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Determination of the persistence of pharmaceuticals in biosolids using liquid-chromatography tandem mass spectrometry

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ABSTRACT

Sludge generated in waste water treatment process can be a major sink for some pharmaceutical and personal care products (PPCPs). The land application of sewage sludge (in the form of biosolids in the United States) can therefore potentially introduce PPCPs into the environment. After treatment, biosolids are often subjected to a storage period before land application. However, little information is available with regard to the fate of PPCPs in biosolids during the storage. In this work, the persistence of seven pharmaceuticals and one antibacterial was evaluated using ultrasonic extraction and liquid-chromatography tandem mass spectrometry (LC–MS/MS). The impacts of aeration and sunlight exposure were investigated. During the experiment, no elimination was observed for carbamazepine, triclosan, and ciprofloxacin while elimination was found for tetracycline, doxycycline, clindamycin, erythromycin, and clarithromycin. Using an availability-adjusted kinetic model, the 50% dissipation time was 37 to >77 d for tetracycline, 53 to >77 d for doxycycline, 1.0–1.6 d for clindamycin, 1.1–1.9 d for clarithromycin, and 7.0–17 d for erythromycin. Those compounds were found more persistent under anaerobic conditions than aerobic condition with a longer 50% dissipation time by a factor of 1.5–2. However, minor impact was observed from sunlight irradiation.

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1. Introduction

Pharmaceuticals and personal care products (PPCPs) are increasingly being used in households, healthcare, and animal husbandry in the United States and worldwide. In 2005, the world pharmaceutical market was 606 billion U.S. dollars, with more than 268 billion located in North America (Enserink, 2006). Over the past decade, growing attention has been drawn to the investigation of the environmental behavior and impact of these compounds (Erickson, 2002; Fent et al., 2006). They are recognized as 'emerging' contaminants due to their bioactivity, wide usage, and potential health and ecological risks (Daughton and Ternes, 1999).

Municipal wastewater is one of the main routes introducing PPCPs into the environment, and as a result much of the research effort has been on the occurrence and fate of those compounds during the wastewater treatment processes (Ternes et al., 2004). Studies have shown that nanogram to microgram per liter concentrations for many PPCPs are commonly found in effluent, indicating an insufficient removal of those contaminants using current wastewater treatment techniques (Miao et al., 2003; Vienoa et al., 2007). Moreover, considerable amounts of PPCPs are sequestrated by suspended solids present in the wastewater and the new biomass generated in the biological processes and subsequently removed by sedimentation as sewage sludge (Ternes et al., 2004; Xia et al., 2005). Residuals up to the milligram per kilogram range are often reported in both activated and digested sludge (Göbel et al., 2005; Kinney et al., 2006).

Sewage sludge is an end product of wastewater treatment process rich in nutrients and organic materials. Treated sewage sludge meeting regulations for pathogens, nutrients, and metals is termed as biosolids in the United States and used as a fertilizer (Kinney et al., 2008). In the United States, about 6.9 million tons of biosolids were generated in 1998, about 41% of which were land applied (USEPA, 1999). The amount of biosolids generated in 2006 was estimated to be more than 8 million dry tons, of which about 50% were land applied (Kinney et al., 2008). Along with land application of biosolids, PPCPs and other pollutants may be transported to soils, having the potential to enter surface water via runoff, leach into the groundwater, or assimilate by vegetation or other living organisms.

Research is limited with regard to the fate of PPCPs in biosolids. In previous research, Heidler et al. (2006) found that 78% of triclocarbon was sequestered in sludge during wastewater treatment and no transformation was observed under anaerobic digestion for 19 d. Carballa et al. (2007) investigated the behavior of 13 PPCPs during anaerobic treatment of sewage sludge using lab-scale digesters. During the sludge digestion, high removal efficiencies were achieved for roxithromycin, sulfamethoxazole, natural estrogens, musks and naproxen, a moderate removal rates were

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achieved for diazepam, ibuprofen, and iopromide and no removal was achieved for carbamazepine. Results from these studies suggest that certain PPCPs can survive the sludge treatment processes. After treatment and before land application, biosolids are typically stored in storage tanks for days to months. Thus the fate of PPCPs during storage is of great importance in determining the amount of contaminants that could potentially be transported into the environment. However, the fate of PPCPs residuals during storage is unclear, and limited information is available to address this question.

The purpose of this study is to investigate the fate of PPCPs during biosolids storage under the influence of different storage conditions. Eight compounds were selected for examination primarily based on their prevalence in biosolids as well as their environmental importance, including antibiotics (ciprofloxacin, tetracycline, doxycycline, clindamycin, clarithromycin, and erythromycin), antiepileptic (carbamazepine), and antibacterial (triclosan). Their structures, selected physico-chemical properties are provided in Table 1.

2. Materials and methods

2.1. Chemicals

Analytical grade standards were purchased from Sigma–Aldrich (St. Louis, MO). Chemicals and solvents were certified ACS or HPLC grade and were purchased from Fisher Scientific (Fair Lawn, NJ). Deionized water (18.3 mΩ) was provided by a NANOpure Infinity Ultrapure Water System (Barnstead, Dubuque, IA). Individual stock standard was made at 50 mg l^{-1} in methanol. Working standards were prepared from the stock standards. All standards were stored at −20 °C. No degradation in the stock standard was observed during the experiment (Supplementary material Fig. S4).

2.2. Experiment setup

Nine high density polyethylene (HDPE) buckets (height: 35 cm, ID: 30 cm) were employed in the experiment. The sorption of selected compounds to the HDPE was found insignificant based on preliminary control tests. The biosolids samples have been treated aerobically and were collected in August 2007 from a wastewater treatment plant (WWTP) in Oregon, OH (see Supplementary material for detail). The initial total suspended solids (TSS) and volatile suspended solids (VSS) of biosolids were 40 g l^{-1} and 24 g l^{-1} approximately. Each bucket was filled with ~17 kg biosolids (28 cm thick approximately) and then transported to the R.A. Stranahan Arboretum, a University of Toledo field research station (Toledo, OH) and set in an open field. Each bucket was spiked with 2.0 mg of each compound in 20 ml methanol. Thus a theoretical concentration of 3000 ng g^{-1} for each compound was reached. Spiked biosolids were then homogenized using an angled steel rod attached to a cordless drill operating at 1000 rpm for about five min. Three storage conditions were used: treatment one ($T1$) simulated a dark and anaerobic condition, buckets were closed with lids; treatment two ($T2$) simulated dark and aerobic conditions, buckets were closed with lids and aerated continuously at a rate of approximately 2 l/min via 100 × 25 mm rubber membrane air diffusers (Oak Park Landscaping and Water Garden, Swanton, OH) placed at the bottom; and treatment three ($T3$) simulated light and aerobic condition, buckets were aerated using the same setup and airflow as $T2$ and were covered with a wooden frame containing 1.27 mm thick Teflon FEP film to prevent rain infiltration while still allowing solar radiation to penetrate. Holes were drilled in the sides of the buckets for $T1$ and $T2$ to release the gases generated during biosolids storage ($T1$) or due to the aeration ($T2$) while no holes was necessary for $T3$ as gases were released through the openings between the wood frame and bucket. These holes and openings were covered with wire mesh to exclude animals and insects. Sketch map of the field experiment setup is illustrated in Fig. 1 (details in Supplementary material).

2.3. Sample collection

The experiment was initiated on 13 August 2007 and lasted 77 d (from summer to late fall). The duration of the experiment was limited by local temperatures dropping to below 0 °C, causing the biosolids to freeze and equipment failure. Samples were collected from each bucket at day 0, 2, 7, 14, 22, 35, 49, and 77. The day 0 samples were collected directly after the experiment setup and the target compounds were measured to represent the initial concentrations. Before sampling, the biosolids were thoroughly mixed using the method described earlier, and then 100 ml of homogenized liquid samples were transferred into two centrifuge tubes from each bucket. One was used for pH, TSS and VSS measurement. The other was lyophilized and used for chemical analysis.

2.4. Temperature, pH, TSS, and VSS measurement

Temperatures of each treatment and air were recorded using HOBO data logger (Onset Corp., Bourne, MA). The pH was measured directly using a Cole-Parmer pH meter with a double junction probe. The TSS and VSS were measured according to standard methods (NWEA, 2000).

2.5. Sample preparation and analysis

Aliquots (0.5 g) of lyophilized samples were extracted by ultrasonication using a mixed solution of methanol, 0.1 M acetic acid and 5% Na_2-EDTA (2:1:1). Extracts were cleaned and concentrated by solid phase extraction using Strata-X (Phenomenex Inc., Torrance, CA) cartridges (200 mg, 6 ml). Determination of target analytes was performed using a ProStar 210 solvent delivery module connected to a 1200 L triple-stage quadrupole mass spectrometer with a dual off-axis electrospray ionization (ESI) interface (Varian Inc., Walnut Creek, CA). Analytes were separated on a 100 × 4.6 mm (3 μm, 100 Å, end capped) Luna C8(2) Silica-based Column with 4 × 2.0 mm packing matched SecurityGuard column (Phenomenex Inc., Torrance, CA). An internal standard calibration curve ($r^2 > 0.99$) was used for quantification. The concentrations of target compounds were reported on dry weight basis. Detailed method information and method validation are provided in Supplementary material.

2.6. Data analysis and kinetic model

Data were collected, quantified and analyzed using Varian MS Workstation Ver 6.8 (Varian Inc., Walnut Creek, CA). Statistical analysis was done using SigmaStat Ver. 3.11 software (Systat Software, Inc., San Jose, CA).

Dissipation of many organic contaminants follows the first-order model. However, deviation from the simple first-order model, such as a biphasic pattern, has also been observed (Beulke and Brown, 2001). Several non-linear models have been developed to describe this kind of kinetics. Here, an availability-adjusted model described by Wang et al. (2006) was adopted. On the assumption that the ratio of target compound concentration in aqueous phase to the total concentration (C) of remaining compound in the sample at time t is λ, the first-order model can be rewritten as:

$$\frac{dC}{dt} = -k\lambda C \quad (1)$$

where k is first-order rate constant. If λ does not change with time, the overall kinetics will follow the first-order kinetic. However, if λ

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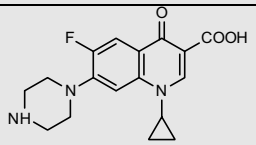
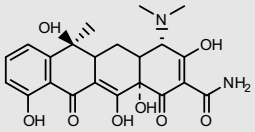
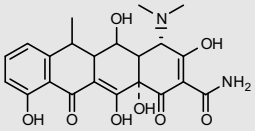
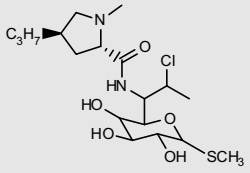
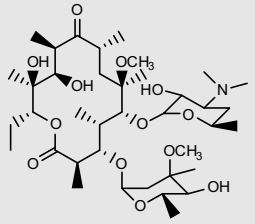
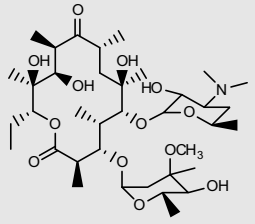
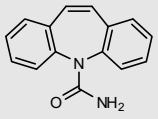
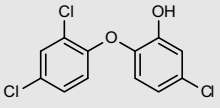
Table 1
Structure, acid dissociation constant (pK_a), octanol–water partition coefficient (K_{ow}) and solid–water distribution coefficients (K_d) of the target compounds

Compound	Structure	p*K*a	log K_{ow}	K_d	
				Activated sludge	Digested sludge
Ciprofloxacin		3.01, 6.14, 8.7, 10.58[a]	0.28[e]	15 849[f]	No data
Tetracycline		3.32, 7.78, 9.58[a]	−1.3[e]	22 600[g]	No data
Doxycycline		3.02, 7.97, 9.15[a]	−0.02[e]	No data	No data
Clindamycin		7.79[a]	2.01[e]	No data	No data
Clarithromycin		8.7[b]	3.18[e]	300–400[b]	No data
Erythromycin		8.90[a]	3.06[c]	No data	No data
Carbamazepine		13.9[c]	2.25[e]	No data	20.4–67.6[h]
Triclosan		8.1[d]	4.8[d]	No data	No data

[a] Qiang and Adams (2004).
[b] Göbel et al. (2005).
[c] Jones et al. (2002).
[d] Aranami and Readman (2007).
[e] Calculated value using USEPA (2007) EPI Suite V3.20 software.
[f] Golet et al. (2003).
[g] Kim et al. (2005).
[h] Carballa et al. (2008).

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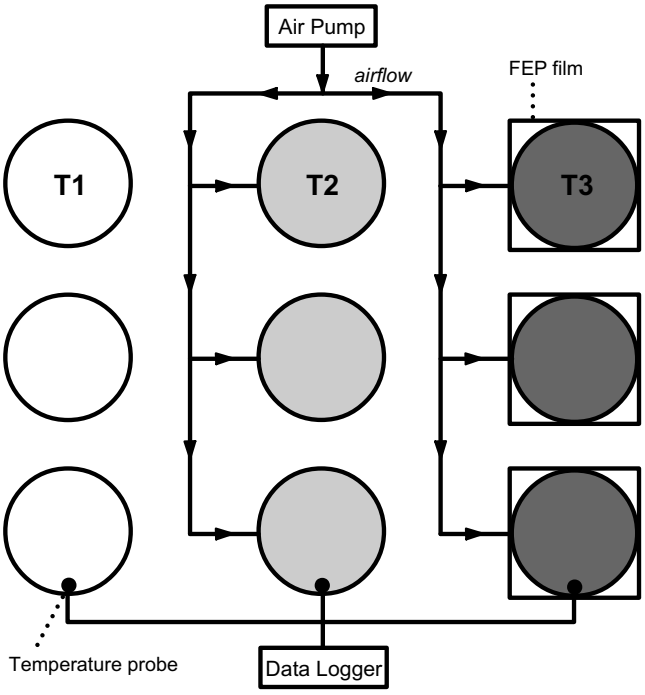

Fig. 1. Schematic map of field experiment setup (see Supplementary material for detail).

varies with time, the kinetics will deviate from the first-order model. Assume the change of λ follows Eq. (2)

$$\lambda_t = \lambda_0 e^{-at} \tag{2}$$

where, λ_0 and λ_t are the fraction of non-adsorbed compound at time 0 and time t, respectively. Constant a is the availability coefficient and a larger a value indicates that the ratio λ decreases faster with time. The modified model can be expressed as below

$$\frac{dC}{dt} = -k' e^{-at} C \tag{3}$$

where $k' = k\lambda_0$, C_0 and C_t are the concentrations of analyte at time 0 and time t, respectively. Integrating Eq. (3), presents a model expressed as

$$C_t = C_0 e^{-\frac{k'}{a}(1-e^{-at})} \tag{4}$$

From Eq. (4), the 50% dissipation time (DT_{50}) can be calculated using Eq. (5).

$$DT_{50} = -\frac{1}{a} \ln\left(1 - \frac{0.693a}{k}\right) \tag{5}$$

3. Results and discussion

3.1. Temperature, pH, TSS and VSS

Biosolids and air temperature were monitored throughout the experiment (Supplementary material Fig. S5). The highest and lowest average diurnal air temperature were 26.5 °C and 3.4 °C, respectively. Change of biosolids temperature followed the trend of air temperature, whereas diurnal temperature fluctuations were less prevalent. Comparing the difference among the treatments, the temperature of biosolids stored in aerobic condition was less stable than those in anaerobic condition, likely attributed to enhanced heat exchange between biosolids and air by the aeration. In addition, the temperature of biosolids in *T*3 appeared to fluctuate more, attributed to sunlight exposure. However, the difference of temperature for three treatments is less than 2 °C for the majority of time. The sample pH and TSS were measured for every sampling. During the experiment, the pH was close to seven with slight variation. The TSS remained constant (40 g l^{-1}) for *T*1 and *T*2 with negligible water loss. However, TSS increased to around 60 g l^{-1} for *T*3, largely attributed to the higher evaporation rates resulting from higher temperature and air exchange rate. No water was added to the buckets to compensate the evaporation. The VSS was only measured for samples collected at day 0 and day 49 and was around 24 g l^{-1} for all samples in *T*1 and *T*2. However, the VSS for samples in *T*3 increased to about 36 g l^{-1} due to the water loss.

3.2. Method performance and background concentrations

The performance of the analytical method is summarized in Table 2. The recoveries for the target compounds at two spiked concentrations (0.2 and 1.0 μg g^{-1}) range from 31% to 83% with relative standard deviations of three replicates less than 20%. Signal suppression was observed for all the compounds due to the matrix effect, especially for ciprofloxacin and triclosan, for which the signal decreased more than 30%. fluoroquinolone and tetracycline antibiotics have been shown to sorb strongly to the solid phase via interaction such as hydrogen bonding with organic matter and complexation with metal cations (Toll, 2001). The low recovery (<50%) of ciprofloxacin, tetracycline, and doxycycline might be attributed to the matrix effect and insufficient extraction even though the strong chelating agent EDTA was added. Due to the low recovery, the data for these three compounds can only be qualitative. However, as the relative standard deviation of the method was less than 20%, the precision was acceptable and the data can still be useful for a kinetic study.

Using the method, background residuals were determined and all target compounds were detected in the biosolids. The highest concentration was 778 ng g^{-1} for ciprofloxacin, followed by triclosan

Table 2
Performance of the analytical method

Compound	Intra-day variation (RSD%)	Inter-day variation (RSD%)	LOD (ng g^{-1})	LOQ[a] (ng g^{-1})	High spike (1 μg g^{-1})		Low spike (0.2 μg g^{-1})	
					ME (%)[b]	RE (%)[c]	ME (%)	RE (%)
Ciprofloxacin	15	13	13	44	48 ± 7	31 ± 6	50 ± 6	38 ± 6
Tetracycline	8.8	11	15	51	89 ± 11	37 ± 3	83 ± 9	44 ± 4
Doxycycline	11	13	8.0	27	73 ± 6	39 ± 4	78 ± 8	37 ± 4
Clindamycin	7.0	7.9	0.1	0.5	85 ± 10	74 ± 6	80 ± 8	79 ± 7
Clarithromycin	6.8	12	0.6	1.9	82 ± 4	77 ± 10	84 ± 6	73 ± 7
Erythromycin-H_2O	9.6	4.2	0.8	2.6	90 ± 5	83 ± 8	88 ± 10	71 ± 4
Carbamazepine	9.6	12	0.2	0.5	81 ± 7	70 ± 3	85 ± 9	72 ± 1
Triclosan	9.0	18	17	57	63 ± 8	53 ± 9	69 ± 7	68 ± 13

[a] LOD: limits of detection; LOQ: limits of quantification.
[b] Matrix effects (mean ± standard deviations, $n = 3$) evaluated by comparing the samples spiked after sample preparation with standards.
[c] Recoveries (mean ± standard deviations, $n = 3$) evaluated by comparing the samples spiked before extraction with standards.

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(320 ng g^{-1}), doxycycline (296 ng g^{-1}), tetracycline (180 ng g^{-1}), carbamazepine (34.5 ng g^{-1}) and clindamycin (23.2 ng g^{-1}). Low concentration were detected for erythromycin-H_2O and clarithromycin, which were 3.6 and 5.2 ng g^{-1}, respectively.

3.3. Elimination of target compounds

The residuals of selected compounds in biosolids during the experiment are presented in Fig. 2. No elimination of carbamazepine, triclosan, and ciprofloxacin was observed throughout the experiment, the concentration of tetracycline and doxycycline decreased slowly, while clindamycin, clarithromycin and erythromycin displayed a relatively fast elimination rate. The dissipation kinetics of these compounds was described using both first-order model and availability-adjusted model (Table 3). The correlation coefficient (r) indicated that the dissipation kinetics of tetracycline, doxycycline, and erythromycin can be well fitted using both models, while the dissipation kinetics of clindamycin and clarithromycin was better fitted using availability-adjusted model, for which the dissipation exhibited a biphasic pattern with a rapid elimina-

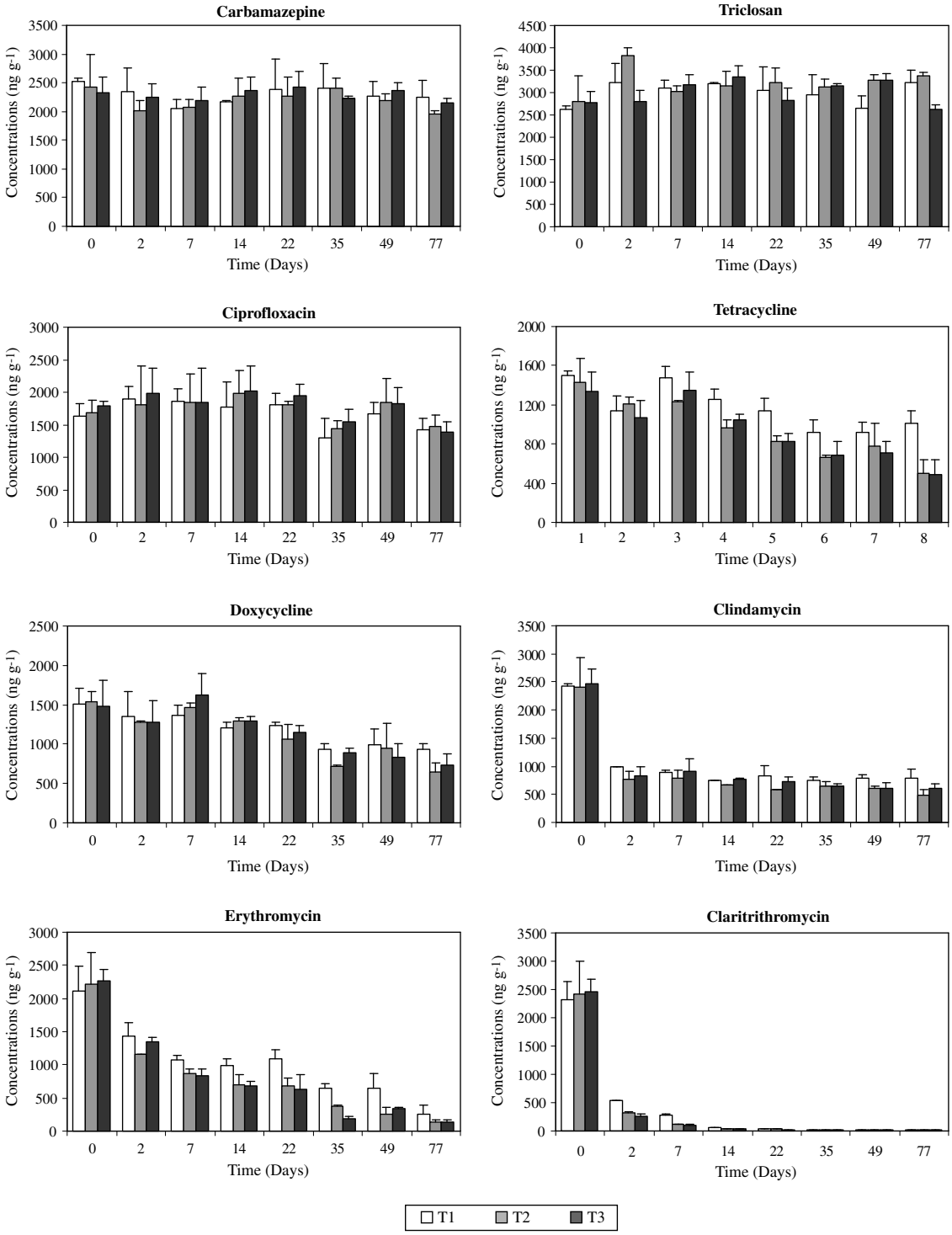

Fig. 2. Degradation of target compounds over time (bar and error bar represent the mean and standard deviation of three replicates from each treatment).

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Table 3
Calculated regression coefficient (r), rate constant (k), availability coefficient (a), and 50% dissipation time (DT_{50}) using first-order and availability-adjusted model

Compound	Treatment	First-order model			Availability-adjusted model			
		r	k	DT_{50}	r	k'	a	DT_{50}
Tetracycline	*T*1	0.73	0.005 ± 0.002	138	0.81	0.023 ± 0.011	0.046 ± 0.032	>77
	*T*2	0.93	0.012 ± 0.002	57	0.96	0.031 ± 0.007	0.030 ± 0.011	37
	*T*3	0.94	0.013 ± 0.002	53	0.95	0.022 ± 0.005	0.015 ± 0.010	43
Doxycycline	*T*1	0.89	0.006 ± 0.001	115	0.95	0.019 ± 0.004	0.036 ± 0.013	>77
	*T*2	0.90	0.011 ± 0.002	63	0.91	0.019 ± 0.015	0.021 ± 0.007	53
	*T*3	0.93	0.010 ± 0.002	69	0.94	0.014 ± 0.004	0.011 ± 0.011	70
Clindamycin	*T*1	0.53	0.008 ± 0.005	86	0.99	0.667 ± 0.093	0.596 ± 0.086	1.6
	*T*2	0.67	0.012 ± 0.006	58	0.97	0.729 ± 0.199	0.536 ± 0.153	1.3
	*T*3	0.65	0.011 ± 0.005	63	0.96	0.965 ± 0.332	0.768 ± 0.274	1.0
Clarithromycin	*T*1	0.83	0.067 ± 0.018	10	0.99	0.399 ± 0.014	0.073 ± 0.003	1.9
	*T*2	0.79	0.063 ± 0.020	11	0.99	0.596 ± 0.056	0.111 ± 0.012	1.2
	*T*3	0.74	0.057 ± 0.021	12	0.99	0.659 ± 0.031	0.125 ± 0.007	1.1
Erythromycin	*T*1	0.96	0.023 ± 0.003	30	0.92	0.045 ± 0.012	0.015 ± 0.011	17
	*T*2	0.96	0.034 ± 0.004	20	0.97	0.085 ± 0.014	0.028 ± 0.008	9.2
	*T*3	0.90	0.032 ± 0.006	21	0.94	0.115 ± 0.027	0.043 ± 0.015	7.0

Rate constant and availability coefficient are estimated value with standard error.

tion during the first seven days and a much slower rate afterward. Better fitting with the modified model supports the assumption of the model that the proportion of available compound in the sample decreases with time. Using the availability-adjusted model, the calculated DT_{50} was 37 to >77 d for tetracycline, 53 to >77 d for doxycycline, 1.0–1.6 d for clindamycin, 1.1–1.9 d for clarithromycin, and 7.0–17 d for erythromycin. According to the DT_{50} value, tetracycline and doxycycline were more persistent during biosolids storage, followed by erythromycin, clarithromycin, and clindamycin. However, due to the biphasic dissipation pattern, clindamycin and clarithromycin could still exist in the biosolids for an extended period at a low concentration.

Previously, persistence of carbamazepine was found in many environmental processes. Removal of carbamazepine during biological wastewater treatment was found less than 10% and sorption to the secondary sludge was insignificant (Joss et al., 2005). Study on the fate of pharmaceuticals in water/sediment systems showed that the 90% dissipation time was more than 365 d for carbamazepine (Löffler et al., 2005). Photodegradation studies indicated that the half-life of carbamazepine was 100 d in the bidistilled water in winter at the highest latitudes (50°N) and the presence of humic acids act as inner filters towards carbamazepine (Andreozzi et al. 2003). Thus photodegradation of carbamazepine in the biosolids might be less significant due to the high organic content and attenuation of light. The result observed here further confirms these persistence trends found for carbamazepine.

Triclosan is widely used in many personal care products. The fate of triclosan during wastewater treatment processes has been investigated using a mass balance approach (Heidler and Halden, 2007). The results suggested that the liquid phase removal efficiency is 98%. However, about 80% particle-associated triclosan was sequestered into wastewater residuals and accumulated in the dewatered and digested sludge. Approximately 50% of the total triclosan mass entering the wastewater treatment plant remained detectable in the sludge. Ying et al. (2007) studied the biological degradation of triclosan in soil under aerobic and anaerobic conditions. A half-life of 18 d was calculated for triclosan in aerobic soil while little removal was found in anaerobic soil during the 70 d experiment. Photodegradation has also been found to be an important process eliminating triclosan from natural water and the formation of 2,7/2,8-dibenzodichloro-*p*-dioxin was observed as a photodegradation product (Aranami and Readman, 2007). However, no elimination was observed here under any tested conditions. This could be attributed to the strong affiliation of triclosan to the organic-rich particles in biosolids and the resulting strong sorption might prevent triclosan from photo and biodegrading.

Study on the behavior of ciprofloxacin during the wastewater treatment processes has found that sorption to the sludge is the main removal mechanism and no significant elimination occurs during sludge treatment, which results in residuals up to mg kg^{-1} detected in the digested sludge (Golet et al., 2003). Photodegradation was also found to be the main process to eliminate ciprofloxacin in the environment, but has been shown to be affected by sorption (Belden et al., 2007). The persistence of ciprofloxacin during biosolids storage could be attributed to the poor biodegradability and strong sorption characteristic.

Tetracycline and doxycycline belong to tetracycline antibiotic group. During the activated sludge process, sorption was also found to be the principal removal mechanism for tetracycline and the removal efficiency increased with the increase in hydraulic and solid retention time (Kim et al., 2005). Study of tetracycline concentrations in a manure-amended soil has shown a slight decline over a 6-month period, and accumulation was found with repeated manure fertilization (Hamscher et al., 2002). Tetracyclines are photodegradable in liquids, but dampening of the photodegradation by sorption in the environment has been observed (Boreen et al., 2003). The slow elimination rate indicated that a considerable portion of tetracycline and doxycycline could survive the long-term biosolids storage.

In previous research, clindamycin was found adsorbed to montmorillonite by a cation exchange mechanism under pH favoring cationic form, and by physical adsorption when the neutral form was present (Porubcan et al., 1978). Detection of clindamycin in effluent and surface water has been reported (Batt et al., 2006), but no study regarding its behavior during wastewater treatment processes can be found in the current literature. Solar photodegradation studies have indicated that clindamycin is less photosensitive (Andreozzi et al., 2006). Half-life of 2033 d (pH 5.5) and 1760 d (at pH 7.5) were calculated in the worst conditions (winter, 50°N). Therefore the elimination of clindamycin in the biosolids could be mainly attributed to the chemical or biological processes. A fast elimination within two days followed by a long-term stable phase found here, suggesting that clindamycin is degradable but further degradation is likely hindered by a nonreversible sorption.

Clarithromycin and erythromycin are macrolide antibiotics. Here erythromycin-H_2O is monitored since erythromycin is known to dehydrate quickly under acidic condition (Hirsch et al., 1999). Similar to clindamycin, clarithromycin degraded rapidly at the

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beginning and slowly at the end of the experiment. Previous research on the behavior of macrolides during wastewater treatment processes has found that the elimination of clarithromycin and erythromycin-H_2O are not efficient, and high residues of both compounds have been detected in effluent, sludge, and receiving waters (Göbel et al., 2005). Relatively fast degradation of erythromycin in soil (Schlüsener and Bester, 2006) and during manure storage (Schlüsener et al., 2006) was also reported with half-lives of 20 and 41 days, respectively. Information on the photodegradation of macrolides in the environment is generally non-available. As many macrolides contain no chromophoric functional groups, their photodegradation may be restricted (Boreen et al., 2003). The results observed here agree with previous observations.

3.4. Influence of storage conditions

Biological degradation of organic substances usually involves electron transfer, and thus, the preferred degradation pathway for a given compound is dependent on the oxidation state of the compound and the environmental conditions, such as the presence or absence of oxygen (Reineke, 2001). No elimination of carbamazepine, triclosan, and ciprofloxacin was found in either aerobic or anaerobic conditions, indicating that these compounds are resistant to biological degradation. Meanwhile, elimination was observed for the remaining compounds in both aerobic and anaerobic conditions and modeling results show that those compounds appeared to be more persistent under anaerobic conditions than aerobic condition with DT_{50} increasing by a factor of 1.5–2 (Table 3). An early laboratory study also found that the biodegradation of four antibiotics (tylosin, olaquindox, metronidazole and oxytetracycline) was significantly slower in surface water in absence of oxygen (Ingerslev et al., 2001). Ying et al. (2007) also reported a faster degradation of triclosan and triclocarban in soil under aerobic condition than anaerobic condition. Thus, aerobic degradation might be a more important mechanism to eliminate PPCPs from the environment. However, more data for compounds from different classes are needed to support this assumption and further research is needed to clarify the degradation pathways and identify the metabolites.

Photodegradation is an important abiotic pathway to eliminate PPCPs and other organic pollutants from the environment. However, the efficiency of photodegradation can be affected by the attenuation of radiation, presence of suspended particles and dissolved organic/inorganic chemicals (Boreen et al., 2003). According to the DT_{50} value (Table 3) for those compounds in *T*2 and *T*3, the impact of sunlight can be less significant. Biosolids, as such complex dirty matrices, may act as sunlight filters and provide suspended particles on which PPCPs can sorb, making those compounds less vulnerable to photodegradation.

4. Conclusion

In this work, the fate of PPCPs during biosolids storage was studied for the first time under field conditions. During biosolids storage carbamazepine, triclosan and ciprofloxacin were found to be persistent. Meanwhile, elimination was observed for the rest of compounds, and their dissipation kinetics can be described using an availability-adjusted model. Aerobic condition appears to be preferred for the elimination of target compounds during biosolids storage. Thus, increasing the aeration time may decrease the amount of PPCPs that could be potentially transported to the soil. The influence of sunlight irradiation has minor impact on the elimination of tested compounds in the biosolids, which may also hold true for other biosolids-borne organic contaminants. Experiments under controlled conditions need to be performed to understand the impact of temperature. Further research is needed to investigate the dissipation of PPCPs in other biosolids treatment and storage processes such as pelletization, chemical stabilization, and composting; and also the transportation and fate of PPCPs following biosolids land application.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2008.06.026.

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