et al., 2010).

165   2.5. Sampling and sample pretreatment

166   The surface water, surface sediment and pore water were sampled at hour 2, day 1, 3, 5, 7, 10,

167   15, 20, 30, 40, 50 after antibiotic spiking in the flume. At each sampling point, three 20 mL of

168   surface water and three 2 g samples of surface sediment at 2-3 cm depth were collected at the

169   front, middle and rear position of the flume. After flushing out residual water in the sampling

170   pipes, three 20 mL of pore water sample from the upper, middle and lower sediment layers

171   were collected in amber glass bottles at the front (pore 1), middle (pore 2) and rear position

172   (pore 3) of the flume (Fig. S3). In addition, three 2 g of sediment samples from the upper,

173   middle and lower sediment layers were collected through three column sampling pores (Fig.

174   S3) at day 10, 20, and 30. The sediments from the different layers were sampled using a steel

175   grooved sampler inserted into sediment sampling pore, which did not impede the system

176   operation for the layer sediment sampling. The used pore was filled with fresh sediment and

177   not sampled again. Meanwhile, water samples from the batch experiments were collected at

178   day 1, 3, 5, 7, 10, 15, 20, and 30 in duplicate. A 975 μL sample of water filtered through

179   syringe filters (0.2-μm PTFE, 13 mm, Agilent, US) was transferred to a vial with 25 μL of 2

180   mg L^{-1} internal standards of deuterated and isotope labelling antibiotic analogues, and stored

181   at -18 °C prior to analysis.

182   The water samples taken from the flume were spiked with 25 μL of 2 mg L^{-1} internal

183 standards, filtered through glass fiber filters (0.7-μm GF/F, Whatman, UK). The pH of

184 filtered samples were adjusted to 3 using H_2SO_4 (30%, v/v). Na_2EDTA (0.2 g) was added into

185 the sample to minimize interference from Ca^{2+} and Mg^{2+}. An Oasis Hydrophile-Lipophile

186 Balance (HLB) cartridge (200 mg, 6 mL, Waters, US) preconditioned with 5 mL methanol

187 and 5 mL Milli-Q water was used to extract and clean up each water sample. The water

188 samples were passed through the HLB cartridges at a flow rate of 5-10 mL min^{-1}. The HLB

189 cartridges were washed by 5 mL Milli-Q water and were dried by vacuum pump for at least

190 10 min. The target compounds were eluted with 3 mL methanol/acetone (85:15, v/v) twice

191 (Hou et al., 2015). The 6 mL extract was blown to near dryness under a gentle stream of

192 nitrogen (37 °C) and dissolved in 1 mL of acetonitrile and Milli-Q water with 0.1% formic

193 acid (5:95, v/v). The final extracts were mixed by vortex mixer, ultrasonicated for 5 min, and

194 finally filtered through 0.22-μm PTFE syringe filters. The filtered extracts were stored at

195 -18°C prior to instrumental analysis.

196 The sediment samples were freeze-dried, ground, and then passed through a sieve (120 mesh).

197 Two-grams of sediment was transferred into centrifuge tubes, and then spiked with the

198 mixture of internal standards containing 50 ng of each compound. The spiked samples were

199 placed at 4 °C overnight. The extraction processes followed that of Zhou et al. (2012) with

200 some small modifications. Ten milliliter of acetonitrile and 10 mL of 0.1 M EDTA-Mcllvaine

201 buffer (Na_2EDTA:citric acid monohydrate:$Na_2HPO_4·12H_2O$ = 12.4:4.3:9.2, pH = 4) was

202 added to each centrifuge tube. The mixture was mixed by vortex mixer, ultrasonicated for 10

203 min, and then centrifuged for 5 min at 6000 rpm. This extraction step was repeated twice, and

204 the supernatant at each step was merged into one bottle. The extracts were diluted with

205 Milli-Q water to 200 mL. The solution was extracted and cleaned up by the same processes

206 as those of water sample described above.

207 2.6. Instrumental analysis

208 The target antibiotic compounds were determined by an Agilent 1290 rapid resolution liquid

209 chromatography tandem an Agilent 6460 Triple Quadrupole mass spectrometer

210 (RRLC-MS/MS, Agilent, US). The separation of target antibiotics compounds was

211 accomplished by Agilent Zorbax Eclipse plus-C18 column (RRHD, 2.1 × 100 mm, 1.8 μm,

212 Agilent, US). The mass spectrometer was operated in multiple-reaction monitoring (MRM)

213 mode with positive ionization (ESI+). The instrumental conditions for the target compounds

214 analysis are shown in Table S2.

215 2.7. Quality control and quality assurance

216 The quantification of 14 antibiotics was achieved by using internal standard method with

217 calibration of working standard solutions. The correlation coefficients (R^2) of calibration

218 curve were between 0.99 and 0.9999. The recoveries were performed by spiking 1 L water

219 samples and 2 g sediment samples with standard solutions to three concentrations of 10 ng

220 L^{-1}, 20 ng L^{-1}, 50 ng L^{-1} and 10 ng g^{-1}, 20 ng g^{-1}, 50 ng g^{-1}, 100 ng g^{-1}, respectively. The

221 recoveries of 14 antibiotics in the water samples ranged from 56 ± 1% to 117 ± 11% and the

222 sediment samples ranged from 57 ± 0.1% to 127 ± 5 %, with relative standard deviation

223 (RSD) less than 15% (Table S3 and Table S4). The method detection limits (MDLs) of 14

224 antibiotics ranged from 0.23 – 5.88 ng L^{-1} for water samples (Table S3) and from 0.25 – 2.94

225 ng g^{-1} for the sediment samples (Table S4). The MDLs were determined by spiking 1 L water

226 samples with the mixed standard solution to 5 ng L^{-1}, and then performing the whole

227 pre-treatment processes. The extracts were gradually diluted until the signal-to-noise ratio

228 was equal to 3.

229 2.7. Attenuation rates calculation for the flume study

230 After the antibiotics were spiked into the flume system, the concentrations would naturally

231 decrease due to dilution and mixing with sediment and pore water. Therefore, in order to

232 obtain the true attenuation rates without the influence of mixing dilution, concentration

233 corrections were conducted by using a conservative tracer bromide as a reference compound

234 (Eq. S1 in SI). One liter potassium bromide solution (3 g L^{-1}) was added into water phase

235 of the flume system simultaneously with the antibiotics. Bromide concentrations in surface

236 water and pore water samples were measured by ion chromatography (881 Compact,

237 Metrohm, Switzerland) at the same intervals as the antibiotic determination. Attenuation rate

238 constants (k) and half-life time ($t_{1/2}$) of antibiotics in the surface water were calculated by

239 fitting a first-order kinetic decay model to these corrected concentrations (Eq. S2 and Eq.S3).

240 3. Results and discussion

241 3.1. Simulation system operation performance

242 During the whole operating period, pH was around 7 and ORP was within 150-170 mV

243 (Table S5). The conductivity was stable at around 300 µs cm^{-1} (Table S5) in the flume, which

12

244 was higher than the on-site value of 80 μs cm^{-1}. However, the conductivities in this flume

245 were not beyond the range values in the natural water (50-500 μs cm^{-1}), which would not

246 influence the experiments. The most likely explanation for the elevated conductivity comes

247 from the addition of the potassium bromide tracer. The temperature was maintained around

248 25 °C and the values of DO were between 7.2 to 9.6 mg L^{-1} (Table S5). The TOCs in water

249 and sediment measured at the initial period and end of the experiment did not show

250 significant changes (Table S6). Therefore, the operational performance of this system was

251 relatively stable, and close to water quality conditions of a natural river.

252 3.2. Dominant attenuation processes

253 The relative importance of the different attenuation processes for these antibiotics was

254 investigated with batch studies. These used river water and sediment from the Tong Yang

255 River, which had a pH of 7.8, conductivity of 80 μs cm^{-1} and sediment TOC of 28.3 g kg^{-1}.

256 Photodegradation proved to be the most important of these processes for all the antibiotics

257 apart from OTC (Fig. 1). Photodegradation was a particularly important loss (estimated >

258 70% of the total) for SDZ, SMZ, STZ, EFC, and OFC. The half-lives controlled by

259 photodegradation alone ranged from 4.40 to 32.9 d (Fig. S4). The importance of

260 photodegradation for antibiotics has also been noted by others (Baena-Nogueras et al., 2017;

261 Batchu et al., 2014; Conde-Cid et al. 2018; Li et al., 2018). Biodegradation and adsorption

262 accounted for the rest of the losses from the water column. Adsorption was the most

263 important process for OTC. Hydrolysis, judged on the basis of the dark sterile control, was

264 not found to be important for any of the antibiotics over 30 d (< 1%).

265   3.3. Attenuation of target antibiotics in the surface water flume study

266   After 50 d, most of the macrolides, tetracyclines and fluoroquinolones had been lost from the

267   water column whilst the more persistent sulfonamides had around 20% remaining (Fig. 2).

268   The losses of the 14 antibiotics in the surface water were corrected for dilution by

269   comparison with the conservative tracer bromide which was simultaneously measured in the

270   surface water (Fig. S5). The k and $t_{1/2}$ of SMR, SMZ, SDM, SMX, STZ, CFC, and OTC were

271   calculated using a first-order kinetic model and these fitted well with the observations ($R^2 >$

272   0.8; $p < 0.01$) ; whilst the fitting for the others presented relatively weakly correlated fitting

273   ($0.6 < R^2 < 0.8$; $p < 0.01$) (Fig. S6). The order of attenuation rate was OTC > RTM > TC >

274   ETM > CFC > NFC > EFC > OFX > STZ > SMZ > SMX > SMR > SDM > SDZ (Table 1).

275   Among these antibiotics, SDZ was the most persistent with 25.6-d $t_{1/2}$. The fluoroquinolones

276   presented moderate attenuation rates with k ranging from 0.06 d^{-1} and 0.13 d^{-1}. OTC and

277   RTM had the shortest half-lives (Table 1), and were completely removed after 15 d (Fig. 2).

278   Overall, the attenuation rates for these antibiotics are rather low and would allow them to

279   travel considerable distances down river. This persistence would increase on cloudy days due

280   to the low contribution of photodegradation.

281   Another way of examining the relevance of these loss rates is to consider the distances

282   travelled down a river after which 50% would be lost. Thus, for these antibiotics half would

283   be lost only following a river travel of 31 km to 444 km at 0.2 m s^{-1} velocity (Table 1). In the

284   case of the Nanfei River (a typical unban river close to the sampling sites) in winter which

285   has a flow velocity 0.15 m s^{-1}, half of the antibiotics loss will take place following a travel

286 distance of 23 km to 333 km. In summer, with a 3.5 m s^{-1} flow velocity, the travel distance

287 would range from 55 km to 777 km before half the antibiotics would be lost. In fact, for the

288 Nanfei River, the distance from the urban discharge to Chaohu Lake is only 25 km. Thus, a

289 considerable portion of the antibiotic discharge from Hefei City would reach this lake without

290 dissipation.

291 3.4. Binding and movement of the antibiotics within pore waters and sediment

292 All antibiotics were detected in the surface sediments, which was attributed to their migration

293 and adsorption to sediment from the water phase (Fig. 3). This is consistent with the

294 adsorption mechanism playing a role in the removals of all antibiotics from the water phase

295 in the batch experiments. For EFC, NFC, TC, OTC and RTM, adsorption played an important

296 role its loss from the water column. This is related to the relatively high hydrophobicity of

297 these compounds ($150 < K_d < 889$ L kg^{-1}) (Table S7). Adsorption made a relatively small

298 contribution to the dissipation of sulfonamides (Fig. 1) due to the low adsorption affinity (K_d

299 < 80 L kg^{-1}). Sulfonamides, as acidic compounds, have a declining sorption capacity with

300 increasing alkalinity due to electrostatic repulsion from sediment (Gothwal and Shashidhar,

301 2015). Therefore, their adsorption capacity decrease in the weakly-alkaline water

302 environment of the flume (Table S5).

303 The sulfonamides concentration in sediment continuously increased until around day 20

304 when it stabilized to $10 - 50$ ng g^{-1} at day 50. Similarly, the concentrations of the other

305 antibiotics in the surface sediments increased rapidly before day 10, and then quickly

15

306 declined until leading to their disappearance at day 50. The two types of behavior were

307 attributed to the difference in their persistence. The sulfonamides have relatively low

308 attenuation rates, thus the part transported to sediment only slowly dissipated compared with

309 the tetracyline, macrolide and fluoroquinolone antibiotics which have higher attenuation rates.

310 For OTC adsorption was shown to be particularly important in the batch studies (58.7%) (Fig.

311 1), which may explain why OTC had the highest concentration in sediment (Fig. 3). In

312 addition, due to its relatively high biodegradation rate (k = 0.0469 d^{-1}) (Fig. S4), OTC in

313 sediment was rapidly dissipated after day 10 and almost disappeared at day 20 (Fig. 3), thus it

314 could not be detected in the lower layer sediments (Fig. 4). All fluoroquinolones including

315 EFC, NFC, OFC, and CFC were detected in the layer sediments at 5 cm, 10 cm and 15 cm

316 depth (Fig. 4), which might be attributed to the relatively strong adsorption to sediment (Fig.

317 1) and the low attenuation rates (Fig. 1 and Table 1).

318 Most of these antibiotics were detected in the pore water from the upper layer (Fig. 5 and Fig.

319 S7). The sulfonamides were present in the upper layer pore water at the highest

320 concentrations. SDZ, SMZ, SDM and STZ were found to be approaching equilibrium with

321 the surface water until day 50, which might be attributed to the higher mobility caused by the

322 low adsorption (Fig. 1). However, in the middle and lower layer pore water, only a few

323 antibiotics were detected, which may have two explanations. One is the limited exchange of

324 surface and pore water caused by the low flow velocity (0.2 m s^{-1}). Another is that most

325 antibiotics were completely retained and dissipating in the upper layer due to the relatively

326 high organic contents and fine texture of sediments (Table S6 and Table S8). Currently,

327 antibiotics have been detected in groundwater of different regions across the world (Kivits et

328 al., 2018; Lopez-Serna et al., 2013; Ma et al., 2015). Thus, further clarification of their

329 transport paths to groundwater is needed.

330 4. Conclusions

331 Photodegradation was the dominant attenuation mechanism of these antibiotics in a

332 water-sediment system. These antibiotics had a wide-range of half-lives with 1.28 d and 25.7

333 d in the water column, which would permit considerable travel distances to take place for

334 many of them in rivers. The adsorption onto the surface sediment in the flume study

335 contributed to part of antibiotic removals from the water phase. All fluoroquinolones and two

336 sulfonamides (SDZ and SDM) migrated further to the deep layer sediments, but there was

337 less presence in the pore water due to the strong adsorption. Adsorption made a relatively

338 small contribution to the dissipation of sulfonamides due to the low adsorption affinity. Thus,

339 the sulfonamides were present in the pore water and approached equilibrium with the surface

340 water at the upper layer, which would permit their high mobility to pore water in hyporheic

341 zone. Therefore, these sulfonamides due to their high mobility and persistence might be

342 important candidates for groundwater contamination.

353 **References**

354 Baena-Nogueras, R.M., Gonzalez-Mazo, E., Lara-Martin, P.A., 2017. Degradation kinetics of

355   pharmaceuticals and personal care products in surface waters: photolysis vs biodegradation.

356   Sci. Total Environ. 590, 643‒654.

357 Batchu, S.R., Panditi, V.R., O'Shea, K.E., Gardinali, P.R., 2014. Photodegradation of

358   antibiotics under simulated solar radiation: Implications for their environmental fate. Sci.

359   Total Environ. 470-471, 299‒310.

360 Bu, Q., Wang, B., Huang, J., Deng, S., Yu, G., 2013. Pharmaceuticals and personal care

361   products in the aquatic environment in China: A review, J. Hazard. Mater. 262, 189‒211.

362 Conde-Cid, M., Fernández-Calviño, D., Nóvoa-Muñoz, J.C., Arias-Estévez, M., Díaz-Raviña,

363   M., Fernández-Sanjurjo, M.J., Núñez-Delgado, A., Álvarez-Rodríguez, E., 2018. Biotic

364   and abiotic dissipation of tetracyclines using simulated sunlight and in the dark. Sci. Total

365   Environ. 635, 1520‒1529.

366 der Beek, T.A, Weber, F.A., Bergmann, A., Hickmann, S., Ebert, I., Hein, A., Kuster, A., 2016.

367   Pharmaceuticals in the environment-global occurrences and perspectives. Environ. Toxicol.

368   Chem. 35, 823–835.

369 Elliott, A.H., Brooks, N.H., 1997. Transfer of nonsorbing solutes to a streambed with bed

370   forms: Theory. Water Resour. Res. 33, 123‒136.

371 Gothwal, R., Shashidhar, T., 2015. Antibiotic pollution in the environment: A review.

372   Clean-Soil Air Water, 43, 479‒489.

373 Hou, J., Wan, W.N., Mao, D.Q., Wang, C., Mu, Q.H., Qin, S.Y., Luo, Y., 2015. Occurrence

374   and distribution of sulfonamides, tetracyclines, quinolones, macrolides, and nitrofurans in

375   livestock manure and amended soils of Northern China. Environ. Sci. Pollut. R. 22,

376   4545‒4554.

377 Jin, G., Tang, H., Gibbes, B., Li, L., Barry, D.A., 2010. Transport of nonsorbing solutes in a

378   streambed with periodic bedforms. Adv. Water Resour. 33, 1402‒1416.

379 Johnson, A.C., Keller, V., Dumont, E., Sumpter, J.P., 2015. Assessing the concentrations and

380   risks of toxicity from the antibiotics ciprofloxacin, sulfamethoxazole, trimethoprim and

381   erythromycin in European rivers. Sci. Total Environ. 511, 747‒755.

382 Kaeseberg, T., Zhang, J., Schubert, S., Oertel, R., Krebs, P., 2018. Abiotic, biotic and

383   photolytic degradation affinity of 14 antibiotics and one metabolite - batch experiments

384   and a model framework. Environ. Pollut. 241, 339‒350.

385 Kivits, T., Broers, H.P., Beeltje, H., van Vliet, M., Griffioen, J., 2018. Presence and fate of

386   veterinary antibiotics in age-dated groundwater in areas with intensive livestock farming."

387   Environ. Pollut. 241, 988-998.

388 Kümmerer, K., 2009a. Antibiotics in the aquatic environment – A review – Part I.

389   Chemosphere 75(4), 417-434.

390 Kümmerer, K., 2009b. Antibiotics in the aquatic environment – A review – Part I.

391   Chemosphere 75(4), 435-441.

392   Li, S., Shi, W., Liu, W., Li, H., Zhang, W., Hu, J., Ke, Y., Sun, W., Ni, J. , 2018. A

393   duodecennial national synthesis of antibiotics in China's major rivers and seas (2005–2016).

394   Sci. Total Environ. 615, 906–917.

395   Li, Y., Rashid, A., Wang, H., Hu, A., Lin, L., Yu, C.P., Chen, M., Sun, Q., 2018. Contribution

396   of biotic and abiotic factors in the natural attenuation of sulfamethoxazole: A path analysis

397   approach. Sci. Total Environ. 633, 1217-1226.

398   Li, Z., Sobek, A., Radke, M., 2015. Flume experiments to investigate the environmental fate

399   of pharmaceuticals and their transformation products in streams. Environ. Sci. Technol. 49,

400   6009–6017.

401   Lopatkin, A.J., Huang, S., Smith, R.P., Srimani, J.K., Sysoeva, T.A., Bewick, S., Karig, D.K.,

402   You, L., 2016. Antibiotics as a selective driver for conjugation dynamics. Nat. Microbiol. 1,

403   16044.

404   Lopez-Serna, R., Jurado, A., Vazquez-Sune, E., Carrera, J., Petrovic, M., Barcelo, D., 2013.

405   Occurrence of 95 pharmaceuticals and transformation products in urban groundwaters

406   underlying the metropolis of Barcelona, Spain. Environ. Pollut. 174,305-315.

407   Luo, Y., Xu, L., Rysz, M., Wang, Y., Zhang, H., Alvarez, P.J.J., 2011. Occurrence and

408   Transport of Tetracycline, Sulfonamide, Quinolone, and Macrolide Antibiotics in the

409   Haihe River Basin, China. Environ. Sci. Technol. 45, 1827–1833.

410   Ma, Y.P., Li, M., Wu, M.M., Li, Z., Liu, X., 2015. Occurrences and regional distributions of

411   20 antibiotics in water bodies during groundwater recharge. Sci. Total Environ. 518,

412   498–506.

413 Qiao, M., Ying, G.G., Singer, A.C., Zhu Y.G., 2018. Review of antibiotic resistance in China

414   and its environment. Environ. Int. 110, 160-172.

415 Ramil, M., El Aref, T., Fink, G., Scheurer, M., Ternes, T.A. 2010. Fate of Beta Blockers in

416   Aquatic-Sediment Systems: Sorption and Biotransformation. Environ. Sci. Technol. 44,

417   962–970.

418 Verraes, C., Van Boxstael, S., Van Meervenne, E., Van Coillie, E., Butaye, P., Catry, B., de

419   Schaetzen, M.A., Van Huffel, X., Imberechts, H., Dierick, K., Daube, G., Saegerman, C.,

420   De Block, J., Dewulf, J., Herman L., 2013. Antimicrobial Resistance in the Food Chain: A

421   Review. Int. J. Environ. Res. Public Health 10, 2643−2669.

422 Wang, F., Stedtfeld, R.D., Kim, O.S., Chai, B., Yang, L., Stedtfeld, T.M., Hong S.G., Kim,

423   D., Lim, H.S., Hashsham, S.A., Tiedje, J.M., Sul, W.J., 2016. Influence of soil

424   characteristics and proximity to Antarctic research stations on abundance of antibiotic

425   resistance genes in soils. Environ. Sci. Technol. 50, 12621−12629.

426 Ying, G.G., He, L.Y., Ying, A.J., Zhang, Q.Q., Liu, Y.S., Zhao, J.L., 2017. China must

427   reduce its antibiotic use. Environ. Sci. Technol. 51, 1072−1073.

428 Zhang, Q.Q., Ying, G.G, Pan, C.G., Liu, Y.S., Zhao, J.L., 2015. Comprehensive evaluation of

429   antibiotics emission and fate in the river basins of China: source analysis, multimedia

430   modeling, and linkage to bacterial resistance, Environ. Sci. Technol. 49, 6772−6782.

431 Zhou, L.J., Ying, G.G., Liu, S., Zhao, J.L., Chen, F., Zhang, R.Q., Peng, F.Q., Zhang Q.Q.,

432   2012. Simultaneous determination of human and veterinary antibiotics in various

433   environmental matrices by rapid resolution liquid chromatography–electrospray ionization

434   tandem mass spectrometry. J. Chromatogr. A 1244, 123−138.

435

436

Figure captions

Fig. 1. Contribution ratio of each individual attenuation processes (including photodegradation, adsorption and biodegradation) in the batch experiments carried out at 25 °C over 30 d periods.

Fig. 2. Temporal profiles of four classes of antibiotics in surface water of the flume study over a 50 d period (mean ± standard deviation).

Fig. 3. Temporal profiles of four classes of antibiotics in surface sediment of the flume study over a 50 d period (mean ± standard deviation).

Fig. 4. Antibiotics in the upper, middle and lower layer sediment at the three sampling time (day 10, day 20 and day 30). The depth of the upper, middle and lower layers was 5 cm, 10cm and 15 cm, respectively.

Fig. 5. Dynamic equilibrium relationships of 14 antibiotics in the pore water with those in the surface water at pore 1. The depth of the upper, middle and lower layers was 5 cm, 10 cm and 15 cm, respectively.
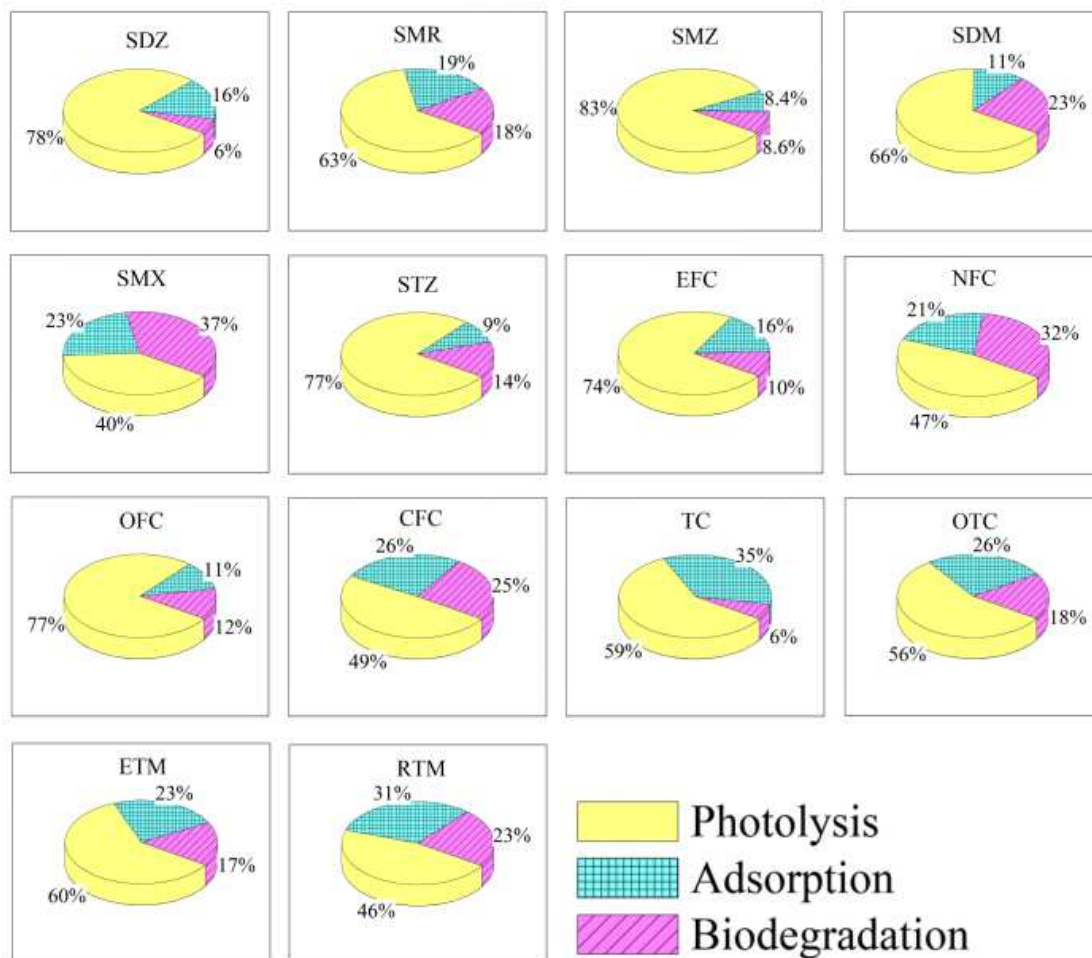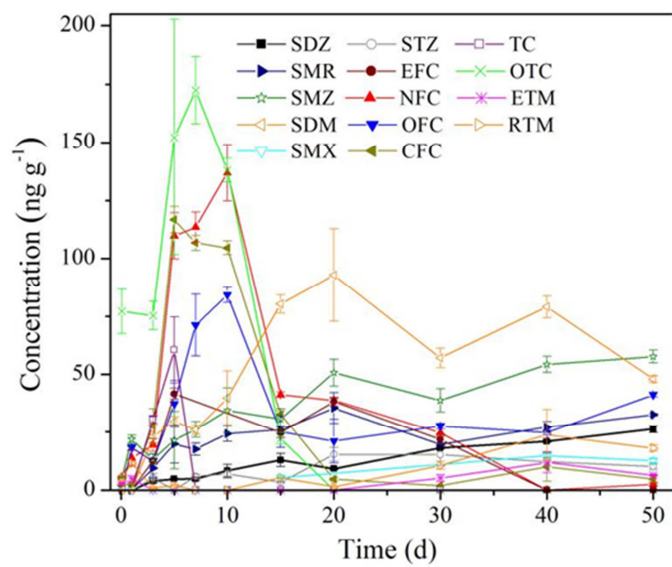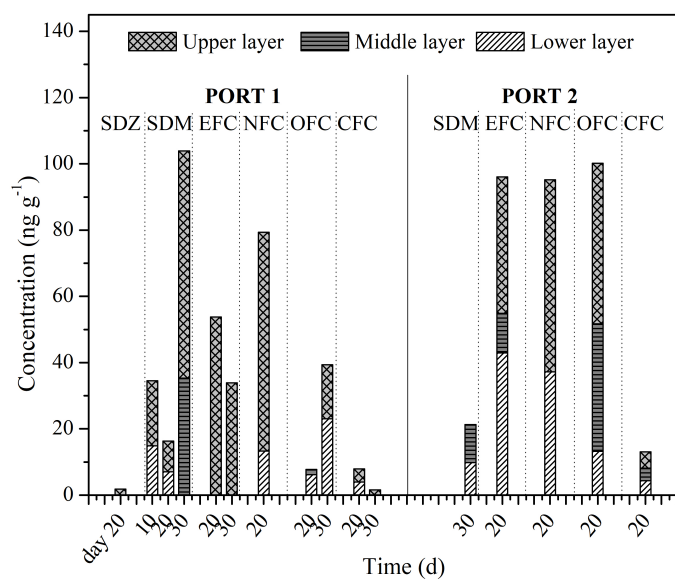
451

Table 1

Attenuation rate constants (k), half-life time ($t_{1/2}$) and half-life distance (d_h)* of 14 antibiotics
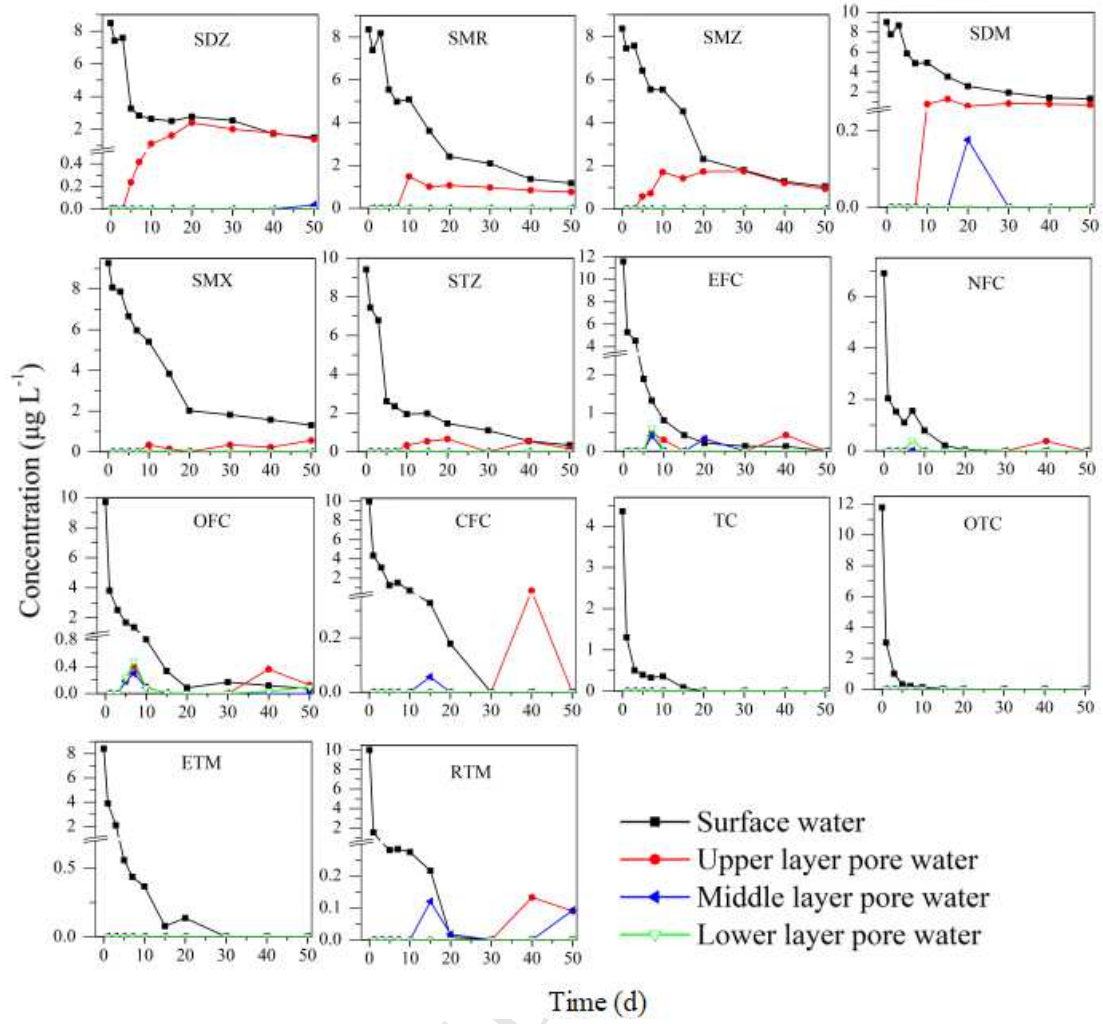
in surface water for the flume experiment.

Compound	k (d^{-1})	$t_{1/2}$ (d)	d_h (km)	Compound	k (d^{-1})	$t_{1/2}$ (d)	d_h (km)
SDZ	0.027	25.7	444	NFC	0.123	5.64	97
SMZ	0.040	17.3	299	OFC	0.062	11.1	192
SMX	0.039	17.8	308	CFC	0.130	5.33	92
SDM	0.038	18.2	314	TC	0.167	4.15	72
SMR	0.039	17.9	309	OTC	0.380	1.82	31
STZ	0.052	13.3	230	ETM	0.164	4.22	73
EFC	0.079	8.78	152	RTM	0.251	2.76	48

d_h was calculated by the average flow velocity (0.2 m s^{-1}) multiplying $t_{1/2}$

SDZ — 16%, 6%, 78%
SMR — 19%, 18%, 63%
SMZ — 8.4%, 8.6%, 83%
SDM — 11%, 23%, 66%
SMX — 23%, 37%, 40%
STZ — 9%, 14%, 77%
EFC — 16%, 10%, 74%
NFC — 21%, 32%, 47%
OFC — 11%, 12%, 77%
CFC — 26%, 25%, 49%
TC — 35%, 6%, 59%
OTC — 26%, 18%, 56%
ETM — 23%, 17%, 60%
RTM — 31%, 23%, 46%

Photolysis
Adsorption
Biodegradation

Highlight:

- Attenuation of 14 antibiotics was studied for 50 d in a simulated stream.

- Persistence was in order of sulfonamides > quinolones > macrolides > tetracyclines.

- Photodegradation was the dominant attenuation mechanism.

- All quinolones were detected in the lower layer sediments at15 cm depth.

- Sulfonamides were present in the sediment pore water with high concentrations.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: