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ILLINOIS SUSTAINABLE
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LIST OF ABBREVIATIONS

Al	aluminum
ASTM	American Society for Testing Materials
Ca	calcium
$CaCl_2$	calcium chloride
CEC	Contaminant of Emerging Concern
Fe	iron
IEPA	Illinois Environmental Protection Agency
K_d	dissociation constant
K_{OC}	soil organic carbon water-partitioning coefficient
P	phosphorus
PPCP	Pharmaceutical and Personal Care Product
USEPA	United States Environmental Protection Agency

Abstract

The potential human and environmental health risks posed by pharmaceuticals and personal care products (PPCPs) have been identified as a research priority at both the federal and state level. It has been well documented that municipal wastewater treatment plants with surface discharge fail to remove many of these emerging contaminants; however, little research has been conducted to determine the capability of lagoon treatment systems to remove PPCPs or of organic-matter-rich clay loam soils to filter PPCPs and reduce surface water pollution. The objective of this study was to determine the fate and transport of selected pharmaceuticals in lagoon-treated wastewater effluent applied as cropland irrigation in Illinois. In this study, we were able to determine the presence of six of the seven priority PPCPs in lagoon-treated wastewater effluent; verify the absence of studied PPCPs in soil and well water prior to treatment; determine characteristics of cropland soil that may impact PPCP transport when wastewater irrigation begins; and conduct sorption isotherm studies to understand the sorption and desorption capabilities of field soils in Lexington, Illinois.

1. Introduction

The potential human and environmental health risks posed by pharmaceuticals and personal care products (PPCPs) are well recognized and are a research priority at both the federal (USEPA, 2010; 2008) and state (Miller and Holm, 2009) level. Ranging from prescription and veterinary drugs to antimicrobials and cosmetic additives, many of these compounds have been found to survive common municipal wastewater treatment systems, posing a risk to aquatic ecosystems and downstream drinking water sources (IEPA, 2008). However, little research is available to determine the fate and environmental health implications of lagoon-treated municipal wastewater effluent applied to farm land. Rural communities often use a series of engineered lagoons to treat sanitary sewage (USEPA, 2002). Effluent from these systems is typically discharged to a receiving stream and can represent a significant nutrient load for these streams (Middlebrooks et al., 1999). One potential solution to this problem is to use the effluent for crop irrigation in nearby fields. The additional water, nutrients, and organic material could enhance soil fertility and crop production while potentially reducing these components in the effluent before it enters receiving streams. Provided that wastewater irrigation does not contribute to contamination of soil, groundwater, or crops, this method is a discharge option for rural communities that could benefit both farmers and the environment.

Given an aging population and medical coverage expansions allowed in the Affordable Care Act, prescription drug use is expected to increase sharply over the coming decades (CMS, 2012). Introduction of these PPCPs into wastewater is generally through excretion and minimally through improper disposal of unused medication. Current municipal wastewater treatment systems are not capable of removing most of these contaminants, and they are discharged directly to surface waters with the treated effluent (Daughton, 2001). The failure of pharmaceutical removal in these natural aquatic environments is evident. A 2002 survey of nearly 140 US streams found that 80% were contaminated with PPCPs (Buxton and Kolpin, 2002). A 2008 assessment of a number of Illinois municipal drinking water supplies that relied on surface water as a source were found to contain 16 PPCPs in the treated drinking water samples (IEPA, 2008). The USEPA has listed PPCPs as contaminants of emerging concern (CEC) (USEPA, 2008).

Current field studies of wastewater use for irrigation have been undertaken mainly in arid to semiarid regions where recycled water is an important source for crops and landscapes. These field soils typically have a higher fraction of sand with lower amounts of clay, silt and organic matter. However, lab studies have shown that soils with higher organic matter and clay composition tend to exhibit greater sorption characteristics for pharmaceutical compounds (Chefetz et al., 2008).

Lexington, a small community in central Illinois, presented a unique opportunity to study PPCP interaction with Loess soils. In 2000, the Illinois Environmental Protection Agency (IEPA) cited the city of Lexington for sewage pollution of nearby surface waters. Up to this time, Lexington homes were connected to individual onsite wastewater treatment systems — some of these systems were merely connections of household plumbing to field tiles. Inappropriate design and maintenance of these systems led to pollution of Turkey Creek and the Mackinaw River. In 2011, a new collection system connected all households to a three-stage lagoon system for wastewater treatment. Since the city is not approved to discharge the effluent to the nearby impaired surface waters, pumps located at the facility transport the effluent water to nearby agriculture fields for center pivot irrigation (Doran, 2013). Irrigation began in early fall of 2013.

Understanding the occurrence of PPCPs in the effluent as well as the fate of PPCPs in the soils will be critical in making informed decisions about irrigation as a means of nutrient control for rural community wastewater treatment systems.

ISU is engaged in a project with the City of Lexington, Illinois, utilizing funding from the U.S. Department of Energy (Project DE-FG36-08GO88039, $967,750) to study the effects of irrigating two 160-acre fields of crops (40 acres of switchgrass, 280 acres in corn) with effluent from the municipal wastewater treatment lagoons.

In this ISTC-funded study, the objectives were to:

- Determine the presence and concentration of seven priority PPCPs in comparable communities' wastewater effluent.
- Determine background concentration of the priority PPCPs in cropland soil and well water at the site prior to irrigation.
- Determine characteristics of cropland soil that may influence the fate and transport of selected PPCPs when wastewater is to be applied.
- Identify sorption properties of cropland soils for selected PPCPs.

2. Methods

2.1. PPCP presence in wastewater effluent

The seven PPCPs listed in Table 1 were identified for analysis in the wastewater effluents. Literature suggests all of the proposed PPCPs are common in municipal wastewater and are likely to be present in effluent from treatment lagoons (Beusse and Recherche, 2004; Beck et al., 2008; Boyd et al., 2005; desMes et al., 2005; Foster and Thomas, 2005; Pederson et al., 2005).

Lexington treatment lagoons had not yet filled with wastewater, but determination of PPCP presence was necessary for determining background sample measurements, so wastewater was sampled from established lagoons to determine likely presence in Lexington wastewater effluents, once those lagoons are established. The nearby communities of Mackinaw and Goodfield had established sewer systems with lagoon treatment and were used for the testing. Table 2 illustrates similarities of the communities in population, age, gender, and income.

Table 1. Pharmaceuticals and personal care products sampled for in wastewater and background soil and groundwater samples.

PPCP	K_{OC*}
Caffeine	22
Carbamazepine	510
17 –α-Ethinyl estradiol	2,884
Gemfibrocil	430
Ibuprofen	3,400
Naproxen	330
Triclosan	9,200

*as reported by toxnet.nlm.nih.gov

Table 2. Comparison of Lexington with Mackinaw and Goodfield on Key Demographic and Economic Characteristics.

	Lexington	Mackinaw	Goodfield
Population	1,968	1,642	994
Female	52.9%	51.7%	51.1%
Median Age (yrs)	40.0	39.1	39.4
Under 18 yrs	14.3%	13.5%	17.7%
65 yrs and older	16.1%	12.7%	13.7%
Median household income ($/yr)	$58,382	$57,352	$71,029

Pharmaceutical and personal care product (PPCP) standards for caffeine, carbamazepine, gemfibrozil, ibuprofen, naproxen, triclosan, and 17-α-ethynylestradiol were obtained from Restek (Bellefonte, PA). Isotope standards including 13C3-Caffeine, D10-Carbamazepine, D6-Gemfibrozil, 13C3-Ibuprofen, 13C4-Naproxen, 13C12-Triclosan, and 13C6-estrone were purchased from Cambridge Isotope (Andover, MA). Solvents used in the study, including methanol, acetone, and acetonitrile, were purchased from Fisher Scientific (Fair Lawn, NJ). Deionized water (>17.6 MΩ-cm) was supplied by a Labconco Water Pro Plus system (Kansas City, MO).

Wastewater influent and effluent samples at the Mackinaw and Goodfield lagoons were collected in September and October 2012 for PPCPs analysis. All samples were collected in 2L glass bottles, prepared in accordance with USEPA Method 1694 (USEPA, 2007), immediately placed in an ice bath and transferred to the laboratory where it was acidified to pH of 2.0 by addition of hydrochloride solution. (Refer to Appendix A for wastewater sampling photos). All water samples were filtered using baked glass fiber filters (GF/F, 0.7-µm Whatman) and stored at 4˚C prior to analysis. Analysis followed EPA Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment and Biosolids by HPLC/MS/MS (USEPA, 2007).

2*.2. PPCPs in cropland soil and well water*

Soil sample collection was accomplished by dividing the cropland into four areas. In each area, forty cores were collected in a zigzagging pattern. Samples from the same area were combined, placed in glass jars prepared in accordance with EPA Method 1694 (USEPA, 2007), covered to prevent photo-degradation , and delivered immediately for analysis. Refer to Appendix B for soil collection photos and field sampling areas. Soils were analyzed following EPA Method 1694 (USEPA, 2007).

Well water samples were collected in glass jars prepared in accordance with EPA Method 1694 from three monitoring wells located within the area to be irrigated. One sample was collected from each well, and a fourth sample was collected as a combination of water from all three wells (although the third well ran dry and comprised about 1/5 of the mixed sample). Samples were placed in an ice bath, covered to prevent photo degradation, and delivered immediately for analysis. Refer to Appendix C for well sample locations. Water was analyzed following EPA Method 1694.

2.3. Cropland soil characterization

For the purposes of this study, distinct areas of the fields were defined by vegetation and slope/elevation. Vegetation would be expected to affect organic soil content (switch grass as opposed to corn), and elevation would be expected to affect particle size distribution. According to vegetative cover and elevation, the area was divided into three sections for sampling; refer to Appendix D for soil sampling divisions. In each of the three divided areas, two sample sites were chosen, and four samples were collected at each sample site. Surface vegetation was removed, and then the top four inches of soil were collected and placed into paper bags. Bags were labeled with the site location and placed into a refrigerator and stored at 4°C to reduce microbial degradation. Soils were combined according to division, passed through a 2 mm sieve to remove remaining vegetation and stones, then ground and oven-dried. Soil samples were analyzed for pH, extractable cations, particle size distribution (% sand, silt, and clay), and organic carbon content. The pH of the soil samples was determined using a 1:1 ratio of oven-dried soil to diluted $CaCl_2$ solution (Thomas and Hargrove, 1984). Extractable iron, aluminum, calcium, and phosphorus of all soil samples was analyzed using the Mehlich 3 extraction procedure that contains 0.2 *M* acetic acid, 0.25 *M* ammonium nitrate, 0.015 *M* ammonium fluoride, 0.013 *M* nitric acid and 0.001 *M* ethylenediaminetetraacetic acid with an extraction ratio of 1:10 (Mehlich, 1984). The Mehlich 3 extractant was gravity-filtered using 2.5 µm Whatman 42 filter paper and analyzed using inductive coupled plasma-optical emission spectrometry. The hydrometer method was employed to determine soil particle size distribution (Day, 1965) and loss on ignition procedure was used to determine the soil organic matter and organic carbon content (Schumacher, 2002).

2.4. Selected PPCP sorption to Lexington cropland soils

The purpose of this task was to help "calibrate" Lexington cropland soils against standard soils used in K_{OC} studies reported in the literature and enable prediction of the behavior of PPCPs in the field. Two of the initial seven PPCPs were evaluated based on their occurrence in wastewater samples and K_{OC} value range (ibuprofen has a high K_{OC} and naproxen a low K_{OC}). Analytical grade ibuprofen and naproxen were purchased from Sygma Aldrich. All glassware was treated according to EPA Method 1694 and glass stoppers or PTFE caps were used when handling solutions.

Equal portions of soils collected for the cropland soil characterization were thoroughly mixed. Pharmaceutical solutions for the sorption study were prepared at concentrations that increased incrementally from 0-10 mg /L with three replicates of each concentration. Methanol was used to keep the solvent isolated in solution (Chefetz et al., 2008), and 0.01*M* $CaCl_2$ was used to simulate the ionic strength. Soil and solution were added at a 1:10 soil to solution ratio to glass centrifuge tubes and immediately capped. Samples were placed on a shaking table, covered to prevent photo-degradation, and shaken at room temperature for 48 hours at 200 rpm. Immediately after shaking, the samples were centrifuged for 10 minutes at 3000g to separate the liquid and solid phases (Lee, et al., 2003). The liquid phase of each sample and the blanks were filtered and refrigerated until the analysis of the selected compounds was performed; the solid phase was kept in the tubes for the desorption study. Data from this experiment along with mass balance calculations, the distribution coefficient (Kd), normalized distribution coefficient with respect to soil organic carbon (K_{OC}) and Freundlich equation parameters were used to elucidate the affinity of the selected compounds for the soils surface (Drillia et al., 2005).

To determine the potential of the selected compounds to desorb from the soil surface, the soil to solution ratio of 1:10 was restored by adding the background matrix solution (0.01M $CaCl_2$) to the centrifuge tubes from the sorption study containing only the solid phase. Samples were then equilibrated by shaking, centrifuged, filtered, and refrigerated in the same manner as for the sorption procedures. Analysis of ibuprofen and naproxen followed modified EPA Method 1694 using LC-UV detector, due to the high spiked concentration of these two compounds.

3. Results

3.1. PPCP presence in wastewater effluent

As indicated in Table 3 and Table 4, six of the seven priority PPCPs tested were present in both Mackinaw and Goodfield municipal lagoons at each sampling event.

Table 3. Concentrations of pharmaceuticals in wastewater sampled in September 2012.

PPCPs	**Goodfield (ng/L)**		**Mackinaw (ng/L)**		**Trip blank (ng/L)**
	Influent	**Effluent**	**Influent**	**Effluent**	
Caffeine	5.13 ± 0.06 x 10^5	n.d.	9.67 ± 0.45 x 10^4	7.34 ± 2.46 x 10^1	n.d.
Carbamazepine	4.75 ± 0.23 x 10^1	2.20 ± 0.41 x 10^2	3.56 ± 0.14 x 10^2	4.89 ± 0.19 x 10^2	n.d.
Naproxen	1.94 ± 0.01 x 10^4	6.19 ± 0.34 x 10^1	3.55 ± 0.10 x 10^3	1.32 ± 0.92 x 10^2	n.d.
Ibuprofen	1.86 ± 0.07 x 10^4	1.47 ± 0.17 x 10^2	1.18 ± 0.01 x 10^4	6.25 ± 0.93 x 10^1	n.d.
Gemfibrozil	1.15 ± 0.02 x 10^4	4.36 ± 0.06 x 10^2	1.09 ± 0.03 x 10^3	3.80 ± 0.08 x 10^2	1.10 ± 0.70
Triclosan	5.44 ± 0.09 x 10^3	1.95 ± 0.11 x 10^1	1.29 ± 0.02 x 10^3	7.30 ± 0.80	n.d.
Ethinylestradiol	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable

Table 4. Concentrations of pharmaceuticals in wastewater sampled in October 2012.

PPCPs	**Goodfield (ng/L)**		**Mackinaw (ng/L)**		**Trip blank (ng/L)**
	Influent	**Effluent**	**Influent**	**Effluent**	
Caffeine	1.16 ± 0.21 x 10^5	5.28 ± 0.41 x 10^2	1.57 ± 0.45 x 10^5	n.d.	n.d.
Carbamazepine	3.38 ± 0.10 x 10^1	2.11 ± 0.41 x 10^2	4.75 ± 0.14 x 10^2	4.79 ± 0.11 x 10^2	n.d.
Naproxen	9.61 ± 0.19 x 10^3	1.96 ± 0.34 x 10^2	1.96 ± 0.10 x 10^4	1.69 ± 0.02 x 10^2	n.d.
Ibuprofen	2.15 ± 0.11 x 10^4	7.78 ± 0.17 x 10^2	2.92 ± 0.01 x 10^4	6.30 ± 0.18 x 10^1	n.d.
Gemfibrozil	8.93 ± 0.85 x 10^2	1.80 ± 0.06 x 10^3	3.64 ± 0.03 x 10^3	3.61 ± 0.03 x 10^2	2.20 ± 0.15
Triclosan	8.08 ± 0.94 x 10^3	3.06 ± 0.11 x 10^1	3.71 ± 0.02 x 10^3	7.90 ± 2.60	n.d.
Ethinylestradiol	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable

3.2. PPCPs in cropland soil and well water

Results for all background soil and well water samples were below the detection levels.

3.3 Cropland soil characterization

As indicated in Table 5, the pH for all sample field areas was found to be slightly acidic. Results for cation exchange capacity can be found in Figure 1. Particle size distribution (Table 6) results indicated that the soils were generally clay loam. Organic matter and organic carbon results are shown in Figure 2.

Table 5. Determination of pH in Lexington field soils*

Soil location characteristics	Mean pH	Standard deviation
Switch grass	5.98	0.095
Corn, upper elevation	6.13	0.064
Corn, lower elevation	6.31	0.095

*Samples measured at 25°C in 0.01M $CaCl_2$.

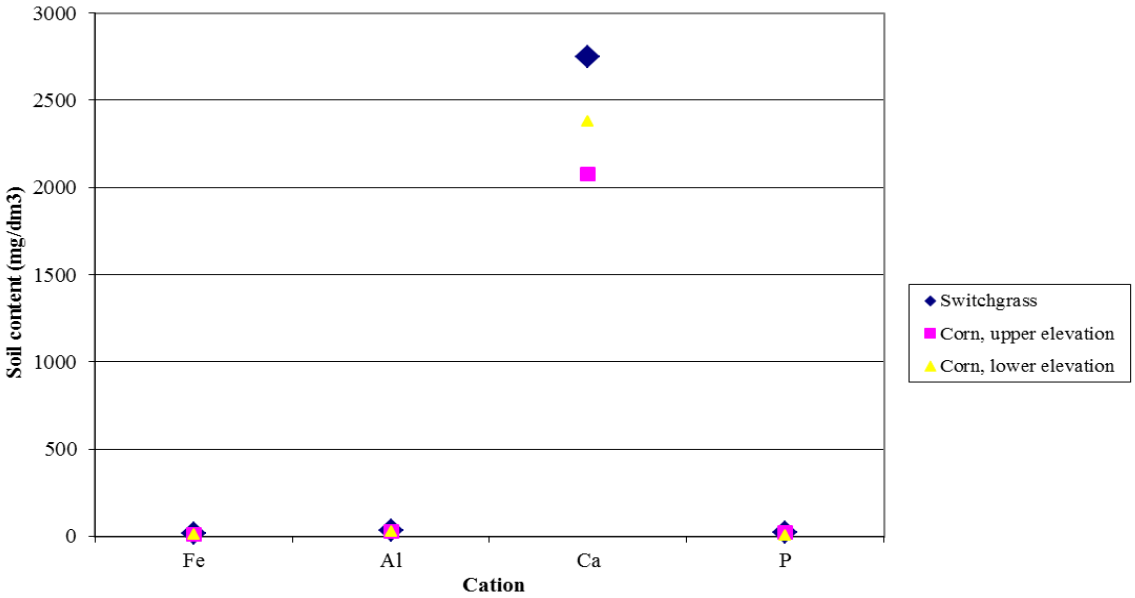

Figure 1. Cation exchange capacity of Lexington field soils. Wavelengths for cations were as follows: Fe: 2598, Al: 3092, Ca: 1840, P: 1774.

Table 6. Determination of particle size distribution in Lexington field soils.

Soil location characteristics	Percent clay	SD	Percent silt	SD	Percent sand	SD
Switch grass	32.3	2.3	35.5	3.1	32.2	5.3
Corn, upper elevation	30.3	3.1	36	2.8	35.4	4.2
Corn, lower elevation	32.3	3.1	39.3	5	28.4	5.3

SD = standard deviation

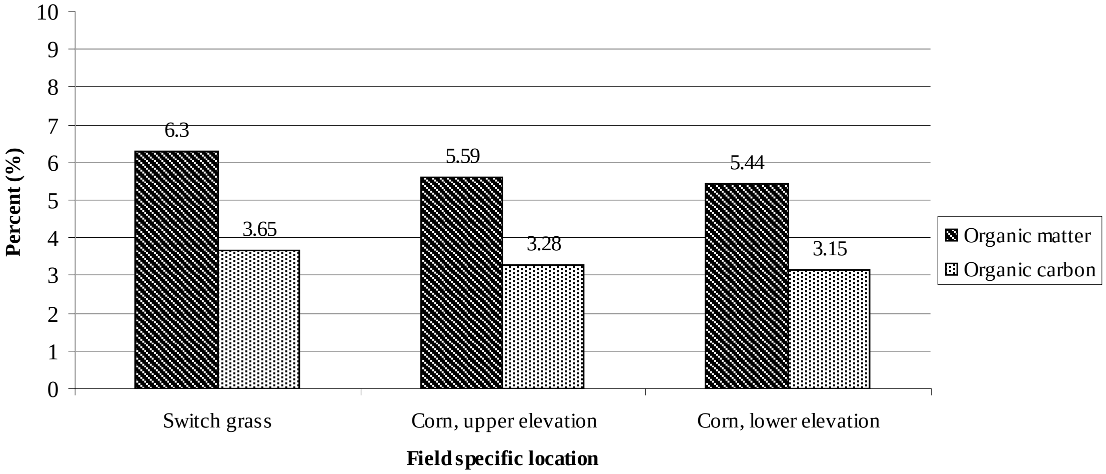

Figure 2. Organic matter and organic carbon content of Lexington field soils.

3.4. Selected PPCP sorption to Lexington cropland soils

The distribution coefficient and water partition coefficient for naproxen and ibuprofen are giving in table 7. Figures 3 and 4 display the results of the sorption and desorption studies for naproxen and ibuprofen.

Table 7. Distribution coefficient (K_d) and water partition coefficient (K_{OC}) determined from Freundlich equation over all concentrations.

PPCP	**K_d**	**R^2**	**K_{OC}**
Naproxen	24.44	0.49	727.4
Ibuprofen	42.368	0.56	1269

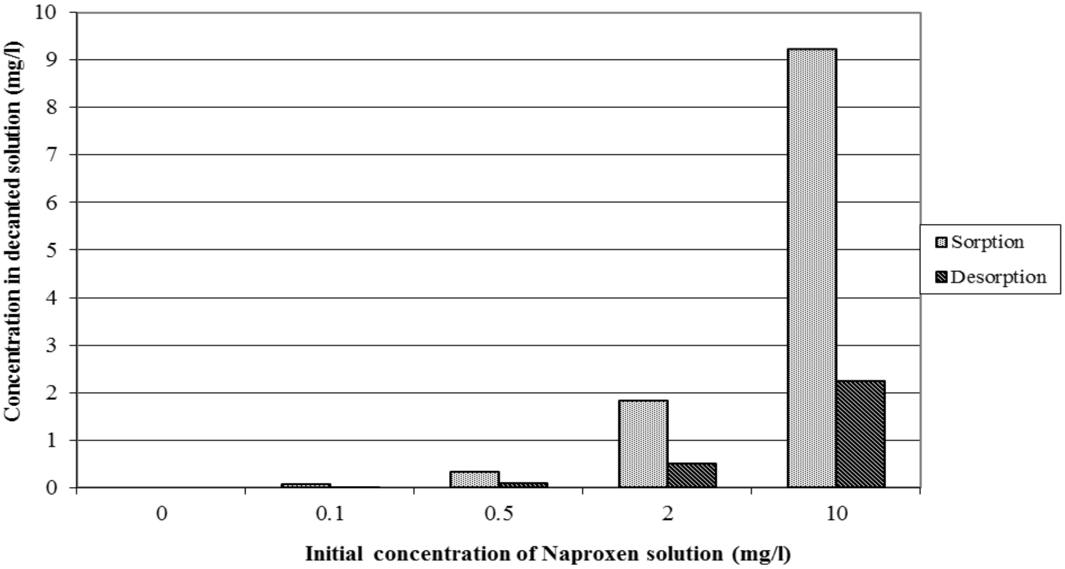

Figure 3. Naproxen batch isotherm. Where no value is presented, value was below detection limits.

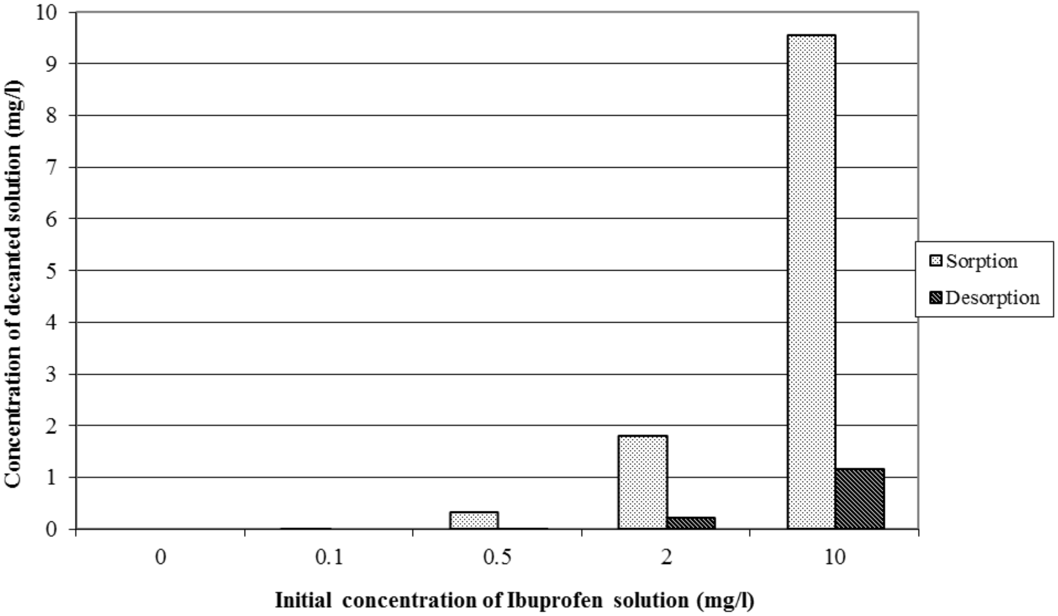

Figure 4. Ibuprofen batch isotherm. Where no value is presented, value below detection limits.

4. Discussion

Six of the seven original PPCPs were found in both Mackinaw and Goodfield communities' wastewater samples on each sampling occasion. For the most part, PPCP concentrations of treated wastewater effluent were lower than the untreated influent. Importantly, PPCPs were present in nearly all finished effluent samples and, without further treatment, would contribute to surface water pollution. No current regulatory limits exist for sanitary discharge of PPCPs, although the USEPA is monitoring discharges at selected sites (USEPA, 2014) and has added PPCPs to its list of contaminants of emerging concern (CEC) (USEPA, 2008).

As expected, background PPCP concentration in soil and well water samples tested below detection levels. Soils in the study area were slightly acidic clay loam with high organic matter content. To rule out the potential effects of small differences in pH, particle size, cation exchange capability, and organic content, soils from different areas of the field were combined for the isotherm study. It was anticipated that soils higher in organic carbon and clay content would yield higher K_{OC} values and decreased mobility, but our results found K_{OC} values lower than values published for both of the PPCPs tested, ibuprofen and naproxen. As indicated by the weak R^2 value, sorption rates did not increase linearly with increasing concentration. This result may have been due to sampling prior to equilibrium during the equilibration procedure, although the time period of 48 hours was consistent with the ASTME1195 method as well as the literature. Some error may have been introduced if the scale used to measure the solid pharmaceuticals was not precise. Percent recovery following sorption was over 100% in all the no-soil-added samples (ranging from 103% to 180% of the initial amount added). Given the error in the recovery estimates for the sorption study, confidence in the measurements for the desorption study may be impractical.

5. Conclusion

Based on results of analyses of wastewater from Mackinaw and Goodfield lagoons, it is likely that PPCPs will be present in wastewater sent from the Lexington lagoons to the agricultural fields' irrigation systems. Six of the seven priority PPCPs were found in lagoon-treated wastewater effluent in two communities with demographics resembling the city of Lexington. No preexisting soil or groundwater contamination was found in the fields prior to irrigation. Relatively high organic carbon and clay content of the fields' soils may increase the affinity for PPCPs with high K_{OC} values, but additional studies are needed to determine other characteristics of the soils that may affect soil and PPCP interactions.

6. Recommendations

There is great potential benefit for cropland irrigation using wastewater effluent — for communities facing restrictive discharge requirements as well as for farm operations. The same nutrients and organics that would pollute surface waters are welcome amendments to agricultural soils. The potential for these soils to filter PPCPs and allow for their degradation is another benefit that has not been well studied. Given the background testing performed and occurrence of PPCPs in rural lagoon effluent waters, it is recommended that further study of Lexington fields include drain tile sampling to better understand field conditions and soil/water/PPCP interaction in addition to sampling of the Lexington lagoons.

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Appendix A

Wastewater collection sites for the determination of the presence of selected PPCPs in Mackinaw and Goodfield lagoons.

Figure A-1. Wastewater influent sample collection weir, Mackinaw lagoons.

Figure A-2. Mackinaw aeration lagoon.

Figure A-3. Wastewater effluent discharge point, Goodfield lagoons.

Appendix B

Soil collection conditions for the determination of the presence of the background concentration of PPCPs in Lexington soils.

Figure B-1. Condition of switch grass field at soil sampling.

Figure B-2. Condition of upper elevation corn field at soil sampling.

Figure B-3. Condition of lower elevation corn field at soil sampling.

Appendix C
Well water collection locations for the determination of the background concentration of PPCPs at Lexington field sites.

Figure C-1. Sampling well locations.

- Sample LW-1
    - Downgradient well 1 from south field (southwest point)
- Sample LW-2
    - Downgradient well 2 from north field (northeast point)
- Sample LW-3
    - Upgradient well 3 from north field (center most point)
- Sample LW-4
    - Near composite of three wells
        - 2/5 LW-1, 2/5 LW-2, 1/5 LW-3

Appendix D

Field site for soil collection for the soil characteristics study and isotherm study on Lexington field soils.

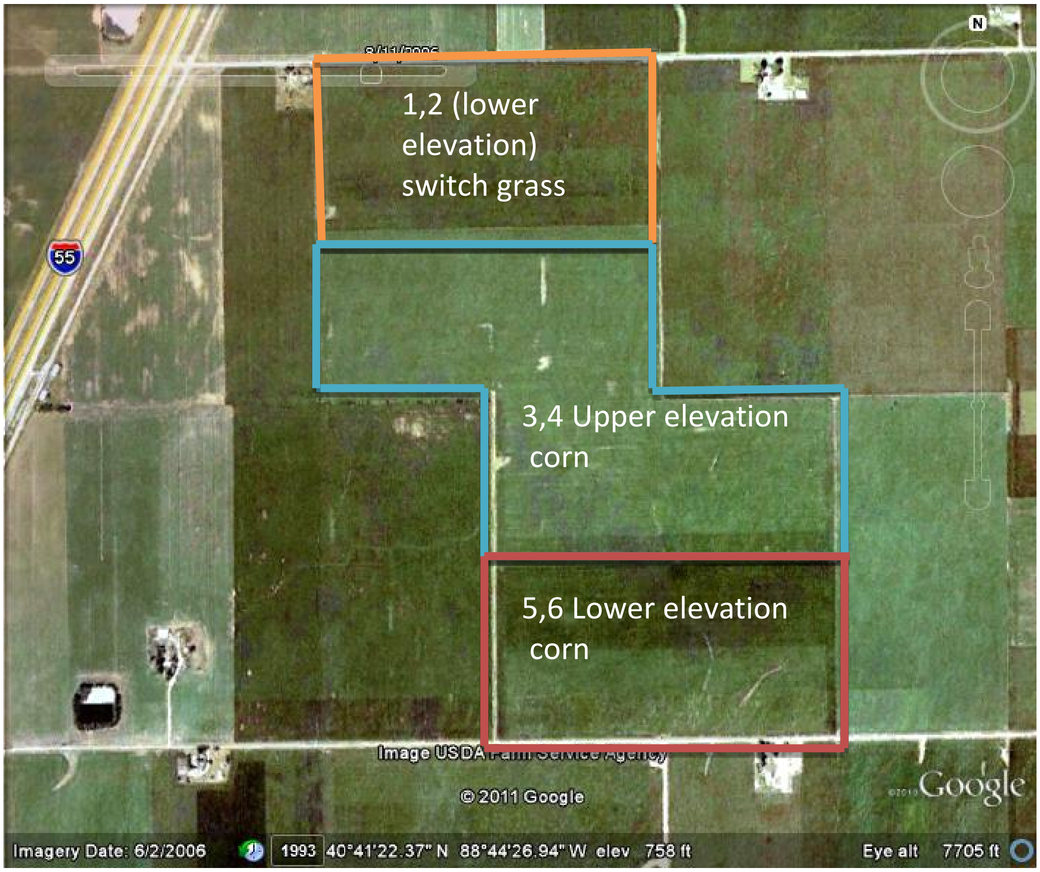

Figure D-1. Division of field site for soil composition for characteristic study.