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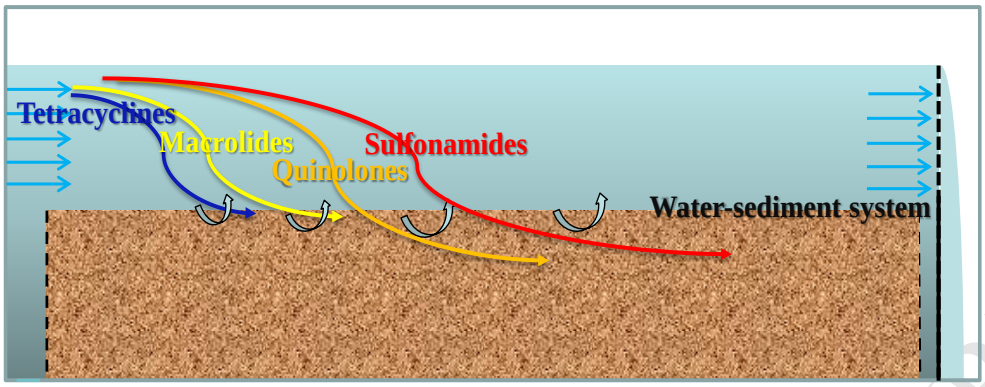

Persistence and migration of tetracycline, sulfonamide, fluoroquinolone, and macrolide antibiotics in streams using a simulated hydrodynamic system

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Abstract: The potential persistence and migration of 14 antibiotics comprising sulfonamides, fluoroquinolones, macrolides and tetracyclines were conducted using a 50-d recirculating flume study supported by batch attenuation experiments with spiked concentrations. The study demonstrated that photodegradation was the dominant attenuation process for these antibiotics in the water environment. The half-lives of 2 to 26 d were in order of sulfadiazine > sulfadimethoxine > sulfamerazine > sulfamethoxazole > sulfamethazine > sulfathiazole > ofloxacin > enrofloxacin > norfloxacin > ciprofloxacin > erythromycin > tetracycline > roxithromycin > oxytetracycline. These modest half-lives meant that the antibiotics were predicted to travel 30-400 km down a typical river before half the concentration would be lost. All antibiotics were detected on the surface sediment in the flume study. Under hyporheic exchange, some of them continually migrated into the deeper sediment and also the sediment pore water. All fluoroquinolones were detected in the sediments. The sulfonamides were detected in the pore water with relatively high concentrations and frequencies. Sulfadiazine, sulfamethazine and sulfathiazole in the upper layer pore water were found to be approaching equilibrium with the surface water. The high presence of sulfonamides in the pore water indicated that their high mobility and persistence potentially pose a risk to hyporheic zone.

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

Capsule: Natural attenuation of antibiotics in streams.

1. Introduction

Antibiotics are now widely used to treat human and animal infections and to promote animal growth in China. The current usage of antibiotics in China recently was estimated at 162 000 tons. The usage with daily doses per 1000 inhabitants per day (DID) is almost six times greater than each of those in European countries and America (Ying et al., 2017). Around half of the un-metabolized human-sourced antibiotics enter waterways following partially effective removal in municipal sewage treatment plants (Kümmerer, 2009a; Qiao et al., 2018). Animal-sourced antibiotics move to waterways via surface runoff from manure applied to land (Zhang et al., 2015). Therefore, rivers can become a major sink for antibiotics, and antibiotics have been widely detected in surface waters across the world (Kümmerer, 2009b; Qiao et al., 2018). Although antibiotics in the water environment rarely pose an acute toxicity risk to aquatic organisms (Johnson et al., 2015), the levels may still induce transfer and selection of antibiotic resistance genes (Lopatkin et al., 2016; Wang et al., 2016). Spread of antibiotic resistance genes via the food chain could have consequences for the safety and health of humans (Verraes et al., 2013).

In order to assess the risk caused by water borne antibiotics, the determination of the dominant attenuation processes and overall attenuation rates including biodegradation, photodegradation, adsorption and hydrolysis are needed. Currently, most research on the fate of antibiotics in water and sediment have mostly focused on individual attenuation processes based on batch experiments (Baena-Nogueras et al., 2017; Conde-Cid et al., 2018; Li et al., 2018; Kaeseberg et al., 2018). However, in the real-world water environment, multiple processes are occurring simultaneously and the key challenges are to assess which one

dominates and to obtain an overall attenuation rate from the multiple processes. Although Luo et al. (2011) provided information on the occurrence and overall attenuation rates of 12 antibiotics in rivers, this still did not distinguish which were the dominant mechanisms. Additionally, the exchange of shallow groundwater and surface water (hyporheic exchange) might cause antibiotics to move into groundwater. Li et al. (2015) has studied sulfamethoxazole fate in the hyporheic zone. Little is known about the transport of other antibiotics in the hyporheic zone.

This study used a recirculating flume to provide hydrodynamic simulation system to mimic material and energy transfer in streams. To complement the flume work, a series of batch experiments were conducted to investigate the major loss mechanism. Fourteen antibiotics which are frequently detected in Chinese rivers including the sulfonamides sulfadiazine (SDZ), sulfamerazine (SMR), sulfamethazine (SMZ), sulfadimethoxine (SDM), sulfamethoxazole (SMX), sulfathiazole (STZ), the fluoroquinolones enrofloxacin (EFC), ofloxacin (OFC), norfloxacin (NFC), ciprofloxacin (CFC), the tetracyclines oxytetracycline (OTC), tetracycline (TC), and the macrolides erythromycin (ETM) and roxithromycin (RTM) (Table S1) (Bu et al, 2013; Li et al., 2018) were selected for this study. It is believed EFC is only used in animal husbandry; the other antibiotics are used both in human health and animal welfare in China (Zhang et al., 2015). The objectives of this study were:

- Assess overall attenuation rates using a flume with local Chinese river water and sediment.
- Use the same flume set-up to study migration in the water-pore-sediments

- Through batch studies, to identify the dominant attenuation mechanism causing these antibiotics to be lost from the water column.
- Assess the consequences of these processes in likely transport of these antibiotics in Chinese rivers

2. Materials and methods

2.1. Chemicals and reagents

Target standards Sulfadiazine (SDZ), Sulfamerazine (SMR), Sulfamethazine (SMZ), Sulfadimethoxine (SDM), Sulfamethoxazole (SMX), Sulfathiazole (STZ) and Enrofloxacin (EFC) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Target standards Ofloxacin (OFC), Norfloxacin (NFC), Ciprofloxacin (CFC) hydrochloride, Oxytetracycline (OTC) hydrochloride, Tetracycline (TC) hydrochloride, Erythromycin (ETM) and Roxithromycin (RTM) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Internal standards Sulfamethazine-$^{13}C_6$ (SMZ-$^{13}C_6$) and Enrofloxacin-D_5 (EFC-D_5) hydrochloride were purchased from Witrga Laboratorien Berlin-Adlershof GmbH (Berlin, Germany); Sulfamethoxazole-D_4 (SMX-D_4) was obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany); Erythromycin-^{13}C, D_3 (ETM-^{13}C, D_3) and Tetracycline-D_6 (TC-D_6) were obtained from Toronto Research Chemicals (North York, ON, Canada). Each antibiotic standard was dissolved in methanol as standard stock solutions (100 mg L^{-1}). The standard stock solutions were stored at -18°C and were used within three months of purchase to reduce error caused by antibiotic degradation. Working standard mixtures (5, 10, 20, 50, 100 μg L^{-1})

were freshly prepared by serial dilution of the stock solutions with acetonitrile and Milli-Q water with 0.1% formic acid (5/95, v/v) at each batch analysis. A mixture of internal standards including SMZ-$^{13}C_6$, EFC-D_5 hydrochloride, SMX-D_4, ETM-^{13}C, D_3 and TC-D_6 were prepared in methanol (2 mg L^{-1}).

HPLC-grade methyl alcohol and acetone were purchased from Tedia Company (Fairfield, OH, USA). HPLC-grade acetonitrile was obtained from Merck (Darmstadt, Germany). HPLC-grade formic acid (purity of 99%) was purchased from Anaqua Chemicals Supply (Wilmington, USA). The other analytical reagents were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China).

2.2. Water and sediment collection and characterization

Water and sediment used in the experiment were taken from the upstream tributary of Tong-yang River in October 2rd 2017 (31°43'14"N; 117°35'29"E; Fig. S1). The Tong-yang River, connecting to the Chaohu Lake in eastern China, was less influenced by human and farming activities. No background antibiotics were found in these samples using sample pre-treatment and instrumental analysis described in detail in Section 2.5 and 2.6. Water was collected in amber containers. Physico-chemical parameters of water (pH, dissolved oxygen, temperature, conductivity, and Oxidation-reduction potential (ORP)) were measured using handheld water quality monitor (Ultrameter II™ 6P, Myronl, US) in situ and in the lab-scale test. Sediment was collected from the top sediment (20-30 mm), and wet sieved (2-mm mesh) in situ. The particle sizes of the sieved sediment were analyzed by a Laser Particle Sizer

(Mastersizer 2000, Malvern, UK). The total organic carbon contents (TOC) in water and sediment samples were determined with the TOC Analyser (Multi N/C 3100, Analytikjena, Gemany). The cooled water and sediment samples (4 °C) were transported to the lab located in Hefei City within 8 hours for use in the flume and batch experiments.

2.3. Hydrodynamic simulation system using flumes

The migration and occurrence of antibiotics in natural water environment was simulated in a recirculating flume with a 5-m long, 30-cm wide and 50-cm deep rectangular channel (Fig. S2). A water pump with 0.75 kw was used to derive water flow. The structure and parameters of the flume were based on descriptions by Elliott and Brooks (1997) and Jin et al. (2010), which are described in the SI and Fig. S3. The sediment was put into the rectangular channel with an approximately 18-cm thickness and 0.3-m^3 sediment. Approximate 0.9-m^3 water was poured into the tank of the flume system with 17-cm water depth in the rectangular channel. Flow velocity was controlled by a valve at 0.2 m s^{-1}, and was monitored by a flow meter (Flowatch, Switzerland). The system was settled beside a window to allow natural sunlight to shine on the apparatus. The system was equilibrated for a week and then run from October 3rd to November 21st 2017. The amount of water lost from the system by evaporation was quantified by using a water gauge every two days. The same amount of the evaporated water was added into the system to maintain water balance. A one hundred-milliliter liter standard solution containing the 14 target antibiotics (9 mg L^{-1} of each compound) was added into water column to obtain an initial concentration of approximately 10 μg L^{-1} for each compound to simulate a high exposure level for a natural water environment level (der Beek

et al., 2016).

2.4. Batch experiments

In parallel to the flume experiment, batch experiments were carried out to explore the dominant attenuation process of each compound. These used water and sediment freshly collected from the Tong-yang River. The experiments were divided into four groups: 1) the sterile water-only group to quantify photodegradation and hydrolysis; 2) sterile water-only group in the dark for hydrolysis only; 3) non-sterile water-sediment group in the dark for biotransformation, adsorption and hydrolysis); 4) sterile water-sediment group in the dark for adsorption and hydrolysis. Each group was set up in duplicate. A one-liter quantity of water was transferred into each glass bottle for the water-only experiments. In the water-sediment groups, 400g (wet) of sediment was put into each glass bottle and then 950-mL water was added (similar to OECD 308). The steady-state photo-degradation test was conducted in an illuminated incubator with sunlight simulators (SPX-250B-G, Boxun, China). The illumination intensity and wavelength were set as 140 W m^{-2} and 300–800 nm, repectively; the photoperiod was eight hours per day. The annual average values of the intensity and photoperiod for Hefei region during October to December were from the NASA Atmospheric Science Data Center (https://eosweb.larc.nasa.gov/). In the sterile test, water was autoclaved at 121 °C for 20 min, and sodium azide (NaN_3, final concentration 0.1%) was added into water-sediment system of groups 1, 2, 4 for inhibiting microbial activity. The initial concentration 50 μg L^{-1} of target compounds was spiked with the antibiotic standards 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:$Na_2HPO_4 \cdot 12H_2O$ = 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

the supernatant at each step was merged into one bottle. The extracts were diluted with Milli-Q water to 200 mL. The solution was extracted and cleaned up by the same processes as those of water sample described above.

2.6. Instrumental analysis

The target antibiotic compounds were determined by an Agilent 1290 rapid resolution liquid chromatography tandem an Agilent 6460 Triple Quadrupole mass spectrometer (RRLC-MS/MS, Agilent, US). The separation of target antibiotics compounds was accomplished by Agilent Zorbax Eclipse plus-C18 column (RRHD, 2.1 × 100 mm, 1.8 μm, Agilent, US). The mass spectrometer was operated in multiple-reaction monitoring (MRM) mode with positive ionization (ESI+). The instrumental conditions for the target compounds analysis are shown in Table S2.

2.7. Quality control and quality assurance

The quantification of 14 antibiotics was achieved by using internal standard method with calibration of working standard solutions. The correlation coefficients (R^2) of calibration curve were between 0.99 and 0.9999. The recoveries were performed by spiking 1 L water samples and 2 g sediment samples with standard solutions to three concentrations of 10 ng 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 recoveries of 14 antibiotics in the water samples ranged from 56 ± 1% to 117 ± 11% and the sediment samples ranged from 57 ± 0.1% to 127 ± 5 %, with relative standard deviation (RSD) less than 15% (Table S3 and Table S4). The method detection limits (MDLs) of 14

antibiotics ranged from 0.23 − 5.88 ng L^{-1} for water samples (Table S3) and from 0.25 − 2.94 ng g^{-1} for the sediment samples (Table S4). The MDLs were determined by spiking 1 L water samples with the mixed standard solution to 5 ng L^{-1}, and then performing the whole pre-treatment processes. The extracts were gradually diluted until the signal-to-noise ratio was equal to 3.

2.7. Attenuation rates calculation for the flume study

After the antibiotics were spiked into the flume system, the concentrations would naturally decrease due to dilution and mixing with sediment and pore water. Therefore, in order to obtain the true attenuation rates without the influence of mixing dilution, concentration corrections were conducted by using a conservative tracer bromide as a reference compound (Eq. S1 in SI). One liter potassium bromide solution (3 g L^{-1}) was added into water phase of the flume system simultaneously with the antibiotics. Bromide concentrations in surface water and pore water samples were measured by ion chromatography (881 Compact, Metrohm, Switzerland) at the same intervals as the antibiotic determination. Attenuation rate constants (k) and half-life time ($t_{1/2}$) of antibiotics in the surface water were calculated by fitting a first-order kinetic decay model to these corrected concentrations (Eq. S2 and Eq.S3).

3. Results and discussion

3.1. Simulation system operation performance

During the whole operating period, pH was around 7 and ORP was within 150-170 mV (Table S5). The conductivity was stable at around 300 μs cm^{-1} (Table S5) in the flume, which

was higher than the on-site value of 80 μs cm^{-1}. However, the conductivities in this flume were not beyond the range values in the natural water (50-500 μs cm^{-1}), which would not influence the experiments. The most likely explanation for the elevated conductivity comes from the addition of the potassium bromide tracer. The temperature was maintained around 25 °C and the values of DO were between 7.2 to 9.6 mg L^{-1} (Table S5). The TOCs in water and sediment measured at the initial period and end of the experiment did not show significant changes (Table S6). Therefore, the operational performance of this system was relatively stable, and close to water quality conditions of a natural river.

3.2. Dominant attenuation processes

The relative importance of the different attenuation processes for these antibiotics was investigated with batch studies. These used river water and sediment from the Tong Yang River, which had a pH of 7.8, conductivity of 80 μs cm^{-1} and sediment TOC of 28.3 g kg^{-1}. Photodegradation proved to be the most important of these processes for all the antibiotics apart from OTC (Fig. 1). Photodegradation was a particularly important loss (estimated > 70% of the total) for SDZ, SMZ, STZ, EFC, and OFC. The half-lives controlled by photodegradation alone ranged from 4.40 to 32.9 d (Fig. S4). The importance of photodegradation for antibiotics has also been noted by others (Baena-Nogueras et al., 2017; Batchu et al., 2014; Conde-Cid et al. 2018; Li et al., 2018). Biodegradation and adsorption accounted for the rest of the losses from the water column. Adsorption was the most important process for OTC. Hydrolysis, judged on the basis of the dark sterile control, was 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

distance of 23 km to 333 km. In summer, with a 3.5 m s^{-1} flow velocity, the travel distance would range from 55 km to 777 km before half the antibiotics would be lost. In fact, for the Nanfei River, the distance from the urban discharge to Chaohu Lake is only 25 km. Thus, a considerable portion of the antibiotic discharge from Hefei City would reach this lake without dissipation.

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

All antibiotics were detected in the surface sediments, which was attributed to their migration and adsorption to sediment from the water phase (Fig. 3). This is consistent with the adsorption mechanism playing a role in the removals of all antibiotics from the water phase in the batch experiments. For EFC, NFC, TC, OTC and RTM, adsorption played an important role its loss from the water column. This is related to the relatively high hydrophobicity of these compounds ($150 < K_d < 889$ L kg^{-1}) (Table S7). Adsorption made a relatively small contribution to the dissipation of sulfonamides (Fig. 1) due to the low adsorption affinity (K_d < 80 L kg^{-1}). Sulfonamides, as acidic compounds, have a declining sorption capacity with increasing alkalinity due to electrostatic repulsion from sediment (Gothwal and Shashidhar, 2015). Therefore, their adsorption capacity decrease in the weakly-alkaline water environment of the flume (Table S5).

The sulfonamides concentration in sediment continuously increased until around day 20 when it stabilized to 10 − 50 ng g^{-1} at day 50. Similarly, the concentrations of the other antibiotics in the surface sediments increased rapidly before day 10, and then quickly

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,

antibiotics have been detected in groundwater of different regions across the world (Kivits et al., 2018; Lopez-Serna et al., 2013; Ma et al., 2015). Thus, further clarification of their transport paths to groundwater is needed.

4. Conclusions

Photodegradation was the dominant attenuation mechanism of these antibiotics in a water-sediment system. These antibiotics had a wide-range of half-lives with 1.28 d and 25.7 d in the water column, which would permit considerable travel distances to take place for many of them in rivers. The adsorption onto the surface sediment in the flume study contributed to part of antibiotic removals from the water phase. All fluoroquinolones and two sulfonamides (SDZ and SDM) migrated further to the deep layer sediments, but there was less presence in the pore water due to the strong adsorption. Adsorption made a relatively small contribution to the dissipation of sulfonamides due to the low adsorption affinity. Thus, the sulfonamides were present in the pore water and approached equilibrium with the surface water at the upper layer, which would permit their high mobility to pore water in hyporheic zone. Therefore, these sulfonamides due to their high mobility and persistence might be important candidates for groundwater contamination.

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436

437 **Figure captions**

438 **Fig. 1.** Contribution ratio of each individual attenuation processes (including
439 photodegradation, adsorption and biodegradation) in the batch experiments carried out at
440 25 °C over 30 d periods.

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

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

445 **Fig. 4.** Antibiotics in the upper, middle and lower layer sediment at the three sampling time
446 (day 10, day 20 and day 30). The depth of the upper, middle and lower layers was 5 cm,
447 10cm and 15 cm, respectively.

448 **Fig. 5.** Dynamic equilibrium relationships of 14 antibiotics in the pore water with those in the
449 surface water at pore 1. The depth of the upper, middle and lower layers was 5 cm, 10 cm and
450 15 cm, respectively.

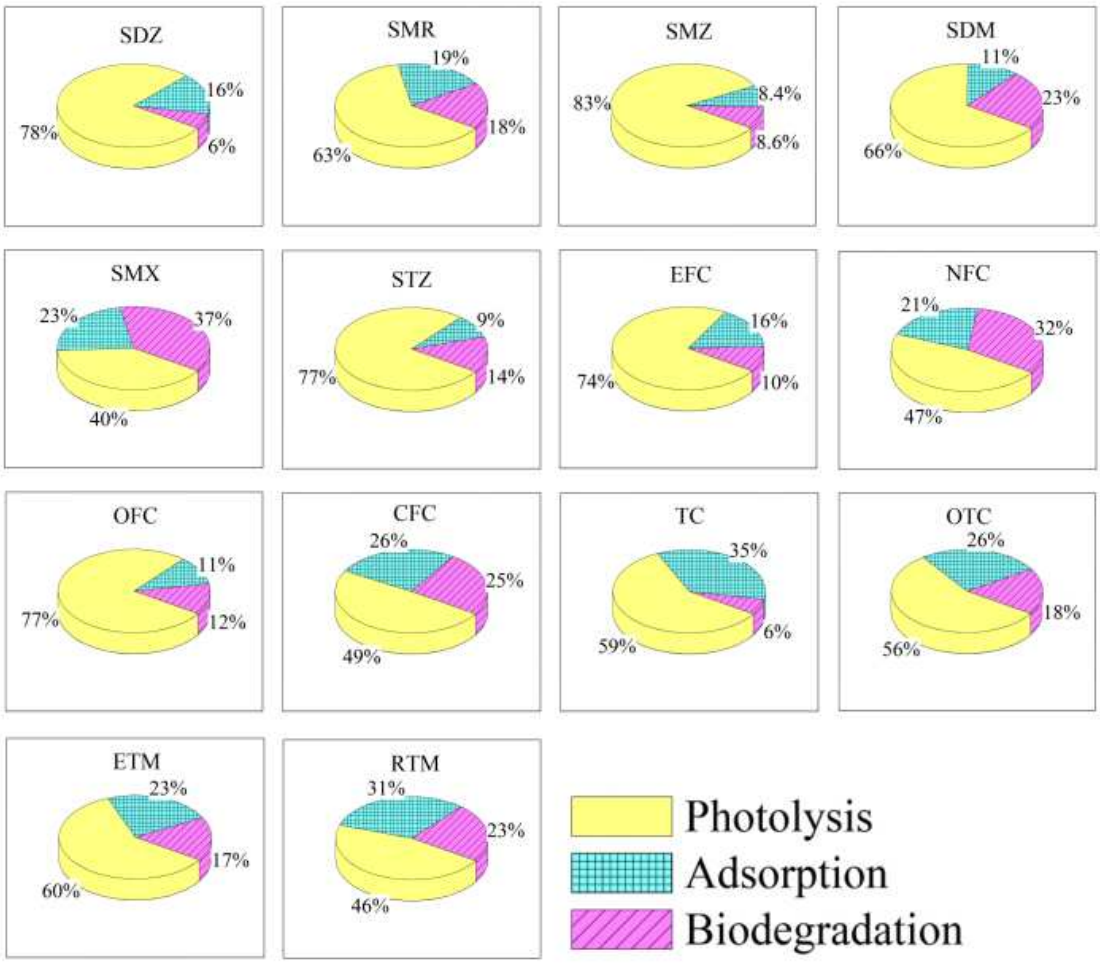
451

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%
78%
6%
SMR
19%
63%
18%
SMZ
83%
8.4%
8.6%
SDM
11%
23%
66%
SMX
23%
37%
40%
STZ
9%
77%
14%
EFC
16%
74%
10%
NFC
21%
32%
47%
OFC
11%
77%
12%
CFC
26%
25%
49%
TC
35%
59%
6%
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31%
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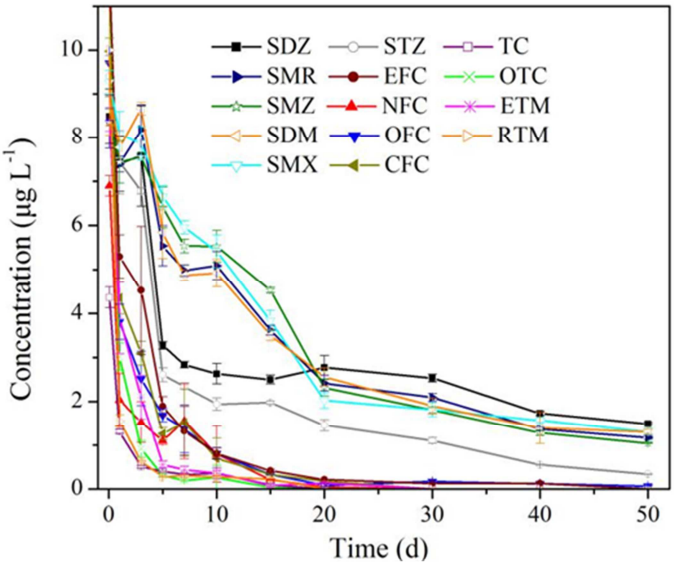
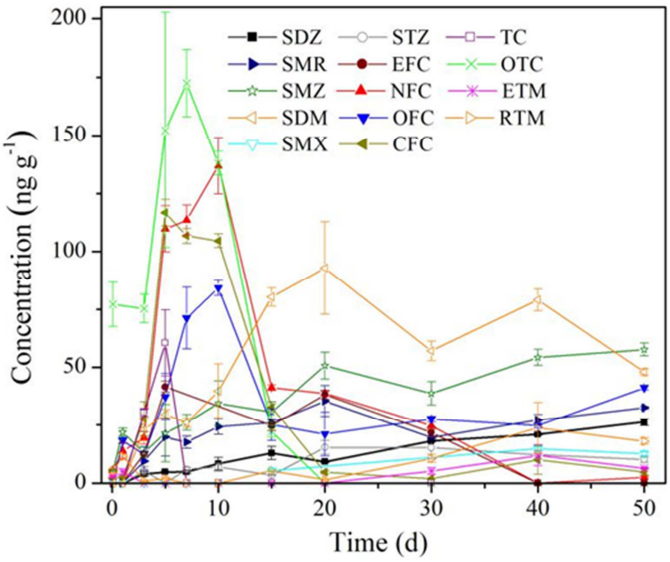
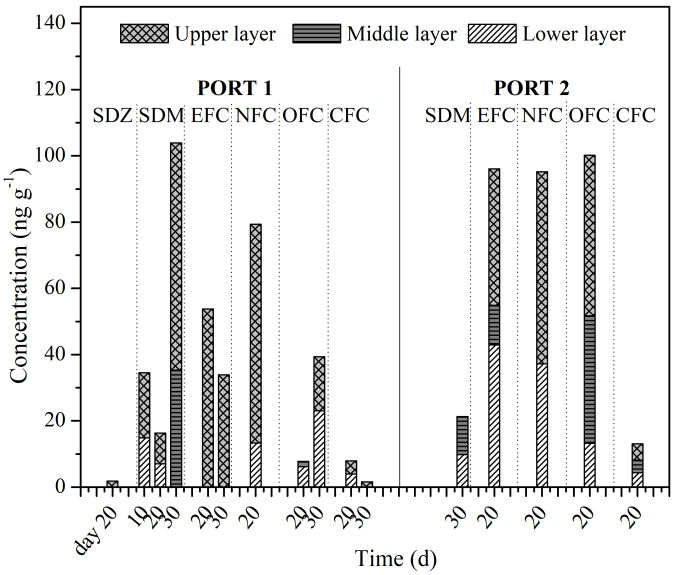
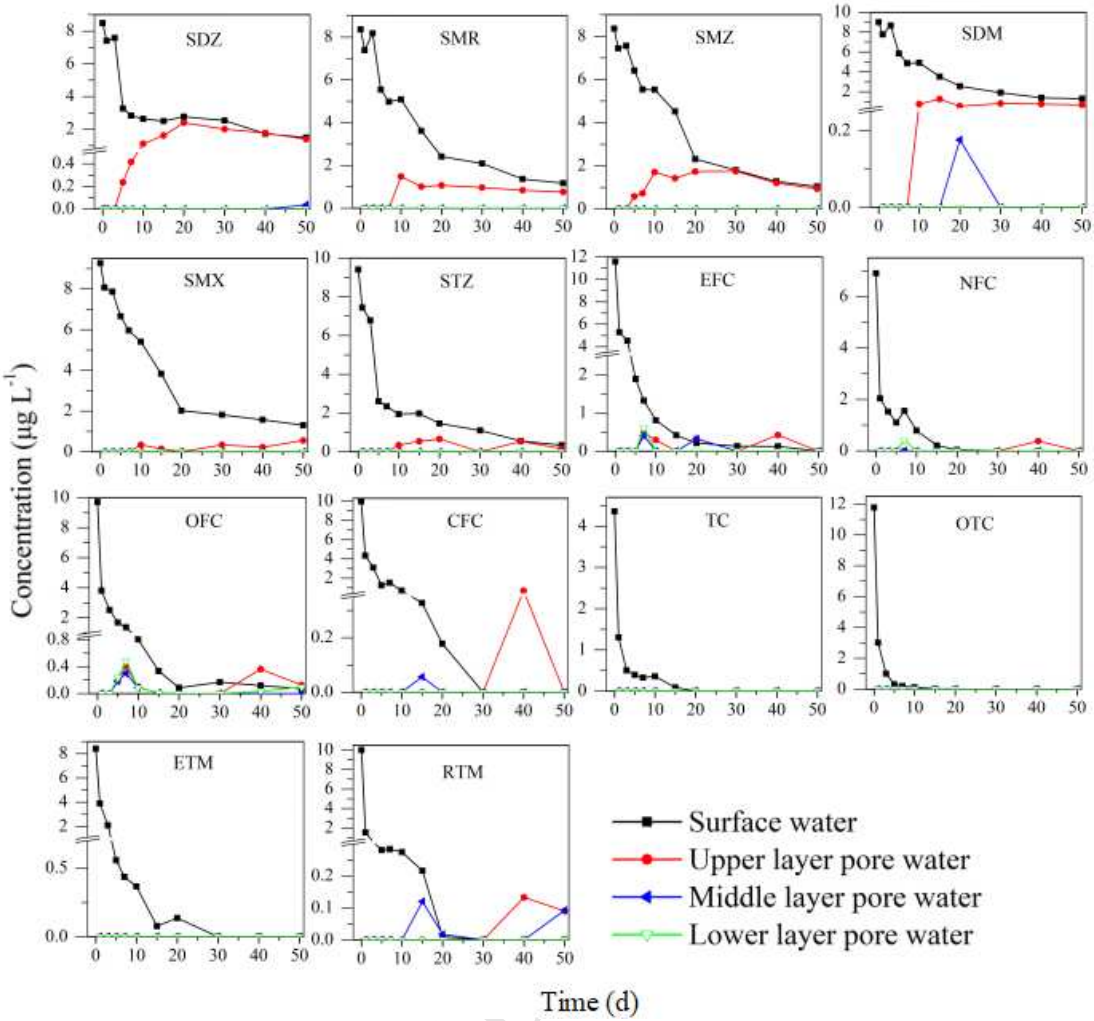
46%
Photolysis
Adsorption
Biodegradation









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: