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Reduction of pharmaceutically active compounds by a lagoon wetland wastewater treatment system in Southeast Louisiana

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ABSTRACT

A number of pharmaceutically active compounds (PhACs) have been detected in the aquatic environment as a result of discharges of municipal wastewater. In the state of Louisiana, USA, many municipalities treat wastewater using natural systems, such as lagoons and wetlands, rather than conventional wastewater treatment technologies. Nearly all research to date has focused on the fate of PhACs in conventional treatment plants, not constructed and natural wetlands. In the wastewater treatment plant (WWTP) for Mandeville, Louisiana, USA, wastewater flows of 7600 $m^3 d^{-1}$ are treated in a series of aeration lagoons (basins), followed by a constructed wetland and UV disinfection, before being discharged into a natural forested wetland (i.e. Bayou Chinchuba) and eventually, Lake Pontchartrain. Thirteen out of the 15 PhACs investigated were detected in the wastewater inflow to the treatment plant. Only 9 of the 13 compounds were above the detection limits at the treatment plant effluent. The concentrations of most compounds were reduced by greater than 90% within the plant, while carbamazepine and sotalol were only reduced by 51% and 82%, respectively. The percent reductions observed in the Mandeville system were greater than reduction rates reported for conventional WWTPs; perhaps due to the longer treatment time (~30 days). Most target PhACs were not completely removed before discharge into Lake Pontchartrain, although their collective annual loading was reduced to less than 1 kg and down to ppb with significant potential for dilution in the large lake.

1. Introduction

The fate of pharmaceutically active compounds (PhACs) in the aquatic environment is an emerging area of research (Ternes, 1998; Daughton and Ternes, 1999; Kolpin et al., 2002, 2004; Ternes et al., 2002; Webb et al., 2003; Jones et al., 2005a). A significant portion of this research has focused on the capacity of wastewater treatment plants (WWTPs) to remove PhACs from wastewater, and the contribution of WWTPs to PhAC loadings to receiving waters (Heberer et al., 2002; Boyd et al., 2003; Miao et al., 2004; Bendz et al., 2005; Joss et al., 2006; Lishman et al., 2006; Gobel et al., 2007). However, there are very few data on the ability of constructed wetlands and natural wetland systems to reduce the concentrations of pharmaceuticals before the release of wastewater into aquatic systems (White et al., 2006; Matamoros et al., 2008).

PhACs enter the environment through a variety of pathways, and the human body plays a major role. A portion (varies by drug and individual) of each pharmaceutical dose is retained in the human body, but residual parent compound and its metabolites are excreted in urine and feces (Daughton and Ternes, 1999; Khetan and Collins, 2007; Lienert et al., 2007). The PhACs are then released either through septic systems or in wastewater effluents (Jones et al., 2005b). Within wastewater treatment plants and in the natural environment, the rates of degradation of PhACs vary, depending on the chemical and physical properties of each compound, and environmental conditions (Jones et al., 2005b). Physical, chemical and biological parameters that influence degradation include; sorption/desorption, redox potential, temperature, pH, photolysis, microbial activity, and select minerals (Tolls, 2001; Zhang and Huang, 2003, 2007; Vogna et al., 2004; Scheytt et al., 2005; ter Laak et al., 2006).

It has been predicted that the discharge of pharmaceuticals into the environment will increase over time (Jones et al., 2005a). For example, in Germany in 1995, 100 tons of prescription drugs were purchased, which does not account for sales of non-prescription drugs and veterinary medicines (Ternes, 1998). As a result of greater reliance on pharmaceuticals and an aging population, the number of prescription and non-prescription drugs dispensed during doctor visits has risen from 190 per 100 people in the USA during 1995–1996 to 226 during 2003–2004 (NCHS, 2006). Monthly prescription drug usage as a percentage of the USA population has risen from 39.1% during 1988–1994 to 45.3% during 1999–2002 (NCHS, 2006).

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Southeast Louisiana has been shaped by deltaic processes over several hundreds of years by the meandering of the Mississippi River. The majority of this region is near, at or below sea level. Due to the low elevation, much of the area is covered by freshwater wetlands. The Mississippi River, which receives treated wastewater from urban centers within the watershed, has the potential to carry significant amounts of contaminants, including PhACs into the coastal waters of Louisiana and the Gulf of Mexico. There is an opportunity in this region to utilize the natural wetlands to provide a final level of treatment (i.e. "polishing") to wastewater, prior to release into surface waters. These wetlands can be used to naturally remove nutrients, organic loads and contaminants, while other regions must use advanced treatment technologies to achieve the same concentration reductions. Natural systems, however, require significantly longer retention times versus conventional wastewater treatment systems due to slower treatment.

Constructed wetlands are effective at removing or reducing the concentrations of nutrients (Braskerud, 2002), pathogens (Karim et al., 2004) and microcontaminants, such as endocrine disruptors, PhACs and personal care products (Belmont et al., 2006; Matamoros et al., 2005a,b; Matamoros and Bayona, 2006; Waltman et al., 2006; White et al., 2006). Natural wetlands are known to mitigate the effects of both point and non-point source pollution (Johnston et al., 1990), but their capacity for removing PhACs has not been previously assessed. Evaluating the benefits and services provided by natural wetlands, and employing these systems, requires an understanding of the system processes, as well as the responses of the systems to point and non-point source pollution. For example, wetlands that are subject to pollution can become impaired as a result of inputs of wastewater, resulting in contamination of local wildlife (Barber et al., 2006; Pelley, 2006).

Two recent publications have identified PhACs and other "down the drain" chemicals in surface waters in southeastern Louisiana. As reported by Boyd et al. (2003) and Zhang et al. (2007), these compounds have been detected in the Mississippi River at New Orleans, in Lake Pontchartrain bordering New Orleans to the north, within the discharge from the Jefferson Parrish East WWTP and at the influent of the drinking water treatment plant. Of the 9 target analytes in the Boyd et al. (2003) study, two were detected (naproxen, triclosan) in WWTP effluent at $ng\,L^{-1}$. The Zhang et al. (2007) study found 10 of the 12 compounds of interest including; naproxen, ibuprofen, carbamazepine, clofibric acid, caffeine, triclosan, acetaminophen, bisphenol A, estrone, 17α-ethinylestradiol and the natural estrogen, 17β-estradiol. It is possible that a range of other PhACs were also present in these samples.

The goal of this study was to evaluate the reduction of a select group of PhACs from untreated municipal wastewater in a lagoon-constructed wetland treatment system discharged into a receiving forested wetland in southeastern Louisiana. The study objectives included: (1) determining concentrations of PhACs loaded to and within the wastewater treatment system, (2) estimating the loading of PhACs to the forested wetland, and to the final receiving waters of Lake Pontchartrain, and (3) comparing reduction rates for PhACs in this natural treatment system to removal rates for more conventional wastewater treatment plants.

2. Methods

2.1. Study area

Mandeville, LA, USA is located on the north shore of Lake Pontchartrain. The Mandeville WWTP is a nontraditional plant that treats the water in a constructed wetland, followed by a natural wetland. Untreated wastewater flows into three $61 \times 183 \times 3\,m$ aerated lagoons in series, (Fig. 1). Each basin has a retention time of nine days, for a total of 27 days of treatment. After retention in the aeration lagoons (basins), the water flows through a surface flow constructed wetland. Water is evenly distributed across

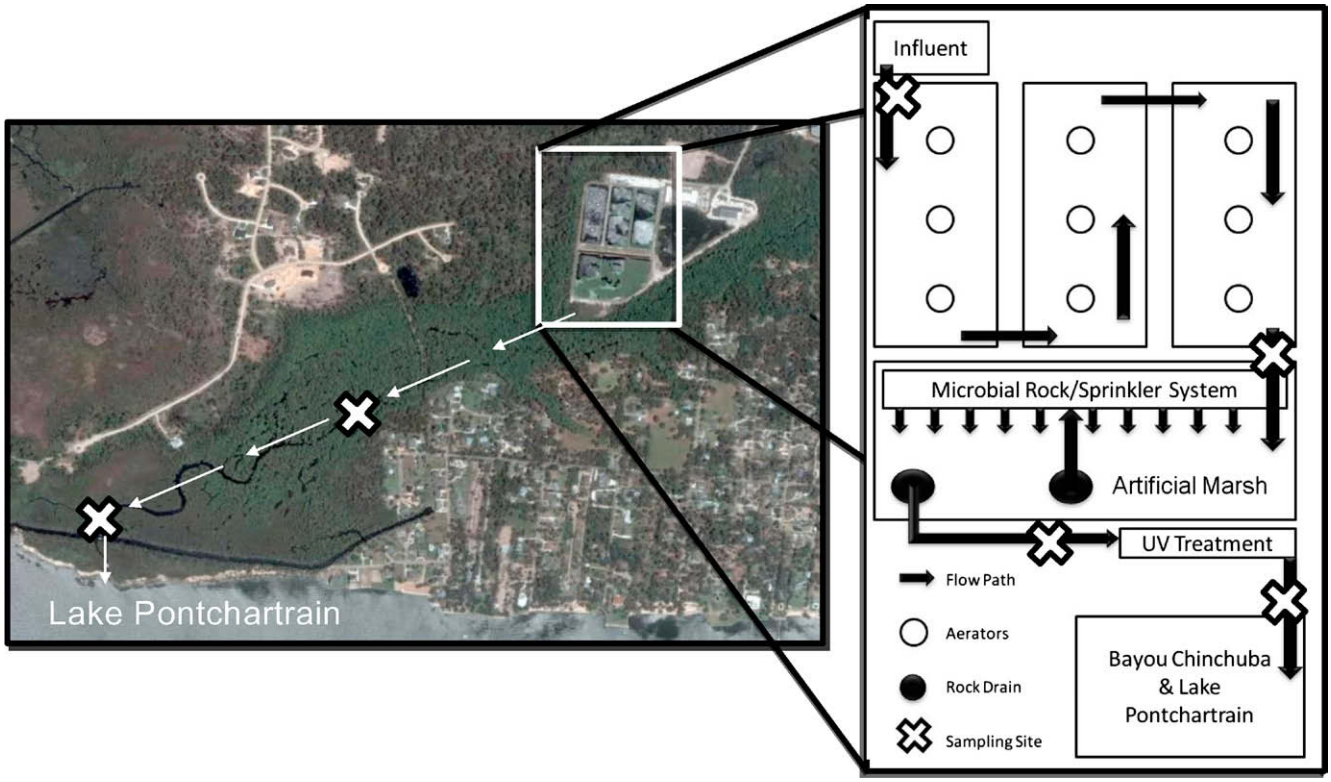

Fig. 1. Schematic of the Mandeville wastewater treatment plant and aerial image of the adjacent forested wetland (Bayou Chinchuba). Arrows depict the direction of surface water flow from the plant, through the forested wetland and into Lake Pontchartrain.

the width of the constructed wetland by percolation through a crushed gravel bed. The water flows through the herbaceous marsh containing several wetland plant species, including Hydrocottle spp. and Phragmites australis. After a 1 day retention time in the constructed wetland, water is collected in two rock basins where 60% of the water is recycled back to the crushed gravel bed and pumped through a series of sprinklers to further aerate the wastewater. The remaining 40% of water is pumped through an 8×1.2 m ultra-violet irradiation channel with 176 UV bulbs for disinfection. The water is then pumped out of a standpipe and into the adjacent forested wetland (i.e. Bayou Chinchuba) for polishing before discharge into Lake Pontchartrain (Fig. 1). The plant has historically discharged into Bayou Chinchuba (since 1989) at a rate of $\sim$7200 $m^3 d^{-1}$. The retention time in the WWTP constructed system is $\sim$30 days and Bayou Chinchuba flow varies by season due to precipitation and evapotranspiration rates.

Water entering the WWTP immediately mixes with the roughly 33 500 m^3 of water already in the first basin. Water is then continuously mixed by fountains and aeration hose along the bottom of the basins. Therefore, sewage entering the WWTP is quickly mixed and pharmaceutical concentrations are normalized over the 9 day retention time within each basin. Therefore variation in loading, whether daily or weekly, of pharmaceutical compounds within the WWTP is minimized in this system.

2.2. Field sampling

All sampling containers were pre-cleaned by washing with soap and water, rinsed with deionized water and then washed with acetone, followed by hexane. The pre-cleaned 4 L amber bottles were used to collect water samples at various locations in the treatment plant and receiving wetland. The sampling locations within the WWTP and constructed wetland (Fig. 1) were selected in order to assess the reduction capacity of the various treatment phases of the plant. Samples were collected May 18, 2007 and chilled to 4 °C during transport to Louisiana State University for extraction.

2.3. Analysis of PhACs

All water samples were stored at 4 °C and processed within 48 h of collection. Samples (250 mL) were filtered with hexane-washed Whatman GF/F filters (Fisher Scientific) to remove all particulate matter and extracted using HLB solid phase extraction (SPE) cartridges purchased from Waters (Millford, Mass). The methods have been previously described for solid phase extraction of acidic drugs (Miao et al., 2002), neutral drugs (Zhao and Metcalfe, 2008), sulfonamide antibiotics (Miao et al., 2004) and beta-blocker drugs (Topp et al., 2008). Briefly, the pH of the sample was adjusted according to the class of compound to be extracted, and stable-isotope labeled surrogates were spiked into the samples at nominal concentrations of 50 ng L^{-1} as internal standards. The four classes of PhACs were extracted by SPE using either HLC Oasis or MCX cartridges. Extraction efficiencies for all analytes have previously been shown to exceed 75%. All samples were extracted in triplicate.

Extracts were shipped overnite in chilled containers from Louisiana State University, Baton Rouge, Louisiana to Trent University, Ontario, Canada for analysis. The extracts were analyzed for the four classes of target compounds summarized in Table 1. Analysis was by liquid chromatography with tandem mass spectrometry (LC–MS/MS), conducted as described previously by Miao et al. (2002) for acidic drugs, Miao et al. (2004) for sulfonamide antibiotics, Zhao and Metcalfe (2008) for neutral drugs, and Topp et al. (2008) for beta blockers. The analytes were detected by monitoring in either negative or positive ion mode by multiple reaction monitoring (MRM). The acidic pharmaceuticals and beta blockers were analyzed with a Quattro LC triple quadrupole mass spectrometer (Micromass, Manchester, UK) fitted with an electrospray interface (ESI). The neutral pharmaceuticals and sulfonamide antibiotics were analyzed with a QTrap mass spectrometer (MDS Sciex, Toronto, ON) equipped with an atmospheric pressure chemical ionization (APCI) ion source.

Table 1
Target PhACs analyzed in samples of wastewater and water collected at the WWTP for Mandeville, LA, USA and the Bayou Chinchuba wetland, including data on the stable isotope surrogates used as internal standards and the limits of quantitation (LOQs)

Class	Compound	Surrogate	LOQ ($\mu g L^{-1}$)	Use
Neutrals	Cotinine	Cotinine-D3	0.002	Nicotine metabolite
	Caffeine	Caffeine-13C3	0.002	Stimulant
	Carbamazepine	Carbamazepine-D10	0.003	Anti-epileptic, psychiatric drug
	Fluoxetine	Fluoxetine-D5	0.010	Psychiatric drug (Prozac)
Beta blockers	Atenolol	Atenolol-D7	0.004	Hypertension
	Nadolol	–	0.002	Blood pressure, migraines
	Propranolol	Propranolol-d7	0.003	Hypertension
	Metoprolol	Metoprolol-d7	0.005	Hypertension
	Sotalol	Sotalol-d6	0.005	Hypertension, arrhythmias
Sulfonamides	Sulfapyridine	Sulfamethazine-$^{13}C6$	0.011	Antibiotic
	Sulfamethoxazole	Sulfamethoxazole-$^{13}C6$	0.007	Antibiotic
Acidics	Acetaminophen	Acetaminophen-D3	0.017	Analgesic/anti-inflammatory
	Naproxen	Naproxen-$^{13}C_1D3$	0.007	Analgesic/anti-inflammatory
	Ibuprofen	Ibuprofen$^{13}C3$	0.011	Analgesic/anti-inflammatory
	Gemfibrozil	Gemfibrozil-D6	0.008	Lipid regulator

A series of external standards were prepared with different concentrations of the target analytes and fixed concentrations of stable isotope surrogates (Table 1). The concentrations of the analytes were determined by comparing the response to each analyte in the samples to the responses to each analyte in the external standards over the range of a calibration curve. These response data were adjusted according to the relative ratios of the responses to the stable isotope surrogates in the sample and external standard. Note that this approach adjusts the quantitative data to compensate for efficiencies of extraction <100% and enhancement or inhibition of the signal due to the effects of the sample matrix. Blanks were prepared by spiking Milli-Q water with labeled surrogates, and extracting and analyzing them as described previously. The limits of quantitation (LOQs), which are listed in Table 1 were estimated as the second lowest point in the linear calibration curve prepared by analysis of the external standards, for which the signal to noise ratio for the analytes in the native samples was >10.

3. Results and discussion

Nearly all of the target compounds were detected in the untreated wastewater entering the treatment plant, with the exception of fluoxetine and propranolol (Table 2). Nadolol, sotalol, and sulfapyridine were the only compounds that were detected in the untreated wastewater but not at the outfall into Lake Pontchartrain, indicating near complete aqueous concentration reduction. The data indicate that the WWTP constructed wetland significantly decreased the concentrations of most target compounds, but not to below the LOQs. The Bayou Chinchuba forested

Table 2
Mean concentrations of target PhACs ($\mu g L^{-1}$; $n = 3$) at sampling locations at the WWTP for Mandeville, LA, USA and the Bayou Chinchuba wetland

Drug class	Compound	WWTP inflow ($\mu g L^{-1}$)	Cell 3 ($\mu g L^{-1}$)	Pre-UV ($\mu g L^{-1}$)	Outfall ($\mu g L^{-1}$)	WL mid ($\mu g L^{-1}$)	WL end ($\mu g L^{-1}$)
Neutrals	Cotinine	1.097 ± 0.060	0.030 ± 0.001	0.014 ± 0.001	0.019 ± 0.002	0.012 ± 0.004	0.015 ± 0.000
	Caffeine	25.567 ± 5.710	0.029 ± 0.006	0.033 ± 0.003	0.028 ± 0.006	0.065 ± 0.020	ND
	CBZ	0.057 ± 0.004	0.082 ± 0.006	0.087 ± 0.001	0.11 ± 0.007	0.028 ± 0.009	0.034 ± 0.001
	Fluoxetine	ND	ND	ND	ND	ND	ND
Acidics	Acetaminophen	39.300 ± 0.685	0.008 ± 0.001	0.015 ± 0.003	0.01 ± 0.001	ND	ND
	Naproxen	10.418 ± 1.530	0.064 ± 0.009	0.193 ± 0.033	0.090 ± 0.010	0.031 ± 0.003	0.020 ± 0.004
	Ibuprofen	9.922 ± 1.177	0.039 ± 0.003	0.080 ± 0.009	0.038 ± 0.002	0.017 ± 0.001	0.013 ± 0.000
	Gemfibrozil	1.652 ± 0.112	0.645 ± 0.031	1.819 ± 0.281	0.600 ± 0.036	0.081 ± 0.003	0.061 ± 0.004
Beta blockers	Atenolol	1.442 ± 0.102	0.284 ± 0.010	0.097 ± 0.009	0.099 ± 0.006	0.015 ± 0.001	0.020 ± 0.002
	Nadolol	0.030 ± 0.003	0.030 ± 0.001	0.007 ± 0.000	0.007 ± 0.001	ND	ND
	Propranolol	ND	ND	ND	ND	ND	ND
	Metoprolol	0.211 ± 0.032	0.025 ± 0.002	0.016 ± 0.001	0.017 ± 0.001	ND	ND
	Sotalol	0.174 ± 0.019	0.148 ± 0.009	0.117 ± 0.005	0.121 ± 0.007	0.031 ± 0.019	0.022 ± 0.003
Sulfonamides	Sulfapyridine	0.068 ± 0.024	0.018 ± 0.008	0.016 ± 0.002	0.016 ± 0.003	ND	ND
	SMX	4.090 ± 0.671	0.918 ± 0.463	0.309 ± 0.055	0.350 ± 0.024	0.328 ± 0.019	0.369 ± 0.124

Standard deviations represent error associated with extraction and analytical precision.
CBZ = carbamazepine; SMX = sulfamethoxazole; ND = not detected at concentrations above the LOQ.

Table 3
Removal rates of pharmaceutically active compounds for the wastewater treatment plant at Mandeville, LA, USA and the receiving forested (Bayou Chinchuba) wetland

Class	Compound	WWTP discharge (%)	B. Chinchuba discharge (%)	Total % removal
Neutrals	Cotinine	>99	0	>99
	Caffeine	>99	0	>99
	Carbamazepine	−53	105	51
	Fluoxetine	ND	ND	ND
Beta blockers	Atenolol	>99	6	>99
	Nadolol	77	23	>99
	Propranolol	ND	ND	ND
	Metoprolol	92	8	>99
	Sotalol	30	52	82
Sulfonamides	Sulfapyridine	76	24	>99
	Sulfamethoxazole	91	1	92
Acidics	Acetaminophen	100	0	>99
	Naproxen	99	1	>99
	Ibuprofen	>99	0	>99
	Gemfibrozil	64	31	95

ND = not detected at concentrations above the LOQ.

wetland was found to further reduce the concentrations of the target compounds.

The total reduction rates of the compounds within the entire treatment system were greater than 90% for all compounds, except carbamazepine at 51% and sotalol at 82% (Table 3). Several other PhACs (i.e. cotinine, caffeine, atenolol, nadolol, metoprolol, sulfapyridine, acetaminophen, naproxen, ibuprofen) were removed by 99% or greater by the entire system. A few compounds also showed reduction rates in the forested wetland between 20% and 31% (i.e. sulfapyridine, nadolol and gemfibrozil). The highest proportion of concentration reduction of the compounds from the aqueous phase occurred in the aeration basin of the WWTP (Fig. 2), which had a 27 day retention time.

3.1. Acidic compounds

Three (acetaminophen, naproxen, Ibuprofen) of the four acidic compound concentrations were reduced below the limits of quantitation within the aeration basins, with gemfibrozil being the exception. The removal of these compounds is similar to concentration reduction observed in previous studies for mechanized wastewater treatment (Ternes, 1998; Heberer et al., 2002; Bendz et al., 2005). The initial gemfibrozil concentration entering the treatment system was $1.65\,\mu g L^{-1}$ and a 61% reduction was observed within the aeration basin.

3.2. Sulfonamides

Sulfamethoxazole (78%) and sulfapyridine (74%) showed large reductions over initial concentrations of $4.090\,\mu g L^{-1}$ and $0.068\,\mu g L^{-1}$ within the aeration basins, respectively. The total concentration reduction by the WWTP and forested wetland for each compound was >99% and 92% for sulfamethoxazole and sulfapyridine, respectively. Both compound concentrations decreased throughout the Mandeville treatment plant, but remained constant after discharge into the forested wetland. These results suggest that the forested wetland provided no treatment and also no dilution. Previous studies have shown that concentrations of these compounds can increase during the wastewater treatment process (Bendz et al., 2005; Gobel et al., 2007). One study found that sulfapyridine and sulfamethoxazole doubled in concentration during certain aspects of wastewater treatment (Gobel et al., 2007). It was hypothesized this increase may be due to the presence of metabolites that were transformed into salfapyridine and sulfamethoxazole during biological treatment. These compounds underwent ~96% reductions in concentrations with activated sludge treatment which is more inline with the removal rates observed in this study.

3.3. Neutral compounds

The neutral compounds, cotinine and caffeine, were both nearly reduced below detection within the aeration basins, while carbamazepine was detected at every step in the treatment process. Fluoxetine was not detected in the treatment system (Table 1). There is an increase in carbamazepine concentration in the plant from $0.057\,\mu g L^{-1}$ at the inflow to a max of $0.087\,\mu g L^{-1}$ at the discharge into Bayou Chinchuba. The carbamazepine concentration increases after the initial measurement at the sewage inflow and remains relatively constant until the measurement of the forested wetland midpoint, where the concentration drops below the initial level. The concentration of carbamazepine continues to decrease

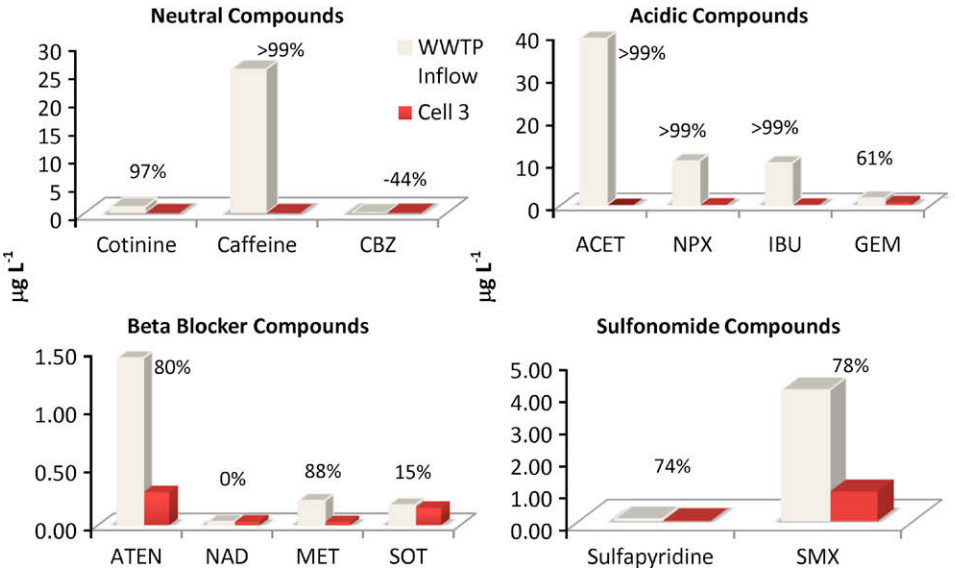

Fig. 2. The mean concentrations ($\mu g\,L^{-1}$) of the target pharmaceutically active compounds at the inflow into the aeration basins and at Cell 3 of the aeration basins of Mandeville wastewater treatment plant, where there is a hydraulic retention time of ~27 days.

and is only $0.028\,\mu g\,L^{-1}$ when discharged into Lake Pontchartrain, down from $0.058\,\mu g\,L^{-1}$ at the inflow. The results support previous research which suggests carbamazepine is a persistent chemical in the environment.

A possible explanation for this concentration increase within the plant is that there was a greater loading of the compound over a period of a couple weeks prior to sampling. Although, this is unlikely as this drug is administered daily in either one or two doses up to 1600 mg to treat chronic symptoms of seizures, ADD, schizophrenia, bipolar disorder and trigeminal neuralgia (USFDA, 2007). An alternate explanation is carbamazepine is retained and persists in the aeration basins. A similar trend was observed in the aeration basins during a November 2006 sampling of the Mandeville WWTP (Unpublished data). During this sampling, the carbamazepine concentration spiked in the aeration basins before dropping below the inflow concentration in the artificial marsh. Miao et al. (2005) suggests that it may be possible that UV irradiation has the ability to convert hydroxyl metabolites of carbamazepine to the parent compound or even modify the dissolved organic matrix in treated wastewater so that the analytes are released from the dissolved organic materials (Miao et al., 2005). A similar trend was observed with synthetic musks treated with UV irradiation (Yang and Metcalfe, 2006).

The USEPA's Estimation Program Interface (EPI) Suite estimates that carbamazepine removal in WWTP to be 2.96% of the total concentration, with 2.86% by sludge and 0.10% due to biodegradation (USEPA, 2007). Previous research has shown that the removal rates of carbamazepine in WWTPs is greater than the EPI Suite estimate and ranges from less than 10% (Ternes, 1998; Heberer et al., 2002) up to 30% (Bendz et al., 2005; Miao et al., 2005). The aqueous concentration reduction observed for the Mandeville WWTP and forested wetland is at 50%, indicating that this natural wastewater treatment system may be more effective at reducing concentrations of carbamazepine than conventional wastewater treatment. Clearly, more investigation is needed on the behavior of carbamazepine in treatment wetlands in order to increase the removal rate.

3.4. Beta blockers

Sotalol has the next lowest removal rate (behind carbamazepine). This drug compound was reduced by 82% compared to removal below the detection limits for the other beta blockers (atenolol, metoprolol). Previous studies have shown that beta blockers are relatively persistent through the wastewater treatment process, with 30–80% removal of concentrations less than 1 ppb in multiple WWTPs studied (Castiglioni et al., 2006; Maurer et al., 2007). The removal rates from this study demonstrate that the Mandeville treatment system may be more effective at reducing the concentration of this class of pharmaceuticals from the aqueous phase. Other studies in conventional WWTPs indicated that atenolol decreased between 30% and 53% and metoprolol from 10% to 83% (Castiglioni et al., 2006; Maurer et al., 2007). These values are also lower than what was observed for the Mandeville WWTP system.

3.5. Compound loading

Estimates of the annual loadings of the PhAC compounds were based on a daily wastewater flow of ~7600 m^3 and on the mean concentrations detected in the samples. The treatment system can potentially remove several hundred kg of PhACs annually, with caffeine (~70 kg) and acetaminophen (107 kg) being the largest contributors (Table 5). There is the potential for competition between compounds for binding sites, where one compound may decrease or prevent sorption due to the presence of another (Li and Werth, 2001; Bonin and Simpson, 2007). Competition could lead to an increase in downstream concentrations of the desorbed compound. However, this may not be significant in vegetated wetland systems that receive nutrient rich, secondarily treated wastewater which can increase vegetative growth. This growth coupled with lower decomposition rates due to low redox (White and Reddy, 2001) leads to increased accrual of organic matter which replenishes organic matter binding sites as new organic matter is deposited (Rybczyk et al., 2002).

None of the PhACs enter Lake Pontchartrain in kilogram amounts annually, and concentrations are likely further diluted in this large lake (1630 km^2). However, it has been shown that some of these compounds can have a detrimental effect on aquatic organisms exposed at ppb concentrations (Huggett et al., 2002; Flaherty and Dodson, 2005; Mimeault et al., 2005; Lienert et al., 2007).

3.6. Conventional versus natural wetlands

Previous studies have shown that conventional wastewater treatment plants reduce the concentrations of PhACs in the aqueous phase, but the efficacy of removal varies widely with the

Table 4
Percent removal and concentrations in treated wastewater reported in the literature for the target pharmaceutically active compounds in conventional wastewater treatment plants, compared to the removal rates of this study

Drug	% Reduction (this study)	% Reduction (Conventional)	Effluent ($\mu g L^{-1}$)	Study	Wastewater treatment method
Atenolol	99	30–53		Castiglioni et. al (2006)	N/I
		50–80	0.16	Bendz et al. (2005)	Clarification, activated sludge, P removal
Caffeine	>99	>99	0.19	Ternes et al. (2001)	Aeration tank, P removal, Clarification
		99	0.18	Heberer et al. (2002)	N/I
		94	0.22	Bendz et al. (2005)	Clarification, activated sludge, P removal
CBZ	51	7	2.10	Ternes (1998)	Clarification, activated sludge, P removal
		8	1.63	Heberer et al. (2002)	N/I
		30	1.18	Bendz et al. (2005)	Clarification, activated sludge, P removal
Gemfibrozil	91	69	0.40	Ternes (1998)	Clarification, activated sludge, P removal
		75	0.18	Bendz et al. (2005)	Clarification, activated sludge, P removal
Ibuprofen	99	90	0.37	Ternes (1998)	Clarification, activated sludge, P removal
		96	0.15	Bendz et al. (2005)	Clarification, activated sludge, P removal
Metoprolol	>99	30–65	0.19	Bendz et al. (2005)	Clarification, activated sludge, P removal
Naproxen	99	66	0.30	Ternes (1998)	Clarification, activated sludge, P removal
		93	0.25	Bendz et al. (2005)	Clarification, activated sludge, P removal
Sotalol	82	25	0.25	Maurer et al. (2007)	N/I
SMX	92	24	0.62	Ternes et al. (2007)	Clarification, activated sludge, N removal

CBZ = carbamazepine ; SMX = sulfamethoxazole; N/I = no info provided.

drug and the treatment technology (Table 4). However, the present study demonstrated that there was a high potential for reduction of PhACs in the constructed wetland within the Mandeville WWTP. A major reason for the high degree of removal is that the Mandeville system functions with a hydraulic retention time (HRT) of approximately 30 days, whereas conventional treatment plants have HRTs of 10–60 h, depending on the treatment technology. The extended treatment time allows for greater removal of microcontaminants, including PhACs, through processes of biodegradation, photolysis, etc. There was an additional concentration reduction between 0% and 50% in the forested wetland, although the mechanism (degradation, sorption, etc.) is unknown. Since several compounds did not decrease in concentration after discharge into the forested wetland, it is unlikely that dilution plays a significant role.

3.7. Seasonal removal

When comparing the sampling event for this study with a previous sampling of the Mandeville WWTP from 11/20/2006 (Unpublished Data) there appears to be seasonal variation (12–300%) with regards to inflow concentrations of several compounds. The greatest variation between seasons occurs with acidic (acetaminophen, naproxen, ibuprophen, gemfibrozil) and neutral (cotinine, caffeine, carbamazepine) compounds, while beta blockers and sulfonamides generally vary less than 50%. With the exception of metoprolol and sulfamethoxazole, all compounds exhibited higher concentrations during November, 2006 compared to May, 2007.

While there may be variation with the inflow concentrations for the Mandeville WWTP, the percent removal within the WWTP

Table 5
Loadings (kg/year) of the target pharmaceutically active compounds to points within the Mandeville, LA, USA wastewater treatment plant and the Bayou Chinchuba receiving wetland

Drug class	Compound	Loading at inflow to WWTP (kg/year)	Loading to Bayou Chinchuba (kg/year)	Loading to L. Pontchart-rain (kg/year)	WWTP reduction (kg/yr)	Bayou Chinchuba reduction (kg/yr)	Total reduction (kg/yr)
Neutral	Cotinine	2.99	0.04	0.03	2.95	0.00	2.95
	Caffeine	69.68	0.09	0.18	69.59	0.00	69.59
	CBZ	0.15	0.24	0.08	−0.09	0.16	0.08
	Fluoxetine	ND	ND	ND	ND	ND	ND
Acidic	Acetaminophen	107.11	0.03	0.00	107.08	0.00	107.11
	Naproxen	28.39	0.25	0.08	28.14	0.17	28.31
	Ibuprofen	27.04	0.11	0.05	26.94	0.06	27.00
	Gemfibrozil	4.50	1.66	0.22	2.85	1.44	4.28
Beta blockers	Atenolol	3.93	0.27	0.04	3.66	0.23	3.89
	Nadolol	0.08	0.02	0.00	0.06	0.02	0.08
	Propranolol	ND	ND	ND	ND	ND	ND
	Metoprolol	0.57	0.05	0.00	0.53	0.05	0.57
	Sotalol	0.47	0.34	0.09	0.14	0.25	0.39
Sulfonamides	Sulfapyridine	0.19	0.04	0.00	0.14	0.04	0.19
	SMX	11.15	0.97	0.91	10.18	0.06	10.24

Compound loading rates were calculated from the observed concentrations at various points in the treatment process, based on a mean flow rate of 7600 $m^3 d^{-1}$.
CBZ = carbamazepine; SMX = sulfamethoxazole; ND = not detected at concentrations above the limits of quantitation.

is very similar for each sampling. Despite the varying inflow concentrations, the November '06 and May '07 samplings had 6, and 8 compounds, respectively, that exhibited >90% removal, while both had 10 compounds with >75% removal. The percent concentration reduction difference between the two samplings was <18% for 10 of the 13 compounds detected, with gemfibrozil, carbamazepine and sotalol being the exceptions.

It is important to note that these data only represent the PhAC compounds in the aqueous phase, since all samples were filtered prior to analysis to remove particulate material. However, previous studies have shown that PhACs adsorbed to suspended particulate material represents a small fraction of the total loads (Miao and Metcalfe, 2007). This sampling event provided only a snapshot of the removal of PhAC compounds in the wastewater stream, and did not take into account temporal variations in PhAC inputs into the WWTP. As mentioned previously, we hypothesize that daily and weekly concentration variations are time-averaged due to basin retention times (~9 day each). Also, national prescription patterns (USFDA, 2007) show that for many of the compounds monitored (excluding the sulfonamide antibiotics, ibuprofen, naproxen, and acetaminophen), the remaining drugs are prescribed for long term usage (e.g. carbamazepine, beta blockers, gemfibrozil, fluoxetine) or otherwise show homogeneous levels of consumption (e.g. caffeine, cotinine). The greatest differences in incoming concentrations therefore, should be seasonal. Future work will focus on the temporal and seasonal variability of PhAC concentrations in wastewater and removal within the wetland system.

4. Conclusions

Results demonstrate that a wastewater treatment system consisting of earthen lagoons and a constructed wetland such as those used in the Mandeville WWTP show a greater reduction in compound concentration than previous investigations of conventional plants. Further polishing in a natural forested wetland produced removal rates for PhACs that averaged 96% for the entire system. There is variation with inflow concentration in the WWTP, but these concentrations are normalized on a daily to weekly basis by mixing within the aeration basins. Seasonal variability may be more pronounced, with greater concentrations entering the facility during colder months. However, despite differences in influent concentrations, removal rates for both November 06 and May 07 were similar. These removal rates are equal or greater than published removal rates in conventional wastewater treatment plants. In particular, carbamazepine and sotalol appear to be more persistent in conventional WWTPs than in the Mandeville wastewater treatment system. The higher removal rates may be due to a longer HRT in the constructed and natural treatment system. The entire system is capable of removing several kilograms per year of PhACs from wastewater, significantly reducing the annual loadings of these compounds to Lake Pontchartrain.

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