

# 1 **Transport and adsorption of antibiotics by marine sediments in a** 2 **dynamic environment**

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12

## 13 **Abstract**

14 *Background, aim, and scope* Bed-sediments are the major sink for many contaminants in  
15 aquatic environments. With increasing knowledge of and research on the environmental  
16 occurrence of antibiotics, there has been growing interest in their behaviour and fate in  
17 aquatic environments. However, there is little information about the behaviour of antibiotics  
18 in a dynamic water/sediment environment, such as river and coastal marine water. Therefore,  
19 the aims of the present study were: (1) to study the transport and distribution of four common  
20 antibiotics between water and sediment in both dynamic and quiescent water/sediment  
21 systems; (2) to understand the persistence and possible degradation of the four antibiotics in  
22 the two different systems.

23 *Materials and methods* A Lid-driven Elongated Annular Flume (LEAF), designed to reduce  
24 the centrifugal effect, was used to simulate a dynamic water environment. In addition, a  
25 quiescent water/sediment experiment was conducted for comparison with the dynamic water  
26 system. The seawater and sediment, used in both experiments of flowing and quiescent  
27 water/sediment systems, were collected from Victoria Harbour, a dynamic coastal  
28 environment in an urban setting. The four antibiotics selected in this study were ofloxacin

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29 (OFL), roxithromycin (RTM), erythromycin (ETM), and sulfamethoxazole (SMZ), the most  
30 commonly used antibiotics in south China.

31 *Results and discussion* Antibiotics in an overlying solution decreased very quickly in the  
32 flume system due to the sorption to suspended particles and surface sediment. There were  
33 significant differences in the adsorption of the four antibiotics in sediment. OFL showed a  
34 high tendency to be adsorbed by sediment with a high  $K_d$  value (2980 L/Kg), while the low  
35  $K_d$  values of SMZ indicated that there was a large quantity in water. The four antibiotics  
36 reached a depth of 20–30 mm in the sediment over a period of 60 days in the flume system.  
37 However, the compounds were only found in surface sediment (above 10 mm) in the  
38 quiescent system, indicating the influence of the dynamic flume system on the distribution of  
39 antibiotics in sediment. OFL showed a moderate persistence in the dynamic flume system,  
40 while other three antibiotics had less persistence in sediment. However, all of the four  
41 compounds showed moderate persistence in the quiescent system.

42 *Recommendations and perspectives* The study showed the rapid diffusive transfer of  
43 antibiotics from water to sediment in the dynamic flume system. The four antibiotics  
44 exhibited larger differences in their adsorption to sediment in both dynamic and quiescent  
45 systems due to their different  $K_d$  values. The high sorption of antibiotics to marine sediment  
46 may reduce their availability to benthic invertebrates.

47 **Keywords:** Antibiotics · transport · adsorption · persistence · sediments · dynamic water  
48 environment · South China.

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## 50 **1 Background, aim, and scope**

51 The occurrence and potential adverse effects of pharmaceutical residuals in aquatic  
52 environments have generated growing interest in recent years due to their potential threat to  
53 the balance of the ecosystem and the risk they pose to the health of humans and animals.  
54 Antibiotics rank among the most important classes of pharmaceuticals because of the large  
55 amounts used in medicines for humans and animals, and in aquaculture.

56 One of the major pathways of antibiotics to the aquatic environment is via municipal  
57 sewage treatment plants (STPs). The removal of antibiotics by STPs has been shown to be  
58 incomplete (Miao et al. 2002; Xu et al. 2007b), and the effects on antibiotics and  
59 antibiotic-resistant bacteria during the wastewater treatment process is largely unknown.  
60 Various groups of antibiotics and some of their metabolites have been detected in the  
61 effluents from municipal STPs (Golet et al. 2003; Ternes et al. 2002). It is known that, as a  
62 result, considerable quantities of antibiotics enter surface water environments, such as river  
63 water and sediments (Golet et al. 2001; Hirsch et al. 1999; Lindberg et al. 2004; Sacher et al.  
64 2001; Xu et al. 2007a), and coastal water and groundwater (Daughton and Ternes 1999;  
65 Heberer 2002; Ternes 1998).

66 With increasing knowledge of the environmental occurrence of antibiotics, interest is now  
67 being focused on their behaviour and fate in the environment (Brannon et al. 2005). For  
68 example, exposure to antibiotics might induce resistance (Kummerer 2004), and lead to the  
69 horizontal transfer of resistance genes in field bacterial populations (Dantas et al. 2008;  
70 Davison 1999; Pruden et al. 2006). Once introduced into surface waters, antibiotics may also  
71 undergo biodegradation and adsorption to sediment. Aquatic sediment is the most important  
72 sink of pharmaceuticals and other contaminants. The distribution of a particular compound  
73 between sediment/suspended particulate matter and water is largely dependent on the  
74 lipophilicity of the compound and on the sorption properties of the sediment. In order to  
75 investigate the distribution kinetics between water and sediment, and the environmental fate  
76 of contaminants, many test systems have been established under a variety of relevant  
77 environmental conditions (Freitag et al. 1985; Freitag et al. 1982; Suzuki et al. 1998). One

78 drawback of most of these systems is that they are based on the quiescent system. Hence,  
79 these systems cannot provide high comparability and reproducibility with dynamic water  
80 systems under real environmental conditions (Sabaliunas et al. 2003). Experimental flumes  
81 with sediment and an overlying solution have proven to be good at mimicking these dynamic  
82 riverine and coastal environments (Allan et al. 2004; Chan and Wai 2004; Wai 2003). So far,  
83 very little work has been conducted on the transport and distribution of antibiotics in dynamic  
84 water environments, such as the discharge points of wastewater effluents in riverbanks and  
85 coastal zones.

86 China has the largest population in the world, and antibiotics are in very common use, with  
87 the annual consumption being over 25,000 tonnes (Kummerer 2003; Xu et al. 2007a). The use  
88 of antibiotics in the fast-developing Pearl River Delta (PRD) region of south China is  
89 especially high (Richardson et al. 2005). The four antibiotics selected in the current study are  
90 representative of three classes of antibiotics that are commonly used in the PRD region. They  
91 have been detected in the Pearl River and other coastal waters in the PRD region at maximum  
92 concentrations of up to 1000 ng/L (Gulkowska et al. 2007; Xu et al. 2007a). The objectives of  
93 this study were: (1) to investigate the distribution of four common antibiotics between water  
94 and sediment in both dynamic and quiescent water/sediment systems; (2) to study the vertical  
95 distribution of antibiotics in 50-mm-bed sediment layers in the flume system, and to compare  
96 it with that in a quiescent system; (3) to understand the persistence and degradation of the four  
97 antibiotics in the two water systems.

98

## 99 **2 Materials and methods**

## 100 2.1 Collecting sediment and seawater

101 Seawater and sediment were collected from Hong Kong's Victoria Harbour in March 2006.  
102 The seawater was transported to the laboratory in 50-litre plastic containers. Sediment was  
103 obtained from a depth of < 10 cm in the harbour. Stones, branches, and other solid materials  
104 in the sediment were carefully removed, and the sediment was then thoroughly mixed before  
105 being introduced into the flume and quiescent systems. The characteristics of the seawater and  
106 sediment are shown in Table 1.

## 107 2.2 Methods

### 108 2.2.1 *Dynamic water/sediment system*

109 A Lid-driven Elongated Annular Flume (LEAF), designed to reduce the centrifugal effect,  
110 was used to perform the dynamic water experiment (Fig. 1). The flume has two identical 3-m  
111 long straight sections, which are meant to create a uniform flow environment. The inner side  
112 of the flume is made of glass in order to reduce the sorption of antibiotics. The depth of the  
113 water and vertical position of the lid can be adjusted. The lid is driven by an adjustable-speed  
114 motor. The water is re-circulated using the butterfly lid controlled by an electromotor. An  
115 ultrasonic velocity monitor was installed in the straight sections of the flume.  
116 The flume was housed in a large laboratory, with the temperature of the room kept at  $20\pm 2$  °C.  
117 About 60 mm of sediment were laid evenly at the bottom of the flume, and 400 litres of  
118 seawater were then slowly added to the flume. The flume was kept running for a week with a  
119 lid rotational speed (RS) of 0.6 m/s (the water velocity was about 20 cm/s) before antibiotics  
120 were added to the water. Then, 16 mg of each of the four selected antibiotics were dissolved  
121 and spiked into the flume system. Following this, the flume started to work at a water velocity

122 of 20 cm/s and the run ended after 60 days. At each sampling period, one litre of surface  
123 seawater (3 cm below the surface) and bottom seawater (3 cm above the sediment), as well as  
124 sediment in the middle of the straight sections of the flume, were collected. After each  
125 sampling programme, two litres of seawater were added to compensate for what had been lost  
126 due to water sampling. Ultra-pure water was also added to keep the volume of the water  
127 constant every day. At the end of the experiment (60 days later), after the overlying seawater  
128 had been cautiously removed, the sediment in the straight section was longitudinally  
129 sectioned at 5-mm intervals down to 20 mm below the sediment–water interface, then 10 mm  
130 down to 30 mm.

#### 131 *2.2.2 Quiescent water/sediment system*

132 A quiescent water/sediment system was designed using a tank in order to compare the  
133 results with the environmental fate of antibiotics in the dynamic flume channel. About 60 mm  
134 of sediment were laid evenly at the bottom, before 40 litres of seawater were added to the tank.  
135 The antibiotics were added as they had been in the flume experiments. Surface seawater and  
136 sediment samples were collected at each sampling period. Appropriate amounts of seawater  
137 and ultra-pure water were added to keep constant the volume of the water in the system.

#### 138 *2.2.3 Extraction and analysis of antibiotics*

139 *Seawater samples:* The extraction of antibiotics from the seawater samples was performed  
140 mainly using the method described by Xu et al. (2007a), based on solid phase extraction  
141 (SPE).

142 *Sediment samples:* Samples of approximately 5 g were accurately weighed (200  
143 ng <sup>13</sup>C<sub>3</sub>-caffeine being added as a surrogate) and then placed into a 50-ml polypropylene

144 centrifuge tube into which 10 ml of extraction buffer had been added. The extraction buffer  
145 consisted of a 2:1:1 mixture of methanol, 0.1 M of a citric acid buffer with the pH adjusted to  
146 6.0, and a 10 mM Na<sub>2</sub>EDTA buffer with the pH adjusted to 6.0. The tubes were vortex mixed  
147 for 1 min and were then placed into an ultrasonic bath for 15 min (water temperature <40°C).  
148 The tubes were then centrifuged (Eppendorf Centrifuge 5810 R) for 10 min at 3000×g. The  
149 supernatant was decanted into a 500 ml glass bottle and the sediment residue was extracted  
150 one more time. The supernatant was combined and diluted to approximately 500 ml with  
151 ultra-pure water. SAX-HLB SPE cartridges were set up in tandem, and pre-conditioned  
152 sequentially with 6.0 ml of methanol, 6.0 ml of ultra-pure water, and 6.0 ml of a 10 mM  
153 Na<sub>2</sub>EDTA buffer (pH 6.0). The samples were then passed through the SPE cartridges and  
154 SPE columns at a flow rate of approximately 5 ml/min. After this, the SAX cartridges were  
155 removed and the HLB cartridges washed with ultra-pure water (10 ml) before being dried  
156 with a flow of nitrogen gas for 1 h. Each cartridge was then eluted with three 2-ml vol of  
157 methanol. The analytes were collected in 10 ml brown glass vials, concentrated under a flow  
158 of N<sub>2</sub> gas to about 20 µl, and then dissolved in 40% aqueous methanol to a final volume of  
159 1.0 ml.

160 The four antibiotics were analysed using high-performance liquid  
161 chromatography-electrospray ionization tandem mass spectrometry. A quantitative analysis of  
162 each compound was performed using LC-ESI-MS/MS with the MRM mode, using the two  
163 highest characteristic precursor ion/product ion transitions. Together with the retention times,  
164 the characteristic ions were used to ensure correct peak assignment and peak  
165 purity. <sup>13</sup>C<sub>3</sub>-caffeine was added as a surrogate standard to all samples prior to the enrichment

166 of the control to avoid possible losses during the analytical procedure. These spiked  
167 antibiotics in seawater and sediment were recovered at mean percentages ranging from 68%  
168 to 87% and from 65% to 72%, respectively. The limit of quantification (LOQ) for each  
169 compound in seawater and sediment are from 1 to 10 ng/L and 10 to 50 ng/g, respectively.

170

### 171 **3 Results and discussion**

#### 172 3.1 Hydrodynamic characteristics of the LEAF

173 To check the uniformity of the flow field in the LEAF, a Preston tube was used to measure  
174 bed shear stress in the straight section of the flume. The stress was calculated according to the  
175 equations described in a previous study (Patel 1965). It was found that the lid rotational speed  
176 (RS) had a quadratic relationship with the flow velocity and the bottom shear stress. Fig. 2  
177 shows the relationship of RS with the flow velocity and shear stress. The maximum bed shear  
178 stress that the LEAF could generate was around  $1 \text{ N/m}^2$ . Therefore, rather broad energy  
179 ranges (induced by shear stress from 0 to  $1 \text{ N/m}^2$ ) can be obtained through the LEAF, with  
180 these energy levels considered to be typical of near bottom shear stresses induced by a tide or  
181 flowing river water (Bokuniewicz et al. 1991). In this study, the RS was set up at 0.6 m/s.  
182 Thus, the induced bed shear stress and water velocity were about  $0.1 \text{ N/m}^2$  and 20 cm/s,  
183 respectively. According to Chan and Wai (2004), the energy level induced in our experimental  
184 conditions ( $0.1 \text{ N/m}^2$ ) was below the critical shear stress of typical non-cohesive sediment  
185 ( $0.15 \text{ N/m}^2$ ). Wai (2003) showed that the concentration of sediment (turbidity signal)  
186 increased and decreased in response to changes in the flow field in the LEAF. This indicated  
187 that the flume that was used was indeed suitable for the study of the erosion and deposition



188 activities of sediment near the sediment-water interface. In addition, the LEAF was also  
189 suitable for carrying out long-term chemical-sediment sorption experiments because it had a  
190 well-controlled environment, and was made of non-reactive materials.

### 191 3.2 Sediment adsorption of antibiotics in both dynamic and quiescent environments

192 The changes over time in the concentration of antibiotics in the overlying seawater,  
193 including the surface and bottom seawater and sediment, in the dynamic flume system are  
194 shown in Fig. 3. The original spiked concentrations of the four antibiotics in the flume were  
195 40 µg/L. However, the concentrations in seawater of all four antibiotics, detected at the first  
196 sampling event (30 min), were much lower than the initial spiked concentrations because of  
197 the rapid sorption to suspended particles and sediment. The antibiotic concentrations in the  
198 original seawater were mainly close to or lower than LOQ, and those in sediment were all  
199 below LOQ (see Table 1). Hence, the concentrations of the original antibiotics in water and  
200 sediment were much lower than the spiked concentrations, and need not be a cause of concern.

201 Concentration profiles in the overlying water suggested that the diffusive transfer of  
202 antibiotics into sediment was a quick process, with the compounds generally detected in  
203 surface sediment at a maximum concentration of more than 3000 ng/g at a very short  
204 sampling interval. Since the antibiotics were spiked into the seawater, their degradation,  
205 especially photodegradation, in the water phase was a competitive process between the  
206 sorption to sediment and a chemical transformation. It is often difficult to distinguish between  
207 sorption and degradation in a natural environment. However, the photodegradation function  
208 can be evaluated in this system based on previous studies under certain controlled conditions.

209 The half-life times of OFL and AMX (amoxicillin) in a solution of water were 2.4 and 10.6 d,

210 respectively in a solar experiment (Andreozzi et al. 2003), and 7.0-17 d for ETM in sludge  
211 (Wu et al. 2008). Generally, the intensity of sunlight is about 50 times greater than the light  
212 emitted by common fluorescent lamps. In addition, the relatively low temperature in the  
213 laboratory may affect the reactivity of antibiotics with radicals formed by photons  
214 (Yamamoto et al. 2009). Together with the shielding from the apparatus, the  
215 photodegradation rates of the antibiotics in this experiment would certainly be greatly reduced.  
216 In a river environment biodegradation would occur at a less rapid rate than would be the case  
217 in photodegradation (Kummerer 2001; Yamamoto et al. 2009). Therefore, the quick changes  
218 in the concentrations of antibiotics in the overlying water at the initial sampling times (i.e., the  
219 first 10 days) were mainly due to sediment adsorption.

220 The concentrations in sediment reached several hundred ng/g at the first sampling event.  
221 This suggests that a water velocity of 20 cm/s can mobilize the small particles in the surface  
222 sediment so that the antibiotic compounds can be adsorbed rapidly to suspended particles, and  
223 then to surface sediment. It can be seen from Table 1 that the small particles (clay content) in  
224 suspended matter increased from 28.4% to 34.7% in comparison with the level in bulk  
225 sediment. On the contrary, the sand content decreased from 12.4% to 1.1%. The adsorption  
226 capacity of suspended particles is strongly related to their size, with larger particles providing  
227 additional surfaces for sorption (Clymo et al. 2005; Pouliquen and LeBris 1996; Thiele-Bruhn  
228 et al. 2004). An X-ray diffraction analysis of clay showed that the sorption of antibiotics can  
229 widen the interlayer spacing of clay. Hence, an increase in the content of clay can lead to an  
230 increase in adsorption capacity (Pouliquen and LeBris 1996). This rapid and extensive  
231 sorption of antibiotics into sediment, which had previously been reported for marine

232 sediments ([Cannavan et al. 2000](#); [Loffler et al. 2005](#)), is mainly attributable to the  
233 lipophilicity of these compounds. The concentrations of antibiotics in the water of the  
234 quiescent environment at the first sampling event were much higher than those in the flume  
235 (see Fig. 4). Correspondingly, the concentrations of antibiotics in sediment were lower than  
236 those in the flume system at the same sampling event due to the lack of dynamic interaction  
237 between water and sediment.

238 In both the flume and quiescent systems, large discrepancies were seen in the adsorption to  
239 sediment of the four antibiotics. The highest concentrations of 3730 ng/g and 1880 ng/g of  
240 OFL in water were detected in the flume and quiescent systems, respectively. However, the  
241 concentrations of SMZ were only 1036 ng/g and 629 ng/g, respectively. The adsorption of  
242 OFL into sediment was particularly strong, while the adsorption of SMZ was found to be  
243 weak. Similar findings were found in previous studies ([Drillia et al. 2005](#); [Sukul et al. 2008](#)).

### 244 3.3 Vertical profiles of antibiotics in sediments

245 In the flume system, the concentrations of the four selected antibiotics were found to be  
246 highest at the top layer of sediment, and to decrease sharply with depth (Fig. 5). At the end of  
247 the experiment, OFL persisted with a residual concentration of 542 ng/g in the top layer (0-5  
248 mm), while the respective figures were 434 ng/g for RTM, 393 ng/g for ETM, and 55 ng/g for  
249 SMZ. The results revealed a pattern of diffusive distribution of the selected antibiotics into  
250 the sediment, due to the dynamic interaction between water and sediments in the flume  
251 system. A different pattern was seen in the quiescent system. Except for approximately 20  
252 ng/g of OFL, no antibiotics were detected below 10 mm in the sediment profile. Allan et al.  
253 investigated the diffusion of the synthetic pyrethroid permethrin into sediment using flume

254 channels (Allan et al. 2005). Their results clearly showed that a large quantity of permethrin  
255 accumulated in the top layer (0-3 mm). Little permethrin was found in the sediment at a depth  
256 of 3 mm below the sediment-water interface. In our work, a high water velocity certainly  
257 affected the normal diffuse boundary layer, which may have resulted in mass transfers and  
258 increased the overall fluxes of antibiotics into the sediment. On the whole, the concentrations  
259 of antibiotics decreased by about one hundred ng/g for every 5 mm in the sediment profile to  
260 a depth of 25 mm, with the exception of the SMZ. No SMZ was found in the sediment at a  
261 depth below 15 mm, probably due to its low distribution coefficient and fast degradation rate  
262 (Holtge and Kreuzig 2007; Wu et al. 2009).

#### 263 3.4 Effects of adsorption/desorption between seawater and sediment

264 The functions of the adsorption/desorption of antibiotics between water and sediment are  
265 rather complex. The distribution coefficient ( $K_d$ ) and the normalized distribution coefficient  
266 ( $K_{oc}$ ) with respect to the organic content (OC) (%) of the solid matrix have often been used to  
267 describe the effects of adsorption between water and sediment.  $K_d$  and  $K_{oc}$  were calculated  
268 according to:

$$269 \quad K_d = C_s / C_{aq}$$

$$270 \quad K_{oc} = 100 K_d / OC,$$

271 where  $C_s$  is the antibiotics equilibrium concentration in a solid matrix, and  $C_{aq}$  is the  
272 equilibrium concentration in an aqueous solution. In the present study, the  $K_d$  and  $K_{oc}$  values  
273 were determined using the concentrations of antibiotics in water and solid after 1 d or later,  
274 and should therefore be close to equilibrium conditions. That no degradation took place  
275 before 1 d was also taken into account. It is known that pharmaceuticals display a wide range

276 of mobility ( $0.2 < K_d < 6000$  L/Kg), and that the variations in  $K_d$  for a given compound in  
277 different soils and sediments can be significant (Tolls 2001). In the present study, the  $K_d$  and  
278  $K_{oc}$  values of each antibiotic did indeed vary significantly (Table 2). The values of  $K_d$  and  
279  $K_{oc}$  decreased in the following order: OFL>RTM>ETM>SMZ. The adsorption of all  
280 compounds was generally higher in sediments with a higher total organic content (TOC)  
281 (Drillia et al. 2005). Hence, it is believed that the high sorption capacity (high  $K_d$ ) to marine  
282 sediment may reduce the availability of antibiotics to benthic invertebrates. The calculated  
283 values showed that OFL has a high tendency to be adsorbed by sediment or solid particles,  
284 while SMZ, with a  $pK_a$  value of 1.69, has a low affinity for sediment. Studies have shown that  
285 the interaction of antibiotics with  $Ca^{2+}$  at clay surfaces is the prevalent sorption mechanism at  
286 low pH levels (Nowara et al. 1997). However, in neutral and weak alkaline pH conditions,  
287 this mechanism cannot play a leading role in the interaction of antibiotics with solids. This  
288 indicates that the interaction of deprotonated carboxylic acid with a clay surface can  
289 contribute significantly to the sorption of fluoroquinolones antibiotics (Nowara et al. 1997). An  
290 X-ray diffraction analysis of clay showed that the sorption of antibiotics can widen the clay  
291 interlayer spacing. Hence, due to the high clay content of the marine sediment in this study,  
292 the mechanism for the fluoroquinolones may be through cation bridging in the diffuse double  
293 layer at the surfaces of the clay. The possible sorption mechanism for the fluoroquinolones  
294 agrees with the high  $K_d$  obtained in previous studies (Tolls 2001). It has been suggested that  
295 electrochemical affinity and hydrophobic interaction can play important roles in the sorption  
296 of macrolides and sulfonamides to sediment/soil (Liu et al. 2002; Pan et al. 2009; Yamamoto  
297 et al. 2009).

298 The fate and mobility of six pharmaceuticals, including ofloxacin and sulfamethoxazole,  
299 were investigated in two types of soils with different values of TOC ([Drillia et al. 2005](#)).  
300 Ofloxacin had the highest  $K_d$  among the six pharmaceuticals. The values of  $K_d$  decreased in  
301 the following order: ofloxacin > propranolol > diclofenac > carbamazepine >  
302 sulfamethoxazole > clofibrac acid. The details of the  $K_d$  and  $K_{oc}$  of the ofloxacin (OFL) and  
303 the sulfamethoxazole (SMZ) are also given in Table 2. It should be noted that the  $K_d$  and  $K_{oc}$   
304 values in the present study were obtained under dynamic flume conditions similar to those of  
305 a subtropical river or coastal environment. Therefore, the  $K_d$  and  $K_{oc}$  values may be different  
306 from those obtained in a steady water/sediment system.

### 307 3.5 The persistence and fate of antibiotics in dynamic and quiescent environments

308 Antibiotics are designed to have a biological effect, and can persist in the human or animal  
309 body after administration. For easy absorption, most antibiotics are made to be water-soluble.  
310 These chemicals can degrade in the body more easily than in the environment. The  
311 persistence of antibiotics in the aquatic environment is a rather complex process, governed by  
312 biodegradation, sunlight photolysis, and other abiotic transformations, such as hydrolysis.  
313 Many antibiotics are relatively resistant to degradation under environmental conditions and  
314 pass through the STP treatment process ([Putschew et al. 2001](#); [Ternes 1998](#); [Ternes and](#)  
315 [Hirsch 2000](#)). At the end of the LEAF experiment (after 60 d), the final average  
316 concentrations of the four antibiotics in the surface water and sediment ranged from 0.26-1.27  
317  $\mu\text{g/L}$  and 36-461  $\text{ng/g}$ , respectively.

318 The degradation rate, often expressed as  $DT_{50}$  and  $DT_{90}$  (the time at which 50% and 90%  
319 of the parent compound has disappeared from sediment or water by transformation or

320 degradation, respectively), has been used to characterize the degradation of pharmaceuticals.  
321 Table 3 shows the degradation rate ( $DT_{50}$  and  $DT_{90}$ ) of the four antibiotics in the human body,  
322 in the flume system, and in the quiescent system. The  $DT_{50}$  values generally varied from  
323 several hours to a day in the human body. However, in the flume environment, the maximum  
324  $DT_{50}$  values in seawater and sediment exceeded 10 days. Thus, the transformation of the  
325 selected antibiotics in the human body is very different from that in the environment. Hence,  
326 appropriate experimental studies and field observations are indispensable for obtaining  
327 reliable data to assess the environmental fate of antibiotics. Great differences in the  $DT_{50}$   
328 values of OFL and SMZ were found in the water and sediment samples due to the different  
329 degradation rates and partitioning process between water and sediment. The expectation is  
330 that OFL is adsorbed relatively quickly by solid matrices in the environment. As for SMZ, it  
331 is likely that a large amount stays in water.

332 The  $DT_{50}$  values, together with the  $DT_{90}$  values, are often used to show the persistence of  
333 antibiotics in the environment because the single  $DT_{50}$  value cannot exactly describe the rate  
334 of degradation. With the exception of SMZ, the  $DT_{90}$  values of the other three compounds (>  
335 60 d) in sediment were longer than the values in water. Many antibiotic compounds  
336 photodegrade in liquids ([Halling-Sorensen et al. 2003](#)). In addition, photodegradation in  
337 sediment can only occur at the surface interface and in the first millimeters of depth. The  
338 chemical removal of antibiotics from sediments is done mainly through scouring or diffusion  
339 processes across the sediment-water interface. The persistence of antibiotics in sediment has  
340 become an important concern in the context of their long-term accumulation in aquatic  
341 environments ([Williams et al. 1999](#)).

342 According to the method described by Hollis (Hollis 1991), with regard to their persistence  
343 in sediment, antibiotics can be grouped into the following four classes: impersistent -  $DT_{50} <$   
344 5 d; slightly persistent -  $DT_{50}$  5-21 d; moderately persistent -  $DT_{50}$  22-60 d; and very  
345 persistent -  $DT_{50} > 60$  d. By this classification, OFL was moderately persistent and the other  
346 three compounds were impersistent. However, in the quiescent system, the  $DT_{50}$  values  
347 ranged from 12.9 to 29 d, and from 24.3 to 41.1 d in seawater and sediment, respectively. The  
348  $DT_{90}$  values were all  $>60$  d for both seawater and sediment. Therefore, all four antibiotics  
349 displayed moderately persistent behaviour in the quiescent system.

350

#### 351 **4 Conclusions**

352 The dynamic environment that we simulated gave some insight into the environmental  
353 behaviours of antibiotic compounds when they are introduced into aquatic environments. The  
354 results showed that the diffusive transfer of antibiotic into sediment was a quick process in the  
355 flume system. The four antibiotics exhibited larger differences in their adsorption to sediment  
356 in both dynamic and quiescent systems due to their different  $K_d$  values. With a high  $K_d$  value,  
357 OFL showed a high tendency to be adsorbed by sediment, while the low  $K_d$  value of SMZ  
358 indicated that a large quantity would remain in water. The experiments revealed that their  
359 high sorption capacity (high  $K_d$ ) to marine sediment may reduce the availability of antibiotics  
360 to benthic invertebrates. In the flume system, the four antibiotics reached sediment layers of  
361 20–30 mm over a period of 60 days. However, in the quiescent system the compounds were  
362 only found in surface sediment (above 10 mm). In the quiescent water system, the four  
363 compounds displayed moderate persistence, with  $DT_{50}$  values ranging from 24.3 to 41.1 d.,



364 and  $DT_{90}$  values of  $\geq 60$  d for most of the compounds. In the dynamic flume system, OFL  
365 displayed a moderate persistence, with  $DT_{50}$  values of  $\geq 22$  d in sediment, while the other  
366 three antibiotics displayed impersistence. Furthermore, the experiment indicated that  
367 antibiotics can resist degradation, with low concentrations persisting in sediment.

368

369 **Acknowledgements:** This work was funded by the Natural Science Foundation of China (No.  
370 40672212) and The Hong Kong Polytechnic University (G-U300). The research for this work was  
371 also supported by the CAS/SAFEA International Partnership Programme for Creative Research  
372 Teams (KZCX2-YW-T001), the Research Grants Council of Hong Kong (PolyU5152/03E), the  
373 Area of Excellence (AoE) project under Grant No. AoE/P-04/2004 from the University Grants  
374 Council of Hong Kong, and the China Postdoctoral Science Foundation (No. 20070420149).

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516 **List of tables and figure captions**

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518

519 **Table 1** Information about bulk seawater and sediment

520 **Table 2** The  $K_d$  and  $K_{oc}$  values of four selected antibiotics

521 **Table 3** The  $DT_{50}$  and  $DT_{90}$  values of the four antibiotics in seawater and sediment

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524 **Fig. 1** The setting of the experimental flume (LEAF)

525 **Fig. 2** Relationship of the lid rotational speed (RS) with the averaged flow velocity ( $\langle u \rangle$ ) and

526 the bed shear stress ( $\tau_b$ ) (adopted from Chan et al. 2006)

527 **Fig. 3** Temporal changes of the four antibiotics in surface water (a), bottom water (b), and

528 sediment (c) of the flume system

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530 quiescent system

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545 **Table 1** Information about bulk seawater and sediment

Type	Organic content	Grain size (%)			Concentration of antibiotics (ng/L)			
		Sand	Silt	Clay	OFL	RTM	ETM	SMZ
Bulk Seawater	2.62 µg/ml	Not available			10	6	< LOQ <sup>b</sup>	<LOQ
Bulk Sediment	0.88 %	12.36	59.22	28.42	<LOQ	<LOQ	<LOQ	<LOQ
Suspended particulate matter <sup>a</sup>	1.13 %	1.14	64.21	34.65	Not available			

546 <sup>a</sup> Suspended particulate matter was collected during the running of the flume for a week, before  
 547 being spiked with antibiotics.

548 <sup>b</sup> The LOQs for OFL, RTM, ETM, and SMZ were 10, 5, 5, and 1 ng/L, and 50, 20, 20, and 10 ng/g  
 549 in seawater and marine sediment, respectively.

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578 **Table 2** The  $K_d$  and  $K_{oc}$  values of four selected antibiotics

Antibiotics	$K_d$ (L/Kg)		$K_{oc}$	
	This study (mean)	References	This study	References
OFL	2982	1192~4525 <sup>a</sup>	447300	50056~1104595 <sup>a</sup>
RTM	1420	470 <sup>b</sup>	213000	-
ETM	337	165 <sup>c</sup>	50550	-
SMZ	89	0.23~43.1 <sup>a</sup>	13350	62.2~607 <sup>a</sup>

579 <sup>a</sup> From (Drillia et al. 2005)

580 <sup>b</sup> From (Gobel et al. 2005)

581 <sup>c</sup> From (Jones et al. 2002)

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615 **Table 3** The DT<sub>50</sub> and DT<sub>90</sub> values of the four antibiotics in seawater and sediment

Antibiotics	In the human body (h)		In the flume system (d)		In the quiescent system (d)	
	DT <sub>50</sub>	DT <sub>90</sub>	DT <sub>50</sub>	DT <sub>90</sub>	DT <sub>50</sub>	DT <sub>90</sub>
OFL	5.0~10.0	— <sup>a</sup>	3.4 <sup>b</sup> (21.4) <sup>c</sup>	7.5 (>60)	12.9 (34.0)	>60 (>60)
RTM	8.4 ~15.5	—	6.7 (2.3)	30 (>60)	29 (41.1)	>60 (>60)
ETM	1.4 ~2	—	7.3 (2.1)	>60 (>60)	18 (27.0)	>60 (>60)
SMZ	8.0~12.0	—	14.7 (3.1)	>60 (29)	14.5 (24.3)	>60 (>60)

616 <sup>a</sup> Not available

617 <sup>b</sup> In seawater

618 <sup>c</sup> In sediment

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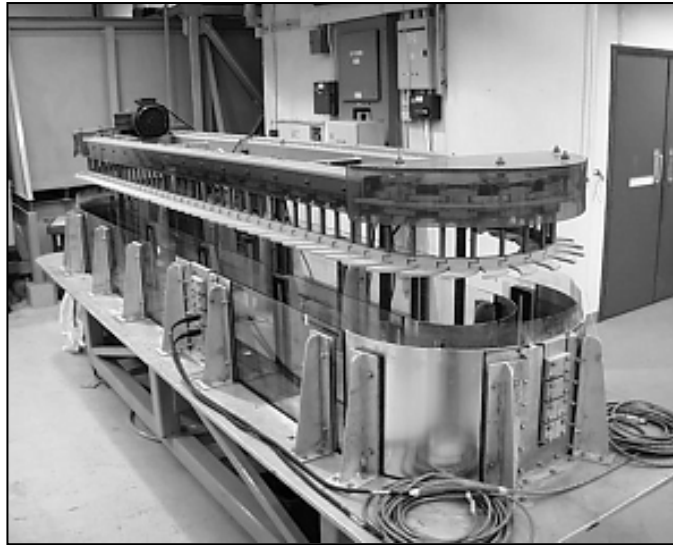
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647 **Fig. 1** The setting of the experimental flume (LEAF)

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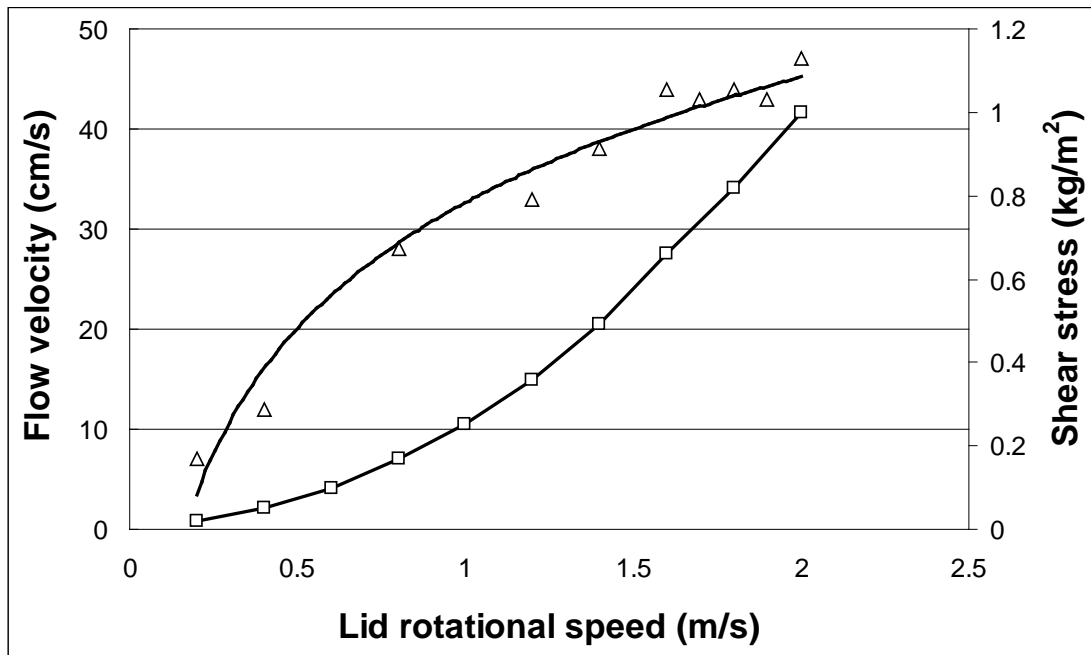
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676 **Fig. 2** Relationship of the lid rotational speed (RS) with the averaged flow velocity ( $\langle u \rangle$ ) and

677 the bed shear stress ( $\tau_b$ ) (adopted from Chan et al. 2006)

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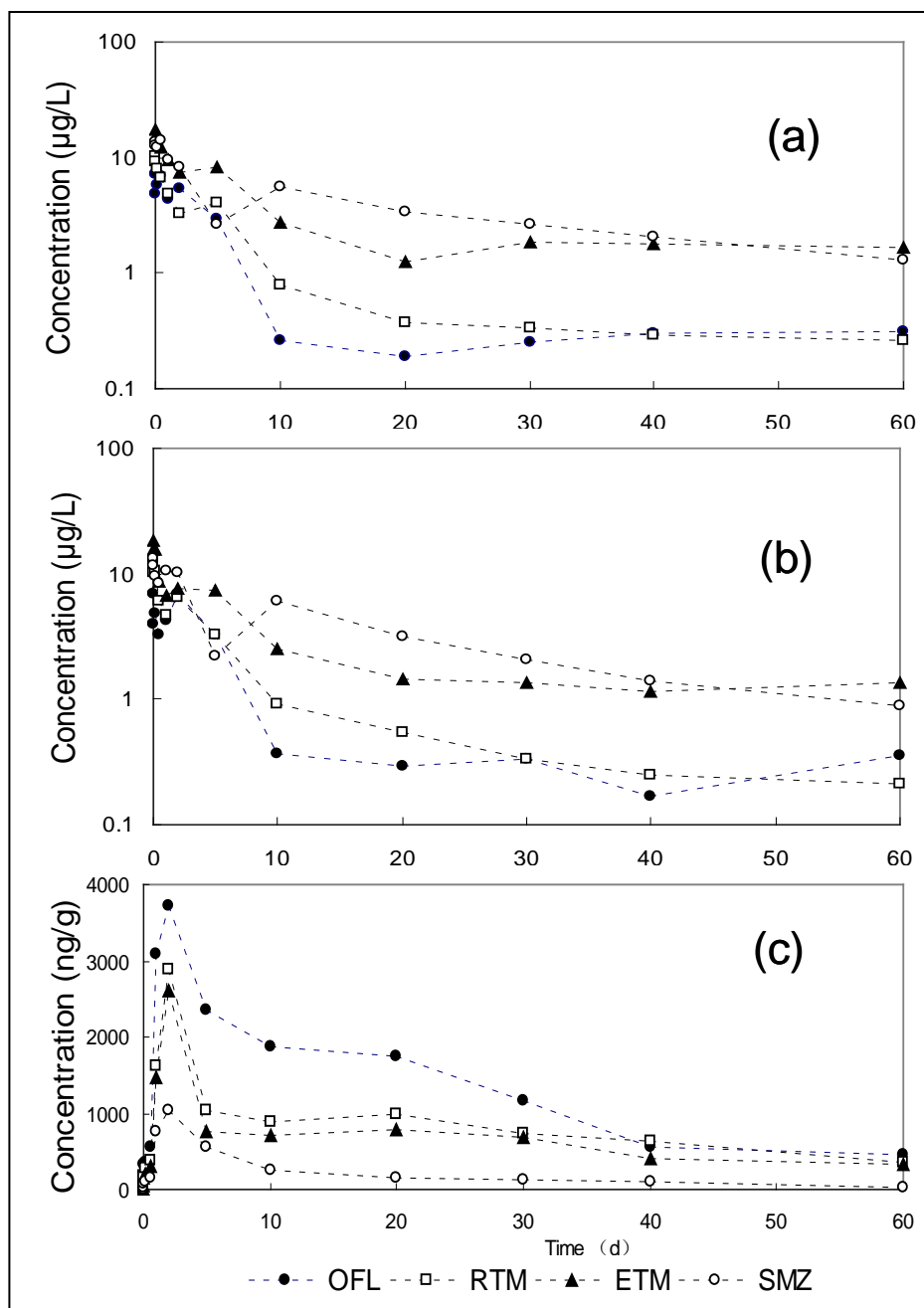
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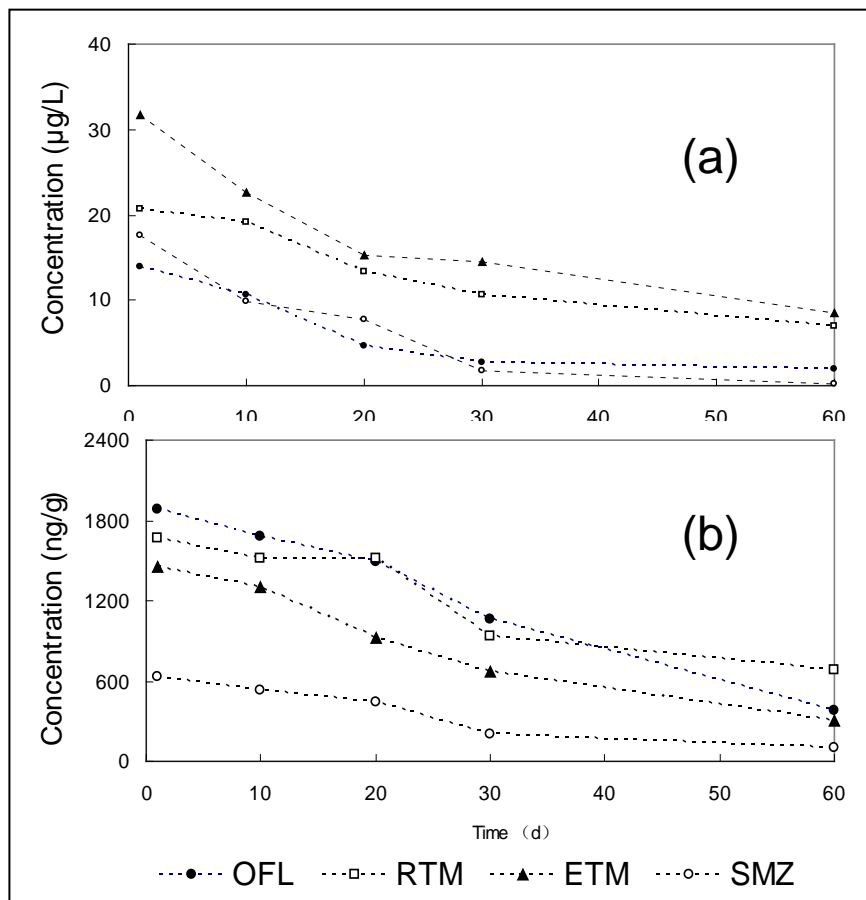
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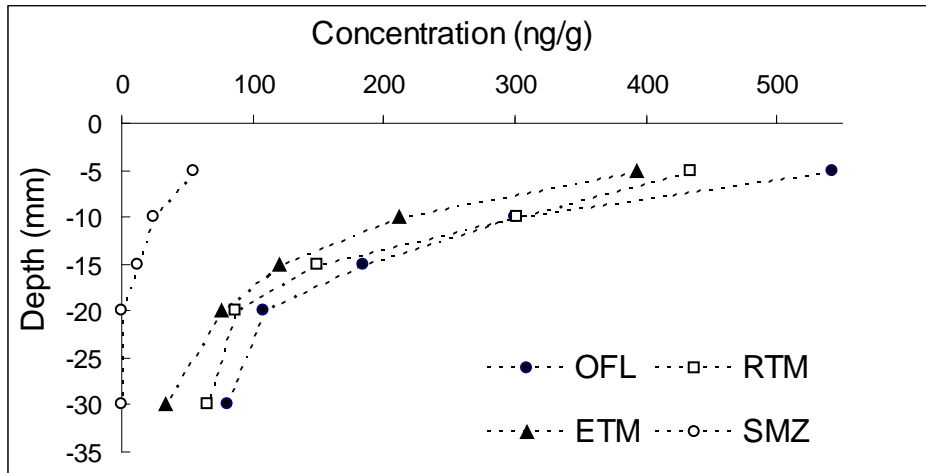
**Fig. 3** Temporal changes of the four antibiotics in surface water (a), bottom water (b), and sediment (c) of the flume system

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767 **Fig. 4** Temporal changes of the four antibiotics in surface water (a) and sediment (b) of the  
768 quiescent system

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783 **Fig. 5** Concentration profiles of the four antibiotics in sediment layers of the flume system

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