Transport and adsorption of antibiotics by marine sediments in a dynamic environment

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Abstract

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

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

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

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

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

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

1 Background, aim, and scope

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

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

With increasing knowledge of the environmental occurrence of antibiotics, interest is now being focused on their behaviour and fate in the environment (Brannon et al. 2005). For example, exposure to antibiotics might induce resistance (Kummerer 2004), and lead to the horizontal transfer of resistance genes in field bacterial populations (Dantas et al. 2008; Davison 1999; Pruden et al. 2006). Once introduced into surface waters, antibiotics may also undergo biodegradation and adsorption to sediment. Aquatic sediment is the most important sink of pharmaceutics and other contaminants. The distribution of a particular compound between sediment/suspended particulate matter and water is largely dependent on the lipophilicity of the compound and on the sorption properties of the sediment. In order to investigate the distribution kinetics between water and sediment, and the environmental fate of contaminants, many test systems have been established under a variety of relevant environmental conditions (Freitag et al. 1985; Freitag et al. 1982; Suzuki et al. 1998). One drawback of most of these systems is that they are based on the quiescent system. Hence, these systems cannot provide high comparability and reproducibility with dynamic water systems under real environmental conditions (Sabaliunas et al. 2003). Experimental flumes with sediment and an overlying solution have proven to be good at mimicking these dynamic riverine and coastal environments (Allan et al. 2004; Chan and Wai 2004; Wai 2003). So far, very little work has been conducted on the transport and distribution of antibiotics in dynamic water environments, such as the discharge points of wastewater effluents in riverbanks and coastal zones.

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

2 Materials and methods

2.1 Collecting sediment and seawater

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

2.2 Methods

2.2.1 Dynamic water/sediment system

A Lid-driven Elongated Annular Flume (LEAF), designed to reduce the centrifugal effect, was used to perform the dynamic water experiment (Fig. 1). The flume has two identical 3-m long straight sections, which are meant to create a uniform flow environment. The inner side of the flume is made of glass in order to reduce the sorption of antibiotics. The depth of the water and vertical position of the lid can be adjusted. The lid is driven by an adjustable-speed motor. The water is re-circulated using the butterfly lid controlled by an electromotor. An ultrasonic velocity monitor was installed in the straight sections of the flume. The flume was housed in a large laboratory, with the temperature of the room kept at 20±2 ℃. About 60 mm of sediment were laid evenly at the bottom of the flume, and 400 litres of seawater were then slowly added to the flume. The flume was kept running for a week with a lid rotational speed (RS) of 0.6 m/s (the water velocity was about 20 cm/s) before antibiotics were added to the water. Then, 16 mg of each of the four selected antibiotics were dissolved and spiked into the flume system. Following this, the flume started to work at a water velocity of 20 cm/s and the run ended after 60 days. At each sampling period, one litre of surface seawater (3 cm below the surface) and bottom seawater (3 cm above the sediment), as well as sediment in the middle of the straight sections of the flume, were collected. After each sampling programme, two litres of seawater were added to compensate for what had been lost due to water sampling. Ultra-pure water was also added to keep the volume of the water constant every day. At the end of the experiment (60 days later), after the overlying seawater had been cautiously removed, the sediment in the straight section was longitudinally sectioned at 5-mm intervals down to 20 mm below the sediment–water interface, then 10 mm down to 30 mm.

2.2.2 Quiescent water/sediment system

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

2.2.3 Extraction and analysis of antibiotics

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

Sediment samples: Samples of approximately 5 g were accurately weighed (200 ng $^{13}C_3$-caffeine being added as a surrogate) and then placed into a 50-ml polypropylene centrifuge tube into which 10 ml of extraction buffer had been added. The extraction buffer consisted of a 2:1:1 mixture of methanol, 0.1 M of a citric acid buffer with the pH adjusted to 6.0, and a 10 mM Na_2EDTA buffer with the pH adjusted to 6.0. The tubes were vortex mixed for 1 min and were then placed into an ultrasonic bath for 15 min (water temperature ＜40℃). The tubes were then centrifuged (Eppendorf Centrifuge 5810 R) for 10 min at 3000×g. The supernatant was decanted into a 500 ml glass bottle and the sediment residue was extracted one more time. The supernatant was combined and diluted to approximately 500 ml with ultra-pure water. SAX-HLB SPE cartridges were set up in tandem, and pre-conditioned sequentially with 6.0 ml of methanol, 6.0 ml of ultra-pure water, and 6.0 ml of a 10 mM Na_2EDTA buffer (pH 6.0). The samples were then passed through the SPE cartridges and SPE columns at a flow rate of approximately 5 ml/min. After this, the SAX cartridges were removed and the HLB cartridges washed with ultra-pure water (10 ml) before being dried with a flow of nitrogen gas for 1 h. Each cartridge was then eluted with three 2-ml vol of methanol. The analytes were collected in 10 ml brown glass vials, concentrated under a flow of N_2 gas to about 20 μl, and then dissolved in 40% aqueous methanol to a final volume of 1.0 ml.

The four antibiotics were analysed using high-performance liquid chromatography-electrospray ionization tandem mass spectrometry. A quantitative analysis of each compound was performed using LC-ESI-MS/MS with the MRM mode, using the two highest characteristic precursor ion/product ion transitions. Together with the retention times, the characteristic ions were used to ensure correct peak assignment and peak purity. $^{13}C_3$-caffeine was added as a surrogate standard to all samples prior to the enrichment of the control to avoid possible losses during the analytical procedure. These spiked antibiotics in seawater and sediment were recovered at mean percentages ranging from 68% to 87% and from 65% to 72%, respectively. The limit of quantification (LOQ) for each compound in seawater and sediment are from 1 to 10 ng/L and 10 to 50 ng/g, respectively.

3 Results and discussion

3.1 Hydrodynamic characteristics of the LEAF

To check the uniformity of the flow field in the LEAF, a Preston tube was used to measure bed shear stress in the straight section of the flume. The stress was calculated according to the equations described in a previous study (Patel 1965). It was found that the lid rotational speed (RS) had a quadratic relationship with the flow velocity and the bottom shear stress. Fig. 2 shows the relationship of RS with the flow velocity and shear stress. The maximum bed shear stress that the LEAF could generate was around 1 N/m^2. Therefore, rather broad energy ranges (induced by shear stress from 0 to 1 N/m^2) can be obtained through the LEAF, with these energy levels considered to be typical of near bottom shear stresses induced by a tide or flowing river water (Bokuniewicz et al. 1991). In this study, the RS was set up at 0.6 m/s. Thus, the induced bed shear stress and water velocity were about 0.1 N/m^2 and 20 cm/s, respectively. According to Chan and Wai (2004), the energy level induced in our experimental conditions (0.1 N/m^2) was below the critical shear stress of typical non-cohesive sediment (0.15 N/m^2). Wai (2003) showed that the concentration of sediment (turbidity signal) increased and decreased in response to changes in the flow field in the LEAF. This indicated that the flume that was used was indeed suitable for the study of the erosion and deposition activities of sediment near the sediment-water interface. In addition, the LEAF was also suitable for carrying out long-term chemical-sediment sorption experiments because it had a well-controlled environment, and was made of non-reactive materials.

3.2 Sediment adsorption of antibiotics in both dynamic and quiescent environments

The changes over time in the concentration of antibiotics in the overlying seawater, including the surface and bottom seawater and sediment, in the dynamic flume system are shown in Fig. 3. The original spiked concentrations of the four antibiotics in the flume were 40 μg/L. However, the concentrations in seawater of all four antibiotics, detected at the first sampling event (30 min), were much lower than the initial spiked concentrations because of the rapid sorption to suspended particles and sediment. The antibiotic concentrations in the original seawater were mainly close to or lower than LOQ, and those in sediment were all below LOQ (see Table 1). Hence, the concentrations of the original antibiotics in water and sediment were much lower than the spiked concentrations, and need not be a cause of concern. Concentration profiles in the overlying water suggested that the diffusive transfer of antibiotics into sediment was a quick process, with the compounds generally detected in surface sediment at a maximum concentration of more than 3000 ng/g at a very short sampling interval. Since the antibiotics were spiked into the seawater, their degradation, especially photodegradation, in the water phase was a competitive process between the sorption to sediment and a chemical transformation. It is often difficult to distinguish between sorption and degradation in a natural environment. However, the photodegradation function can be evaluated in this system based on previous studies under certain controlled conditions. The half-life times of OFL and AMX (amoxicillin) in a solution of water were 2.4 and 10.6 d, respectively in a solar experiment (Andreozzi et al. 2003), and 7.0-17 d for ETM in sludge (Wu et al. 2008). Generally, the intensity of sunlight is about 50 times greater than the light emitted by common fluorescent lamps. In addition, the relatively low temperature in the laboratory may affect the reactivity of antibiotics with radicals formed by photons (Yamamoto et al. 2009). Together with the shielding from the apparatus, the photodegradation rates of the antibiotics in this experiment would certainly be greatly reduced. In a river environment biodegradation would occur at a less rapid rate than would be the case in photodegradation (Kummerer 2001; Yamamoto et al. 2009). Therefore, the quick changes in the concentrations of antibiotics in the overlying water at the initial sampling times (i.e., the first 10 days) were mainly due to sediment adsorption.

The concentrations in sediment reached several hundred ng/g at the first sampling event. This suggests that a water velocity of 20 cm/s can mobilize the small particles in the surface sediment so that the antibiotic compounds can be adsorbed rapidly to suspended particles, and then to surface sediment. It can be seen from Table 1 that the small particles (clay content) in suspended matter increased from 28.4% to 34.7% in comparison with the level in bulk sediment. On the contrary, the sand content decreased from 12.4% to 1.1%. The adsorption capacity of suspended particles is strongly related to their size, with larger particles providing additional surfaces for sorption (Clymo et al. 2005; Pouliquen and LeBris 1996; Thiele-Bruhn et al. 2004). An X-ray diffraction analysis of clay showed that the sorption of antibiotics can widen the interlayer spacing of clay. Hence, an increase in the content of clay can lead to an increase in adsorption capacity (Pouliquen and LeBris 1996). This rapid and extensive sorption of antibiotics into sediment, which had previously been reported for marine sediments (Cannavan et al. 2000; Loffler et al. 2005), is mainly attributable to the lipophilicity of these compounds. The concentrations of antibiotics in the water of the quiescent environment at the first sampling event were much higher than those in the flume (see Fig. 4). Correspondingly, the concentrations of antibiotics in sediment were lower than those in the flume system at the same sampling event due to the lack of dynamic interaction between water and sediment.

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

3.3 Vertical profiles of antibiotics in sediments

In the flume system, the concentrations of the four selected antibiotics were found to be highest at the top layer of sediment, and to decrease sharply with depth (Fig. 5). At the end of the experiment, OFL persisted with a residual concentration of 542 ng/g in the top layer (0-5 mm), while the respective figures were 434 ng/g for RTM, 393 ng/g for ETM, and 55 ng/g for SMZ. The results revealed a pattern of diffusive distribution of the selected antibiotics into the sediment, due to the dynamic interaction between water and sediments in the flume system. A different pattern was seen in the quiescent system. Except for approximately 20 ng/g of OFL, no antibiotics were detected below 10 mm in the sediment profile. Allan et al. investigated the diffusion of the synthetic pyrethroid permethrin into sediment using flume channels (Allan et al. 2005). Their results clearly showed that a large quantity of permethrin accumulated in the top layer (0-3 mm). Little permethrin was found in the sediment at a depth of 3 mm below the sediment-water interface. In our work, a high water velocity certainly affected the normal diffuse boundary layer, which may have resulted in mass transfers and increased the overall fluxes of antibiotics into the sediment. On the whole, the concentrations of antibiotics decreased by about one hundred ng/g for every 5 mm in the sediment profile to a depth of 25 mm, with the exception of the SMZ. No SMZ was found in the sediment at a depth below 15 mm, probably due to its low distribution coefficient and fast degradation rate (Holtge and Kreuzig 2007; Wu et al. 2009).

3.4 Effects of adsorption/desorption between seawater and sediment

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

$$K_d = C_s/C_{aq}$$

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

where C_s is the antibiotics equilibrium concentration in a solid matrix, and C_{aq} is the equilibrium concentration in an aqueous solution. In the present study, the K_d and K_{oc} values were determined using the concentrations of antibiotics in water and solid after 1 d or later, and should therefore be close to equilibrium conditions. That no degradation took place before 1 d was also taken into account. It is known that pharmaceuticals display a wide range of mobility ($0.2<K_d<6000$ L/Kg), and that the variations in K_d for a given compound in different soils and sediments can be significant (Tolls 2001). In the present study, the K_d and K_{oc} values of each antibiotic did indeed vary significantly (Table 2). The values of K_d and K_{oc} decreased in the following order: OFL>RTM>ETM>SMZ. The adsorption of all compounds was generally higher in sediments with a higher total organic content (TOC) (Drillia et al. 2005). Hence, it is believed that the high sorption capacity (high K_d) to marine sediment may reduce the availability of antibiotics to benthic invertebrates. The calculated values showed that OFL has a high tendency to be adsorbed by sediment or solid particles, while SMZ, with a pK_a value of 1.69, has a low affinity for sediment. Studies have shown that the interaction of antibiotics with Ca^{2+} at clay surfaces is the prevalent sorption mechanism at low pH levels (Nowara et al. 1997). However, in neutral and weak alkaline pH conditions, this mechanism cannot play a leading role in the interaction of antibiotics with solids. This indicates that the interaction of deprotonated carboxylic acid with a clay surface can contribute significantly to the sorption of fluoroquinoloes antibiotics (Nowara et al. 1997). An X-ray diffraction analysis of clay showed that the sorption of antibiotics can widen the clay interlayer spacing. Hence, due to the high clay content of the marine sediment in this study, the mechanism for the fluoroquinoloes may be through cation bridging in the diffuse double layer at the surfaces of the clay. The possible sorption mechanism for the fluoroquinoloes agrees with the high K_d obtained in previous studies (Tolls 2001). It has been suggested that electrochemical affinity and hydrophobic interaction can play important roles in the sorption of macrolides and sulfonamides to sediment/soil (Liu et al. 2002; Pan et al. 2009; Yamamoto et al. 2009).

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

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

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

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

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

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

4 Conclusions

The dynamic environment that we simulated gave some insight into the environmental behaviours of antibiotic compounds when they are introduced into aquatic environments. The results showed that the diffusive transfer of antibiotic into sediment was a quick process in the flume system. The four antibiotics exhibited larger differences in their adsorption to sediment in both dynamic and quiescent systems due to their different K_d values. With a high K_d value, OFL showed a high tendency to be adsorbed by sediment, while the low K_d value of SMZ indicated that a large quantity would remain in water. The experiments revealed that their high sorption capacity (high K_d) to marine sediment may reduce the availability of antibiotics to benthic invertebrates. In the flume system, the four antibiotics reached sediment layers of 20–30 mm over a period of 60 days. However, in the quiescent system the compounds were only found in surface sediment (above 10 mm). In the quiescent water system, the four compounds displayed moderate persistence, with DT_{50} values ranging from 24.3 to 41.1 d., and DT_{90} values of ≥ 60 d for most of the compounds. In the dynamic flume system, OFL displayed a moderate persistence, with DT_{50} values of ≥22 d in sediment, while the other three antibiotics displayed impersistence. Furthermore, the experiment indicated that antibiotics can resist degradation, with low concentrations persisting in sediment.

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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[b]	＜LOQ
Bulk Sediment	0.88 %	12.36	59.22	28.42	＜LOQ	＜LOQ	＜LOQ	＜LOQ
Suspended particulate matter[a]	1.13 %	1.14	64.21	34.65	Not available			

[a] Suspended particulate matter was collected during the running of the flume for a week, before being spiked with antibiotics.

[b] The LOQs for OFL, RTM, ETM, and SMZ were 10, 5, 5, and 1 ng/L, and 50, 20, 20, and 10 ng/g in seawater and marine sediment, respectively.

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[a]	447300	50056~1104595[a]
RTM	1420	470[b]	213000	-
ETM	337	165[c]	50550	-
SMZ	89	0.23~43.1[a]	13350	62.2~607[a]

[a] From (Drillia et al. 2005)

[b] From (Gobel et al. 2005)

[c] From (Jones et al. 2002)

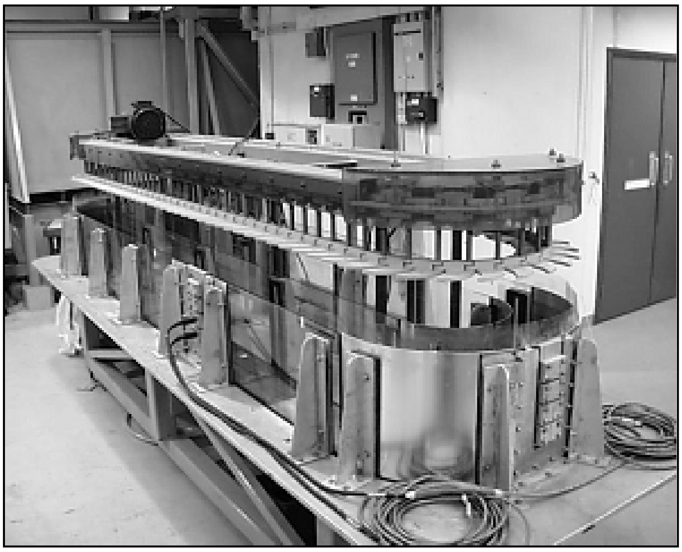
Table 3 The DT_{50} and DT_{90} values of the four antibiotics in seawater and sediment

Antibiotics	In the human body (h)		In the flume system (d)		In the quiescent system (d)	
	DT_{50}	DT_{90}	DT_{50}	DT_{90}	DT_{50}	DT_{90}
OFL	5.0~10.0	—[a]	3.4[b] (21.4)[c]	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)

[a] Not available

[b] In seawater

[c] In sediment



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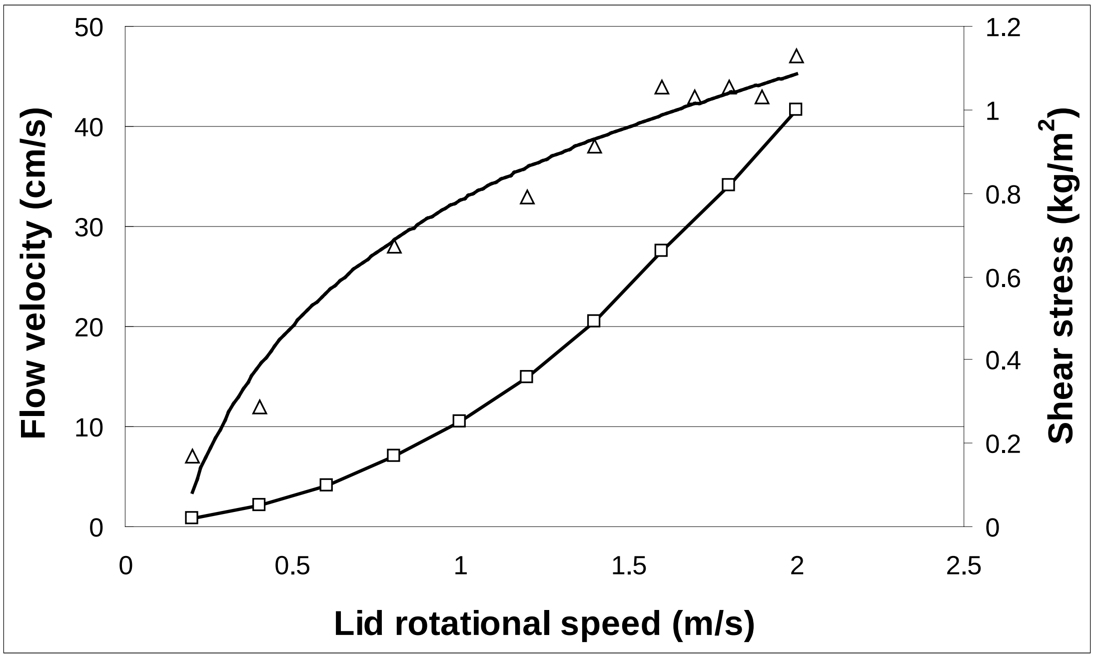

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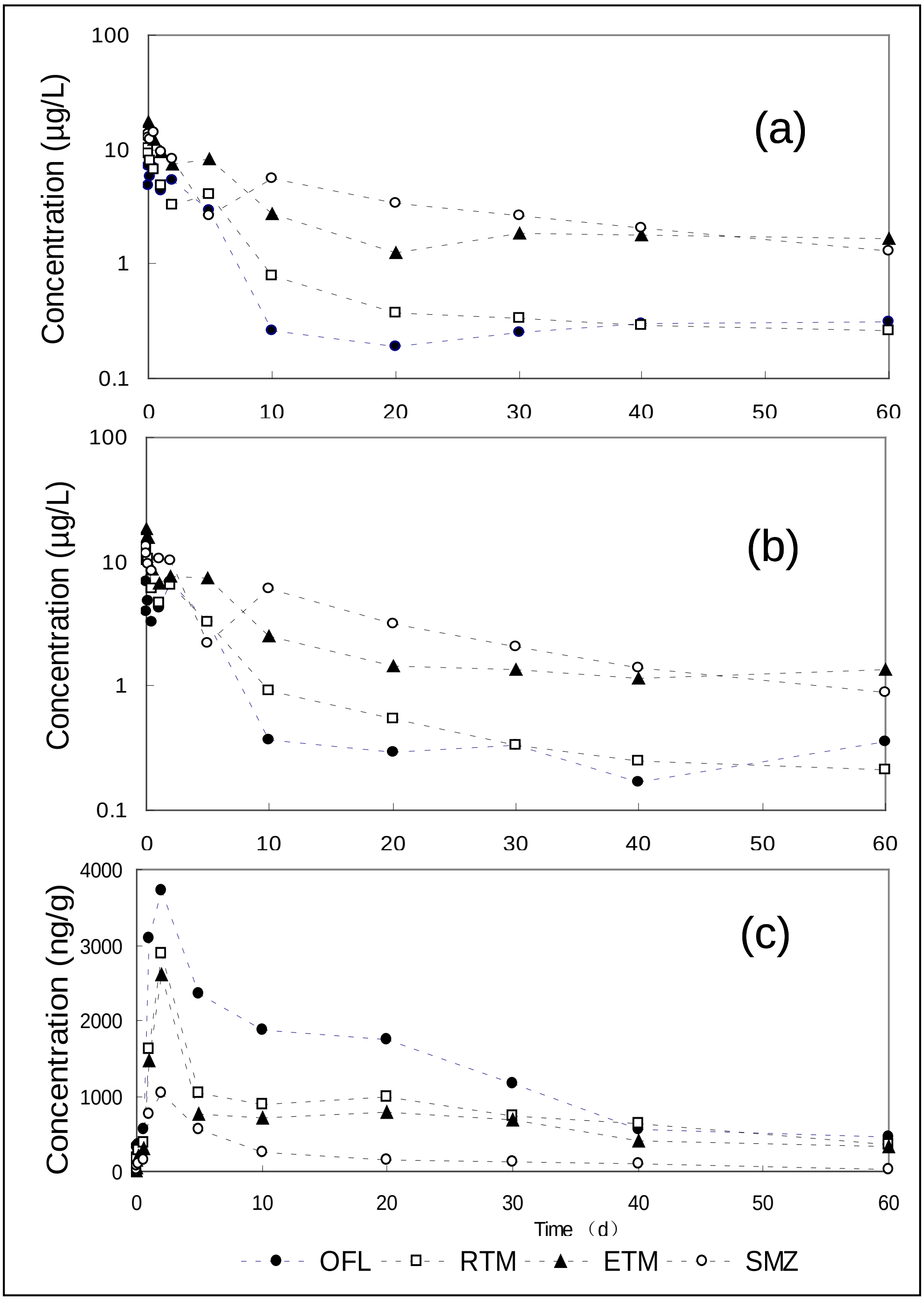

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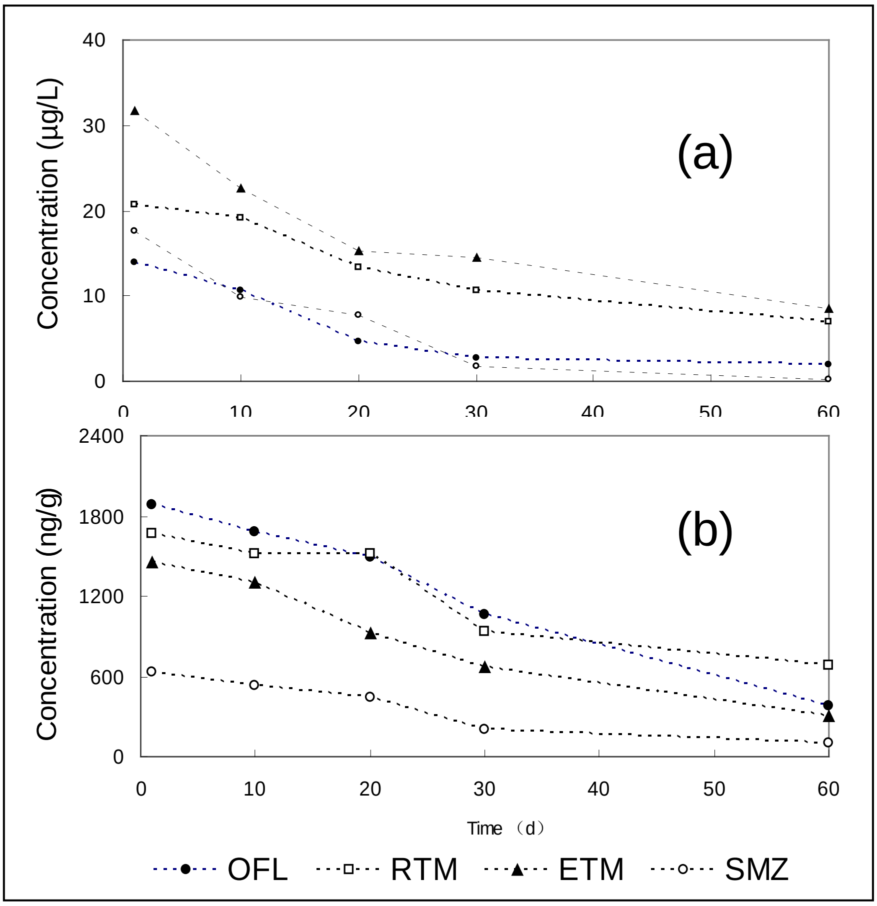

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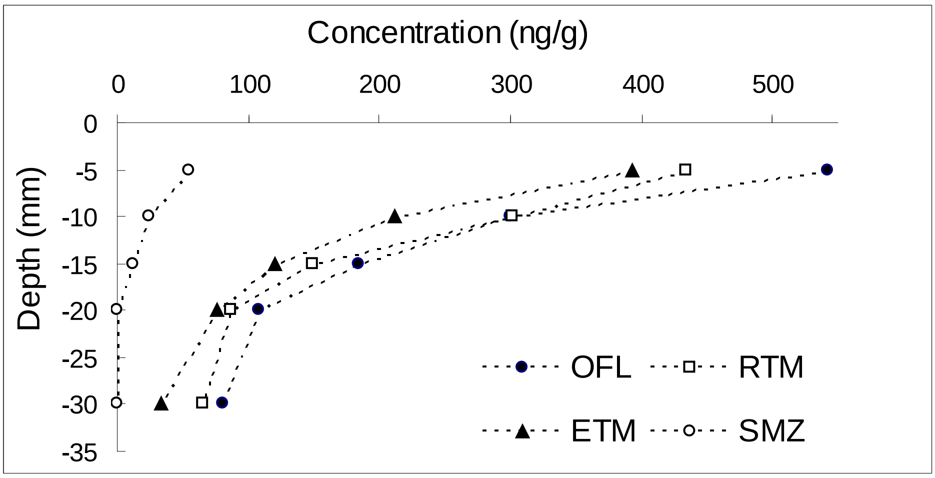

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