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Occurrence and removal of pharmaceutical and hormone contaminants in rural wastewater treatment lagoons

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HIGHLIGHTS

- Develop methods to analyze thirteen pharmaceuticals and eight steroid hormones in a variety of aqueous samples.
- Investigate the occurrence of pharmaceutical and hormone contaminants in rural wastewater treatment lagoons.
- Explore the removal efficiency of pharmaceutical and hormone contaminants by an aerated lagoon treatment system.
- Assess the water quality of watersheds which are receiving effluents from a rural lagoon treatment plant.

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ABSTRACT

Rural communities in the United States usually use a series of aerated lagoons to treat domestic wastewater. Effluents from these systems are typically discharged to receiving watersheds, which leads to a potential transfer of pharmaceuticals and personal care products (PPCPs) and steroid hormones from sanitary sewage to the environment. The primary objectives of this study are to identify and quantify PPCPs and steroid hormones in rural sewage treatment lagoons, to investigate the removal efficiency of these emerging contaminants in the treatment processes, and to monitor their occurrence in the surrounding watershed. In this study, a method has been developed to analyze thirteen PPCPs and eight steroid hormones in various water samples. Among all of the PPCPs considered, ten chemicals were detected in sewage influents, lagoon waters of different treatment stages, or effluents at concentrations in the ng/L to low μg/L range. Three hormones were observed in the influents at total concentrations as high as 164 ng/L, but no hormone residues were detected in the effluents. This indicates that the aerated lagoons may effectively remove hormone contaminants. With the exception of carbamazepine, removal rates for the other detected PPCPs were relatively high in the range of 88 to 100% in September with average air temperature equal to 20 °C. However, the removal efficiency of nine PPCPs in the rural wastewater treatment plant exhibited large temporal variability. The concentrations of PPCPs in the lagoon waters and effluents collected in November, with average air temperature equal to 4.4 °C, were 1–2 orders of magnitude higher than those samples collected in September. Occurrence of these PPCP contaminants in the surrounding watershed was also monitored. The discharge of effluents significantly elevated the PPCP concentrations in the receiving creek and increased their occurrence in the adjacent river.

1. Introduction

The widespread occurrence of pharmaceuticals and steroid hormones in the aquatic environment has been recognized as an emerging environmental issue (Heberer, 2002; Kolpin et al., 2002; Boyd et al., 2003; Snyder et al., 2003; Yu et al., 2011). Sewage treatment plants (STPs) and concentrated animal feeding operations (CAFOs) are identified to be major sources discharging pharmaceuticals and personal care products (PPCPs) and naturally occurring hormones to surrounding watersheds via wastewater effluent (Kolpin et al., 2002; Snyder et al., 2003; Benotti and Brownawell, 2007; Zheng et al., 2008). Additionally, septic tank systems have also been considered as a potential source introducing emerging contaminants into groundwater (Swartz et al., 2006; Carrara et al., 2008). Previous studies mainly focused on monitoring occurrence of PPCPs and steroid hormones in urban municipal STPs, CAFO lagoons, and septic tank systems and investigating their

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removal efficiency of contaminants (Heberer, 2002; Zuehlke et al., 2006; Kim et al., 2007; Hutchins et al., 2007; Carrara et al., 2008; Sui et al., 2011; Zheng et al., 2008, 2012). Some investigations showed that most hormone and some PPCP contaminants could be quickly broken down in conventional activated sludge processes (Zuehlke et al., 2006; Kim et al., 2007; Sui et al., 2011). Moreover, the use of advanced oxidation processes such as ozonolysis and photocatalysis as tertiary treatments in STPs could further improve the removal efficiency of these contaminants (Ternes et al., 2003). Unfortunately, not all PPCP contaminants could be eliminated completely in the municipal STPs. For example, some PPCPs such as clofibric acid and carbamazepine, up to the μg/L-level, have been detected in sewage effluents and adjacent surface water (Heberer, 2002; Kolpin et al., 2002).

Currently, traditional and modern municipal STPs have been widely used to treat urban wastewater in the world. Engineered lagoons are often used to treat domestic wastewater generated from rural communities in the United States and Europe (USEPA, 2011). Over 8000 sewage treatment lagoons are in place, accounting for more than 50% of the wastewater treatment facilities in the U.S. (USEPA, 2011). Compared to three-stage municipal STPs, using sewage treatment lagoons is a more feasible and economic wastewater removal approach for rural communities, which comprise approximately 19.3% of the population of the U.S. They usually contain at least one artificial aerated lagoon plus additional aerated and/or anaerobic lagoons in series, in parallel, or both (USEPA, 2002). For typical aerated lagoons, a variety of contaminants in wastewater can be removed through physical, chemical and biological processes with the help of oxygen and microorganisms. The removal efficiency varies with different lagoon systems and operation conditions. Although extensive work has been undertaken on monitoring PPCP and hormone contaminants in municipal STPs, the information concerning the occurrence and removal of emerging contaminants in the rural lagoon treatment systems is essentially blank.

The lagoon treatment plants are generally ineffective at nutrient removal compared to the STPs. Effluent from these systems is often directly discharged to a receiving stream, resulting in a significant nutrient load for these streams. One potential solution to reduce nutrient loading is to use the effluent for crop irrigation in nearby fields, which can provide nutrients and organic matter for plant growth. Also, this water reuse practice can offer an alternative water source to reduce the demand for high quality water. However, the effluent derived from the aerated lagoons also retains heavy metals, pathogens, and organic pollutants besides excess amounts of nutrients. To assess the potential risks of using the effluent for land application and understand the consequences of discharging organic pollutants to the natural environment, it is of the utmost importance to evaluate the occurrence of PPCPs and steroid hormones in the effluent from rural lagoon systems. Therefore, more research on rural wastewater treatment facilities is required to better understand removal efficiency of emerging organic contaminants in such lagoon treatment systems; removal mechanisms of the contaminants in aerated lagoons; and, if any, potential environmental risks arising from the use of the effluents for irrigation.

This study aims to: (i) develop robust analytical methods for thirteen PPCPs, five steroid estrogenic hormones and three estrogen sulfate conjugates, which were chosen because of their widespread use and high frequency of detection (Kolpin et al., 2002; Boyd et al., 2003; Swartz et al., 2006; Kim et al., 2007); (ii) detect the occurrence of targeted PPCPs and estrogenic hormones in a typical rural wastewater lagoon system and adjacent watersheds; (iii) investigate removal efficiency of detected emerging contaminants at various stages of the treatment; and (iv) compare the effect of seasonal variation on occurrence and removal of the contaminants. Data collected in this study will be used to evaluate the human and environmental health risks associated with using treated rural wastewater to irrigate cropland in a nearby field beginning in 2013.

2. Experiment

2.1. Chemicals

PPCP standards caffeine (CAF), carbamazepine (CBZ), diphenhydramine (DPA), erythromycin (ERY), fluoxetine (FLU), gemfibrozil (GEM), ibuprofen (IBU), naproxen (NAP), triclocarban (TCC), triclosan (TCS), trimethoprim (TMP), sulfamethazine (SMI), and sulfamethoxazole (SMO), internal standard florfenicol, and hormone standards 17α-estradiol-3-sulfate (αE2-3S), 17β-estradiol-3-sulfate (βE-3S), estrone-3-sulfate (E1-3S), estriol (E3), 17α-estradiol (αE2), 17β-estradiol (βE2), estrone (E1) and ethynylestradiol (EE2) were obtained from Restek (Bellefonte, PA, USA). Isotope standards including $^{13}C_3$-caffeine, D_{10}-carbamazepine, D_3-diphenhydramine, $^{13}C_2$-erythromycin, D_6-fluoxetine, D_6-gemfibrozil, $^{13}C_3$-ibuprofen, $^{13}C_4$-naproxen, $^{13}C_6$-triclocarban, $^{13}C_{12}$-triclosan, $^{13}C_3$-trimethoprim, $^{13}C_6$-sulfamethazine, $^{13}C_6$-sulfamethoxazole, and $^{13}C_6$-estrone were purchased from Cambridge Isotope (Andover, MA, USA). Solvents used in the study, including methanol, acetone, and acetonitrile, were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Deionized (DI) water (>17.6 MΩ-cm) was supplied by a Labconco Water Pro Plus system (Kansas City, MO, USA).

2.2. Sample collection

Samples were collected from a rural wastewater treatment plant in a small town of Illinois, USA. As shown in Fig. 1, this treatment system consists of a primary treatment with a bar screen, followed by two aerated lagoons in series (containing 1.4 and 1.0 million gallons of wastewater, respectively) and a sand tank for filtration. Samples were collected in both September and November 2011. Wastewater samples were sequentially collected from the influent, the 1st and 2nd aerated lagoons, and effluent of the treatment plant. The effluent is directly discharged to a creek, from which water samples were also collected at two sites: (i) about 30-meters upstream and (ii) two-kilometers downstream of the effluent outlet. The creek flows into the Mackinaw River; therefore, an additional water sample was taken from the Mackinaw River about 10 kilometers downstream of the creek entrance site in November. Water samples within the treatment plant were collected by an extended scoop and then stored in glass jars. Surface water samples from the creek were collected directly by submerging the glass jars. Water samples from the Mackinaw River were collected by a commercial water sampler (Forestry Suppliers, Jackson, MS, USDA) from a bridge above the river. All aqueous samples were collected in 2 and 4-L glass bottles, immediately transferred to the laboratory in an ice bath, acidified to pH of 2.0 by hydrochloric acid, and passed through glass fiber filters (GF/F, 2.0-μm Whatman) to remove duckweeds or algae within the same day. All water samples were extracted within three days. All glassware and GF/F filters used in this study were baked for 8 hours at 475 °C. Basic physicochemical parameters of collected samples are shown in the supporting information (Table S1).

2.3. Solid phase extraction of PPCPs

PPCPs in all collected water samples were extracted using solid phase extraction (SPE) by EPA Method 1694 with some modifications. In brief, the water samples (0.1 L for influent, 0.25 L for lagoon and effluent samples, and 1 L for surface water) were spiked with stable isotopic standards as surrogates (50 ng for each surrogate standard in 0.1 mL). Before loading the samples, the Oasis HLB cartridge (200 mg/6 mL, Waters, Milford, MA) was preconditioned with 10 mL methanol, 10 mL water, and 10 mL pH = 2.0 water in series by gravity. All water samples were passed through the SPE cartridge with the aid of a vacuum to control the flow rate at 3–5 mL/min. The cartridge was then washed with 10 mL water and dried under

Fig. 1. Schematic diagram of the rural wastewater treatment facility.

vacuum for about 30 minutes. The sample was eluted with 10 mL methanol and 6 mL acetone:methanol (1:1) by gravity. Combined sample extracts were evaporated to dryness under gentle nitrogen gas and reconstituted with 0.5 mL acetonitrile:water (1:1).

2.4. Solid phase extraction of steroid hormones and conjugates

Aqueous samples (0.25 L for influent, lagoon and effluent samples; 1 L for surface water) were spiked with 50 ng $^{13}C_6$-estrone isotope standard as a surrogate standard. A modified SPE method (Reddy et al., 2005) was used for the hormone extraction. Before loading the water samples, Oasis HLB cartridges were preconditioned with 10 mL methanol, 10 mL water, and 10 mL pH = 2.0 water in series by gravity. Similarly, water samples were passed through the SPE cartridge, using a vacuum to control the flow rate at 3–5 mL/min. After loading each water sample, the cartridge was washed with 5 mL methanol:water (5:95) and dried under vacuum for about 30 minutes. Fraction 1 for steroid hormones was eluted by gravity with 6 mL of ethyl acetate: methanol (9:1) followed by 5 mL of 5% methanol in water containing 2% acetic acid and 5 mL of 5% methanol in water containing 2% ammonium hydroxide. After drying for another 30 minutes, fraction 2 for hormone conjugates was eluted with 5 mL methanol containing 2% ammonium hydroxide by gravity. Fractions 1 and 2 were combined, evaporated to dryness under gentle nitrogen gas, and reconstituted with 1.0 mL acetonitrile:water (1:1).

2.5. Separation of PPCPs

Internal standard (100 ng florfenicol) was spiked into the sample extract and 30 μL of sample was injected for analysis. All PPCPs investigated in this work were separated on a Symmetry C_{18} column (3.5 μm particle size, 2.1 × 150 mm, Waters) by a high performance liquid chromatography (HPLC) system (2695 module, Waters). A gradient separation was achieved using two mobile phases: solvent A, water containing 0.1% ammonium acetate and 0.1% acetic acid; and solvent B, 1:1 methanol:acetonitrile. The gradient started with 90% solvent A and 10% solvent B and was maintained for 2 minutes. Then the gradient was ramped up to 5% solvent A and 95% solvent B linearly in 13 minutes and maintained for 8 minutes. The gradient was changed back to 90% solvent A and 10% solvent B after 0.5 minutes and re-equilibrated for 5.5 minutes.

2.6. Separation of steroid hormones and conjugates

Similarly, the sample extract was spiked with 100 ng of internal standard florfenicol. Separation of hormones and conjugates was performed on the same C_{18} column used for PPCPs. Two mobile phases were applied for separation: solvent C, water with 10 mM ammonium hydroxide; and solvent D, acetonitrile with 10 mM ammonium hydroxide. The gradient was started with 90% solvent C and 10% solvent D and maintained for 2 minutes. The gradient was then ramped up to 5% solvent C and 95% solvent D linearly in 13 minutes and maintained for 8 minutes. The gradient was changed back to 90% solvent C and 10% solvent D and re-equilibrated for 5.5 minutes.

2.7. Detection by mass spectrometer (MS)

A tandem triple quadrupole MS/MS equipped with an electrospray ionization (ESI) source (Quattro Macro QA1140, Waters) was used for detection in this study. For PPCP analysis, the MS/MS was operated in both positive and negative ESI modes simultaneously with the following optimized instrument conditions: desolvation gas flow rate at 650 L/min and capillary voltage of 3.0 kV for positive and 3.5 kV for negative mode. Multiple reactions monitoring (MRM) was applied for detection. Collision energies, cone voltages, and retention times for PPCPs are listed in Table S2. For steroid hormones and conjugates, negative ESI mode was applied with the same desolvation gas flow and capillary voltage. Optimized collision energies, cone voltages, and retention times for each compound are listed in Table S3.

3. Result and discussion

3.1. Method validation

The performance of the developed methods was evaluated by considering response linearity, recoveries, and limits of detection (LODs) of PPCPs and hormones in DI water, effluent, and influent samples. At least one standard spike and one solvent blank was analyzed every 10 injections to check the fluctuation of the instrument and possible internal contamination or sample carryover. Five point calibration curves (0.1–500 ng/mL) were produced for each PPCP and its isotope compound. For the hormones, calibration curves were estimated as response of each compound relative to the $^{13}C_6$-estrone surrogate. Good linearity was achieved for all the compounds and the squares of correlation coefficients (r^2) were all higher than 0.999.

Recovery was obtained by spiking 100 ng of each PPCP or hormone compound in 1 L DI water. The recoveries of the thirteen PPCPs and eight steroid hormones in DI water ranged from 71%–113% and 85%–116%, respectively (Table 1). The relative standard deviation (RSD) for most PPCPs and hormones was less than 5% (Table 1).

Limits of detection (LOD) for each compound in DI water, influent, and effluent were obtained by spiking isotope standards into DI water (1 L), influent (0.1 L) and effluent samples (0.25 L). Sub-nanogram-per-liter levels of PPCPs (0.010–0.70 ng/L) and steroid hormones and conjugates (0.59–5.5 ng/L) could be detected in DI water (Table 1). LODs for the influent (2.2–40 ng/L PPCPs; 3.3–75 ng/L hormones) and the effluent (0.47–6.0 ng/L PPCPs; 2.1–33 ng/L hormones) were greater than those for DI water due to matrix effects in both influent and effluent samples (Table 1). PPCPs and steroid hormones were not detected in trip blanks except for small amounts of GEM that were detected in both sample trips (Table 2) at concentrations which were less than 1% of what were found in the downstream surface water samples.

3.2. Occurrence and removal of PPCPs in the aerated lagoon system

The occurrence of all selected PPCPs and steroid hormones was investigated in the lagoon system in September and November 2011. PPCP concentrations are summarized in Table 2. Ten out of the thirteen PPCPs were detected in the influent in both September and November.

Table 1
Recoveries, precision, and method limit of detection (LOD) of the investigated compounds.

	Recovery (%)	Precision relative standard deviation (%RSD, n = 6)	LOD (ng/L)		
			Water	Effluent	Influent
Caffeine	92	10	0.70	6.0	6.3
Carbamazepine	109	6	0.20	0.93	2.2
Naproxen	107	2	0.50	2.1	11
Ibuprofen	71	5	0.30	0.94	4.9
Gemfibrozil	84	4	0.020	0.47	5.9
Triclosan	98	5	0.40	1.6	40
Trimethoprim	93	5	0.040	2.4	4.8
Triclocarban	98	6	0.010	0.29	4.2
Sulfamethoxazole	89	5	0.040	1.9	6.7
Diphenhydramine	113	1	0.090	0.66	2.9
Erythromycin	90	1	0.010	5.7	13
Fluoxetine	77	1	0.63	1.0	6.8
Sulfamethazine	94	8	0.020	2.7	11
Ethynylestradiol	116	3	1.3	3.4	11
Estrone	86	3	0.73	4.2	10
17-α-Estrodiol	91	2	2.6	33	75
17-β-Estrodiol	94	1	0.97	7.3	27
Estriol	85	1	5.5	26	43
Estone-3-sulfate	94	1	0.59	2.1	3.3
17-α-estrodiol-3-sulfate	89	1	1.8	14	15
17-β-estrodiol-3-sulfate	91	1	0.97	6.0	6.7

LOD defined as the amount of each compound that produced a signal-to-noise ratios of 3 in 1 L DI water, 0.25 L effluent, or 0.1 L influent samples concentrated to 0.5 mL for injections.

ERY, FLU and SMI were not detected in any samples collected in this study. Concentration levels of PPCPs found in the influent of this aerated lagoon system ranged from 0.048–58 μg/L, with caffeine detected at the highest level. Most PPCP levels decreased along the treatment path from influent to effluent, with the exception of CBZ in both months (Table 2).

Removal of PPCPs was calculated using R = (Ca − Cb) / Ci, where R is removal efficiency at each treatment stage, Ca is the concentration of PPCP detected in the influent or aerated lagoons, Cb is the concentration of PPCP detected in the next adjacent aerated lagoons or effluent, and Ci is the concentration of PPCP detected in the influent. This equation can be used to measure the removal efficiency of PPCPs at each treatment step relative to the original influent. Total removal is the difference in concentrations in the wastewater influent and effluent relative to the influent concentration. Removal of PPCPs within the lagoon system in the two sample trips are summarized in Fig. 2 and Table S4. The lagoon system was found to efficiently remove most PPCPs except CBZ in September, with overall removal ranging from 88.0% to 100%. This result indicates that the efficiency of PPCP contaminant removal in this rural aerated lagoon system is comparable to most urban STPs and pilot treatment plants (Benotti and Brownawell, 2007; Hijosa-Valsero et al., 2010; Reyes-Contreras et al., 2011).

Elimination of the PPCPs from rural wastewater mainly occurred in the first treatment lagoon with removal efficiencies ranging from 70.1% to 100%. However, CBZ was concentrated about three and two times respectively in September and November in the first treatment lagoon compared to their influents. In addition, the concentrations of GEM and TMP were higher in the treatment lagoons than in the raw influent in samples collected in November (Table 2). These three compounds have been reported to persist in STPs and natural environments (Benotti and Brownawell, 2009; Araujo et al., 2011; Reyes-Contreras et al., 2011). CBZ especially has been proposed as a sewage marker because of its resistance to degradation in municipal STPs (Clara et al., 2004; Kim et al., 2007; Reyes-Contreras et al., 2011; Kuroda et al., 2012). Extensive evaporation in the lagoons may be another factor that elevates concentrations of these compounds in the effluent. For example, the total wastewater inflow (4.6 million gallons) was more than two times higher than the total outflow (2.1 million gallons) according to the daily record of the treatment plant in September, 2011. The loss of water volume in this open lagoon system is primarily attributable to evaporation, resulting in the concentration of recalcitrant contaminants in the lagoon system.

3.3. Effect of seasonal variation on PPCP occurrence and removal in the lagoon system

Most PPCP concentrations measured in the rural lagoon-treated wastewater effluent collected in September are comparable to concentrations detected in urban municipal wastewater effluents (Boyd et al., 2003; Benotti and Brownawell, 2007; Kim et al., 2007; Sui et al., 2011). However, significantly higher concentrations ($p = 0.02$) were found in the aerated lagoon and effluent samples collected in November (1st lagoon: 158–13,900 ng/L; 2nd lagoon: 71–5480 ng/L; and effluent: 150–5030 ng/L) compared to the samples collected in September (1st lagoon: n.d. − 3430 ng/L; 2nd lagoon: n.d. − 1220 ng/L; and effluent: n.d. − 436 ng/L) for most PPCPs (Table 2). This result suggests that high concentrations of PPCPs could be discharged into the surrounding watersheds in the month of November.

As shown in Fig. 2, the removal efficiencies of PPCPs in each treatment step of the lagoon system in November were relatively lower than those in September. The monthly average temperatures in the small town of IL, are 20 °C in September and 4.4 °C in November (data from weather.com). This suggests that ambient temperature

Table 2
Concentrations of PPCPs in the trip blank, wastewater influent, aerated lagoon, effluent, and adjacent surface water samples collected in September and November, 2011.

Sample		CAF (ng/L)	CBZ (ng/L)	NAP (ng/L)	IBU (ng/L)	GEM (ng/L)	TCS (ng/L)	TCC (ng/L)	TMP (ng/L)	SMO (ng/L)	DPA (ng/L)	ERY	FLU	SMI
Trip blank	Sep.	n.d.	n.d.	n.d.	n.d.	1.14(61)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Nov.	n.d.	n.d.	n.d.	n.d.	2.20(7)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Influent	Sep.	51,300(1)	47.5(5)	19,400(1)	18,600(4)	1140(2)	5440(2)	1120(2)	1170(1)	3800(3)	1800(1)	n.d.	n.d.	n.d.
	Nov.	57,700(5)	67.3(6)	38,800(4)	26,200(6)	893(1)	4650(3)	829(5)	223(8)	928(5)	1570(3)	n.d.	n.d.	n.d.
Lagoon1	Sep.	n.d.	198(1)	608(1)	1840(3)	3430(3)	107(10)	278(3)	148(1)	207(1)	283(5)	n.d.	n.d.	n.d.
	Nov.	5310(2)	187(4)	6850(0.2)	13,900(3)	1500(2)	592(2)	345(2)	854(1)	158(0.3)	674(2)	n.d.	n.d.	n.d.
Lagoon2	Sep.	n.d.	181(1)	143(2)	184(6)	1220(1)	31.0(9)	148(2)	82.6(2)	123(2)	209(2)	n.d.	n.d.	n.d.
	Nov.	615(11)	159(1)	1030(4)	5480(0.3)	1730(1)	216(9)	218(2)	602(1)	71.0(4)	522(1)	n.d.	n.d.	n.d.
Effluent	Sep.	n.d.	220(19)	62.0(5)	146(12)	436(1)	19.5(6)	135(2)	30.0(33)	43.2(5)	38.5(1)	n.d.	n.d.	n.d.
	Nov.	486(9)	150(1)	912(7)	5030(2)	1630(4)	218(13)	243(2)	586(4)	173(23)	501(1)	n.d.	n.d.	n.d.
Upstream	Sep.	n.d.	0.59(10)	n.d.	1.77(28)	1.87(23)	2.27(8)	2.60(50)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Nov.	n.d.	n.d.	1.85(41)	4.65(9)	0.87(12)	8.72(18)	5.74(15)	n.d.	n.d.	1.62(15)	n.d.	n.d.	n.d.
Downstream	Sep.	n.d.	104(2)	18.3(4)	43.6(7)	142(9)	16.1(22)	14.6(1)	n.d.	56.8(4)	n.d.	n.d.	n.d.	n.d.
	Nov.	n.d.	141(1)	179(7)	1210(0.1)	1280(0.3)	54.8(8)	19.8(1)	8.88(7)	43.5(6)	2.65(5)	n.d.	n.d.	n.d.
Mackinaw River	Sep.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Nov.	9.1(9)	13.7(1)	5.65(13)	4.75(22)	2.53(4)	3.08(51)	5.06(0.4)	1.72(2)	42.2(4)	1.74(3)	n.d.	n.d.	n.d.

Values in parentheses are relative standard deviation. n.d. = not detected. n.a. = not available.

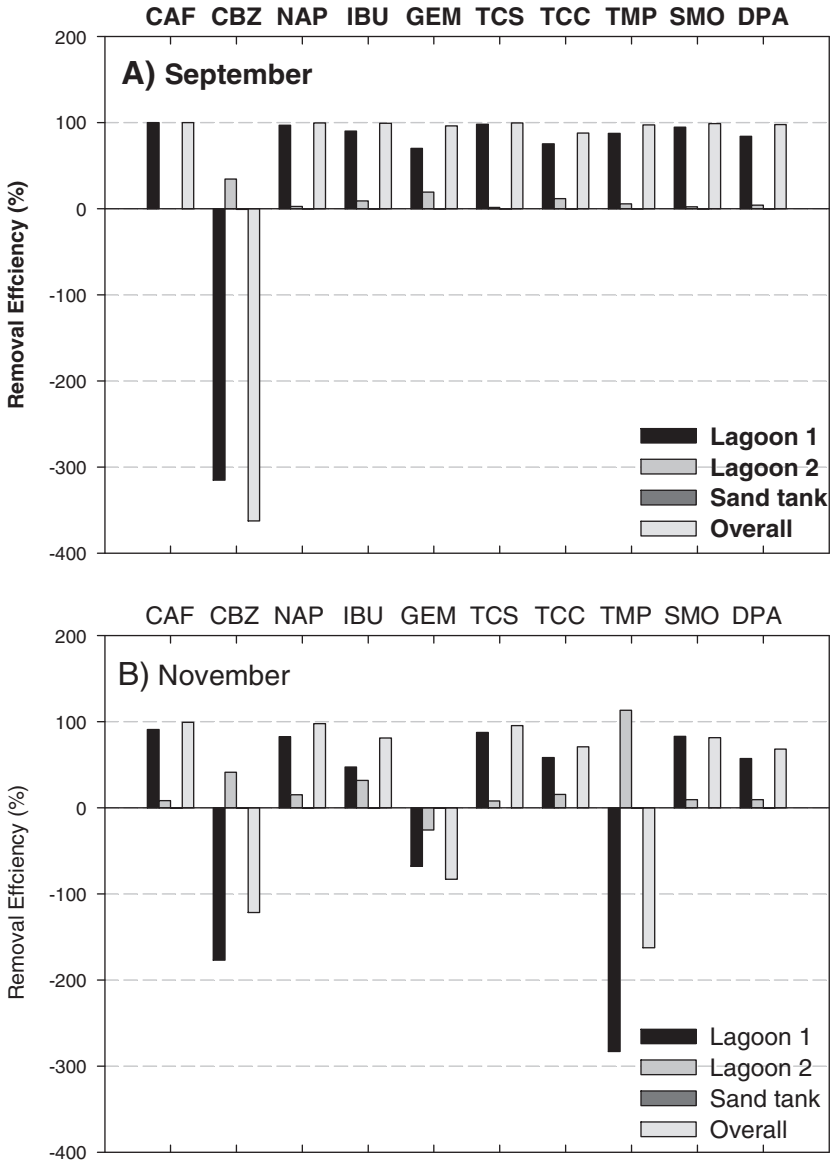

Fig. 2. Removal efficiencies (%) of each detected PPCP in the rural wastewater treatment system: (A) September; and (B) November.

could play an important role for removal efficiency of PPCP contaminants in these open lagoon treatment systems. Previous studies of municipal STPs evaluated the effect of seasonal variations on PPCP occurrence and removal in different treatment processes (Loraine and Pettigrove, 2006; Sui et al., 2011). It has been reported that treatment of PPCPs by activated sludge or membrane bioreactors was a temperature dependent process (Zuehlke et al., 2006; Sui et al., 2011).

There are numerous mechanisms including sorption, photodegradation, hydrolysis, and biodegradation to eliminate PPCPs in the lagoon treatment system. In general, biologically mediated degradation is a major process for PPCP removal in the aerated lagoons. Biodegradation rates of organic contaminants are highly temperature-dependent because microorganisms used in these processes have optimal activity at physiological temperature. For example, Li et al. (2011) reported that biodegradation rates of an antibiotic in CAFO wastewater increased with increasing temperature up to 37 °C, which is the most suitable temperature for microorganisms. Similarly, the cold weather could inhibit the activity of microorganisms in the aerated lagoon system and thereby reduce the removal efficiency of PPCPs in November.

3.4. PPCP occurrence in the surrounding watershed

As shown in Fig. 3, PPCPs in the creek upstream water ranged from below detection limits to levels of several ng/L, and elevated levels of PPCPs were found in the downstream sample due to the treated wastewater effluent input. Concentrations of PPCPs in the sample collected in the receiving creek downstream of the rural sewage treatment lagoon in September ranged from below detection to 142 ng/L, which is within the range reported by previous studies of surface water that received sewage effluent (Kolpin et al., 2002). In November, concentrations of NAP (179 ng/L), IBU (1210 ng/L) and GEM (1280 ng/L) in the downstream surface water exceeded the maximum values of a national investigation by Kolpin et al. (2002). The outflow of effluent from this lagoon treatment plant is about 50,000–80,000 gallons per day, which usually dominates the stream flow, especially in the dry seasons. Without sufficient dilution, the direct discharge of the effluent significantly increased the PPCP concentration in the receiving creek.

Although dilution, degradation, and sorption largely decreased the PPCP concentrations in the Mackinaw River compared to the

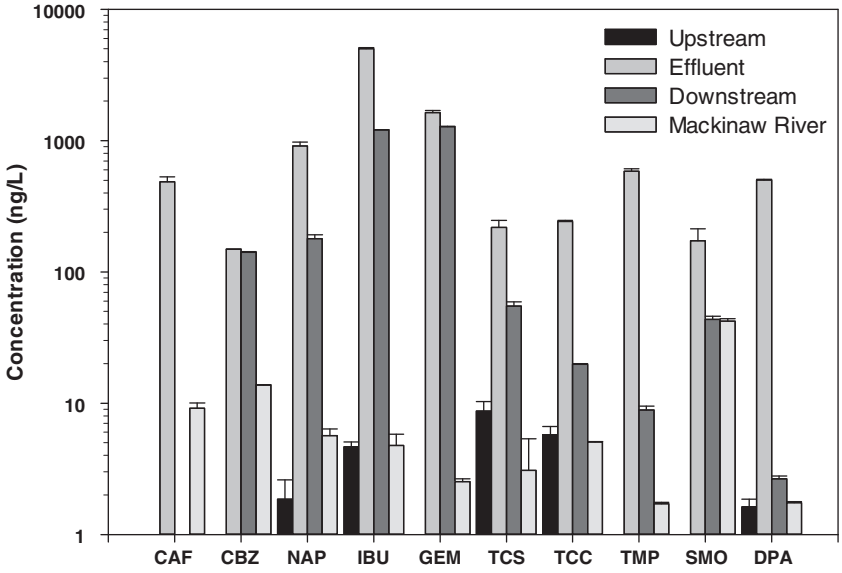

Fig. 3. Measured concentrations of the PPCPs in the creek upstream, effluent, creek downstream, and Mackinaw River water samples collected in November.

receiving creek, the occurrence of these contaminants was still observed, ranging from 1.7 to 42 ng/L in November (Fig. 3). This study indicates that the discharge of effluents from rural wastewater treatment lagoons may increase the occurrence of PPCPs and elevate their concentrations in surrounding watersheds, thereby potentially impacting the rural aquatic environment.

3.5. Occurrence of steroid hormones in the lagoons and the surrounding watershed

The influent sample collected in September was the only sample in which hormones E1 (16.9 ng/L), E3 (126 ng/L) and E1-3S (21.2 ng/L) were detected (Table S5). No steroid hormone residues were detected throughout the aerated lagoons and effluents, suggesting that the aerated lagoon system may effectively remove hormone contaminants. This is consistent with previous studies that showed that aeration is a very effective approach at eliminating hormone contaminants due to rapid biodegradation of these chemicals under aerobic conditions (Gadd et al., 2010; Yang et al., 2011). Reddy et al. (2005) detected E1-3S (34 ng/L), E2-3S (3.2 ng/L), E1 (24 ng/L) and E2 (7.6 ng/L) in municipal wastewater influent, and smaller amounts of E1-3S (0.3 ng/L), E1 (0.7 ng/L) and E2 (0.2 ng/L) in effluent. Other studies have reported rare detections and low concentrations of EE2, 17b-E2, E1-3S and E2-3S in municipal wastewater effluent (Ternes et al., 1999; Ferguson et al., 2001; Kolpin et al., 2002; Kim et al., 2007).

By contrast, wastewater from concentrated animal feeding facilities is more likely to display much higher levels of steroid hormones and their conjugates (Hutchins et al., 2007; Zheng et al., 2008, 2012). In this study, no detectable hormone residues were found in all collected upstream, downstream, and river samples (Table S5). This implies that steroid hormones derived from the sewage wastewater lagoons or livestock farms around this rural area have a negligible contribution to the environment.

4. Conclusion

This study on the removal of PPCPs and steroid hormones by a rural wastewater treatment facility demonstrated that concentrations of most of the selected compounds can be effectively reduced by this lagoon treatment system. There were no detectable steroid hormones in the aerated lagoons and effluents, suggesting this lagoon treatment may effectively remove hormone contaminants. Except for CBZ, the removal efficiencies of other detected PPCPs by the lagoon system in September were relatively high, with overall removal ranging from 88.0 to 100%. Also, the removal of PPCPs in the aerated lagoon system showed seasonal performance variation due to the effect of ambient temperature. This study indicates that the effluent discharge from the lagoon system may increase the occurrence of PPCPs and elevate their concentrations in surrounding watersheds. In addition, this research provides background levels of PPCPs and steroid hormones in effluent from rural lagoon treatment systems, which is very useful to evaluate potential risk from the use of effluent for crop irrigation. Further research is needed to investigate the fate and transport of PPCPs and hormones in the environment, and explore whether these emerging contaminants can transfer to crop plants that are irrigated with treated wastewater effluents and thereby impact public health.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.12.035.

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