Evaluation of the Treatability of Pharmaceuticals, PAHs and Pesticides during Wet Weather Flows in a Wastewater Treatment Plant

Kenya L. Goodson[1], Dr. Robert Pitt[1], Dr. Sam Subramaniam[2], Dr. Shirley Clark[3]

[1] Dept. of Civil, Construction, and Environmental Engineering, the University of Alabama, Tuscaloosa, AL 35487.
[2] Dept. of Chemistry, Miles College, Birmingham, AL
[3] Penn State Harrisburg, Middletown, PA, 17057

Abstract

Pharmaceuticals and personal care products (PPCPs) are of particular interest to scientists, because of the lack of information on their effects on ecosystems and lack of regulations affecting their discharges. These pollutants are produced in very large quantities and discharged in sewage where partial treatment occurs before their discharge. They have been detected in surface waters throughout the country. Some of the pharmaceuticals excreted from the body are unmetabolized into the domestic wastewater stream and are more toxic and untreatable than their parent compound.

Wastewater treatment systems receive PPCPs, along with other poorly understood contaminants including PAHs and pesticides. Wastewater treatment systems were not designed to treat these chemicals. Factors that can influence their treatability by wastewater treatment systems include the physical and chemical characteristics of the pollutants, the retention time in the unit treatment processes, and flow rates that can be influenced by rainfall. During this EPA-funded study, we are looking for the relationship in wastewater treatment efficiency and weather conditions, specifically examining treatment during wet weather flow. The operation of a local wastewater treatment facility was examined at several locations during seven wet weather events and seven dry weather events for these compounds.

During wet weather, there was an increase in mass discharges to the treatment plant for both PAHs and some of the pharmaceuticals. Gemfibrozil had a higher mass during dry weather. Although, the mass entering the treatment plants increased for the analytes, there were still significant reductions in the secondary treatment phase of the facility. Based on these data, treatability appeared to remain similar during both wet and dry weather. Hydraulic retention times and hourly flow variations are being examined during the final portion of this project.

Introduction

Emerging contaminants are newly recognized chemicals that have been detected in surface waters and groundwater. Emerging contaminants have been chemicals of concern because of their potential effects on aquatic wildlife. There is also a potential risk to humans who are exposed to these chemicals, but little is known about the effect on human populations.

Research has increased on the fate and transport of emerging contaminants. The EPA is working in conjunction with the US Geological Survey to compile a list of these contaminants that are in the US waterways (*A National Reconnaissance*). Samples were taken from a total of 139 US streams and waterways to analyze 95 organic wastewater contaminants [1]. These chemicals will be analyzed to identity the chemicals that are in our waterways, to study their composition and to determine their fate and transport, and their effect on the environment. Analytical equipment has been improved to be able to detect targeted contaminants at lower concentrations.

Wastewater treatment plant discharges has been identified as a common source of emerging contaminants in waterways. Wastewater treatment plants (WWTPs) are designed to treat organic matter that enters the systems. Typically, the constituents they are designed to treat consist of organic matter that deletes oxygen (measured by CBOD, BOD, and COD), nutrients (nitrogen and phosphorus), total suspended solids (TSS) and fecal coliform bacteria. With the increase of pharmaceutical and personal care products (PPCPs) consumption, more of these chemicals are being released into the wastewater stream and into wastewater treatment plants. Some of these PPCPs are going through the treatment plants only partially treated and are being discharged with the final effluent into the environment. PAHs have also been identified in treatment plant influent, likely from stormwater. Pesticide concentrations in municipal treatment system influents are also indicators that stormwater is entering the wastewater sysem.

In our study, we are collecting sample sets from each major unit process at the Tuscaloosa wastewater treatment facility (the Hilliard K. Fletcher treatment plant). Seven sample sets are being obtained during significant rain events and during dry weather conditions from four areas in the treatment plant. The dry weather samples will be compared to the wet weather samples for concentrations and for mass of pollutants for each constituent.

Description of Targeted Analytes

To understand the process of treatability, there has to be knowledge concerning the constituent that enters the treatment plant and their predicted behavior. Each chemical behaves a certain way during certain chemical conditions. The pH of the solution and the temperature affects how chemicals react in wastewater. The pH of wastewater usually ranges between 6 and 8. The temperature of the treatment system is usually between 20°C and 25°C. The chemical characteristics of wastewater constituents that affect treatability under these typical conditions are therefore of greatest interest. The solubility and the sorption coefficients are inversely proportional in most cases. The sorption values of the chemicals are evaluated using the log of the octanol-water coefficient (Kow).

Chemical Name (Pharmaceutical)	Molecular Weight	Log Octanol-water coefficient	Solubility (mg/L)
Carbamazepine [2]	236.1	2.45	17.7

Fluoxetine [3]	309.3	4.05	38.4
Gemfibrozil	250.12	4.78	5.0
Ibuprofen[4]	206	3.5-4.0	41.5
Sulfamethoxazole	253	0.9	600
Triclosan	289.5	4.8-5.4	2-4.6
Trimethoprim	290.32	0.79	400

Pharmaceuticals and personal care products with low log Kow values tend to be less hydrophobic and generally are soluble in water, whereas higher log Kow values indicate a higher affinity to sorb to particles in the water-sediment matrix. PPCPs that are problematic are those that are highly soluble in water and typically do not sorb to particles.

Of all the pharmaceuticals that are targeted for this study, Sulfamethoxazole and Trimethoprim show the lowest log Kow values. These chemicals theoretically will remain aqueous in solution and can only be removed by a secondary treatment process, compared to compounds that sorp to particulates and can be readily removed by sedimentation processes. Fluoxetine, Gemfibrozil, Ibuprofen and Triclosan have high Kow and correspondingly very low water solubility values. Primary sedimentation should remove a substantial amount of these pollutants, although many other factors determine sorption, such as the amount of particulates and the velocity of the flowing water. Carbamazepine has low solubility and low sorption. This compound is highly resistant to biodegradation and has shown very little removal during the monitoring.

Many PAHs are commonly found in stormwater. Infiltration of stormwater into sewer lines increases the presence of the PAHs in the wastewater stream. PAHs are typically insoluble in water and are very lipophilic. However, those having small molecular weights have increased solubility in water. Solubility of some PAHs, such as anthracene, increase with increasing temperatures. PAHs are differentiated by the number of carbon rings in their molecular structure and the placement of hydrocarbons connected to them. This structure determines their physical and chemical properties. During wastewater treatment, they maybe undergo changes in their physical and chemical structure.

Chemical Name (PAH)	**Molecular Weight (g/mol)**	**Solubility (mg/L)**	**log octanol-water coefficient**
naphthalene	128.2	31.5	3.30
acenaphthylene	152.2	3.93	4.07
acenaphthene	154.2	16.1	3.94
fluorene	166.2	1.98	4.23
anthracene	178.2	0.07	4.54
phenanthrene	178.2	1.12	4.57
pyrene	202.2	0.135	5.18
fluoranthene	202.2	0.264	5.14
benzo[a]anthracene	228.3	0.014	5.66
chrysene	228.3	1.8 x 10-3	5.71

Some wastewater treatment systems treat industrial wastes which can include pesticides. However, pesticide contaminants can enter wastewater treatment plants by surface runoff from locations treated by the pesticides, from contaminated rinses during cleaning of pesticide applicators and containers, and/or from disposal of unused pesticides [5]. Pesticides in stormwater can enter the sanitary sewers by inflow or infiltration. Katsoyiannis et al 2004 categorizes pesticides as persistent organic pollutants (POPs). These POPs tend to have low water and high fat solubility, stability slowing degradation processes, low vapor pressure, and are persistent in the environment [6].

Chemical Name (Pesticides)	**Molecular Weight (g/mol)**	**Solubility in water (mg/L)**	**log octanol-water coefficient**
Methoxychlor[7]	345.65	0.1	4.68-5.08
Aldrin	364.91	0.027	6.5
Dieldrin	380.91	0.1	6.2
Chlordane	409.76	insoluble*	~5.54
Arochlor Σ	257.9-453	insoluble*	5.6-6.8
Lindane	290.83	17	3.8
Heptachlor[8]	373.32	0.056	6.10
Heptachlor-epoxide	389.40	not found	5.40

Although physical and chemical characteristics play a factor in the removal of emerging contaminants, hydraulic retention rates (HRT) and solid retention rates at the treatment plant also factor into the removal ability of these organic compounds.

Site Description

Description of area

Tuscaloosa is the fifth largest city in the state of Alabama, with a population of about 83,000, according to the 2006 Census Bureau estimate [9]. The total area of Tuscaloosa is 66.7 mi^2 with 10.5 mi^2 comprised of surface waters of Lake Tuscaloosa and the Black Warrior River (source: tuscaloosacountyalabama.com). Typical weather is humid, with total annual rainfall being about 55 inches. Slightly more occurs during the winter months. Tuscaloosa wastewater needs are met by the Earl Hilliard Wastewater Treatment Plant.

Earl Hilliard Wastewater Plant

Tuscaloosa's wastewater treatment system contains approximately 550 miles of City maintained assets with another 50 miles of privately owned collection lines [10]. Over 60 sanitary sewer lift stations carry wastewater to the wastewater treatment plant. Tuscaloosa's wastewater facility was built in 1960 and upgraded in 1974[11]. A 33 million dollar expansion was designed in 1995, increasing the capacity of the treatment plant to 24 million gallons per day [11](City of Tuscaloosa). Earl Hilliard Wastewater facility has a primary and secondary treatment system. The primary and secondary system is duplicated in case a part of the plant has to shut down for maintenance or repairs., The Earl Hilliard Wastewater Treatment facility is a typical secondary treatment plant with a pretreatment phase, a primary clarifier, an aeration tank, a secondary clarifier, and disinfection system. Tuscaloosa's wastewater treatment plant currently uses ultra-violet disinfection instead of chlorine. For the solids that are filtered out of the effluent, an anaerobic digester uses microbes grown at the facility to feed on the solid material to stabilize and dewater the sludge.

Sampling and analysis

Sampling method

During each rain event sampled, one liter samples of wastewater were manually collected from four areas of the facility: the inlet of the treatment plant before pre-treatment, the effluent from the primary clarifier, the effluent from the secondary clarifier and at the final discharge outlet, after disinfection. Each sample was a composite sample taken during a two hour time period. Six one liter sample bottles were used at each sampling location for the analysis of acidic and basic pharmaceuticals, PAHs, and pesticides. Each sample was stored in amber glass bottles, and refrigerated before extraction.

Analysis

The acidic pharmaceuticals were extracted using SPE extraction (EPA method 1694). Samples for acidic pharmaceutical analysis were acidified to 2.0 ± 0.1 pH using hydrochloric acid. Sodium ethylenediaminetetraacetic acid (Na-EDTA) was added for chelation of any heavy metals that might be present. SPE cartridges were eluted with methanol and 2.0 pH reagent water before extraction.

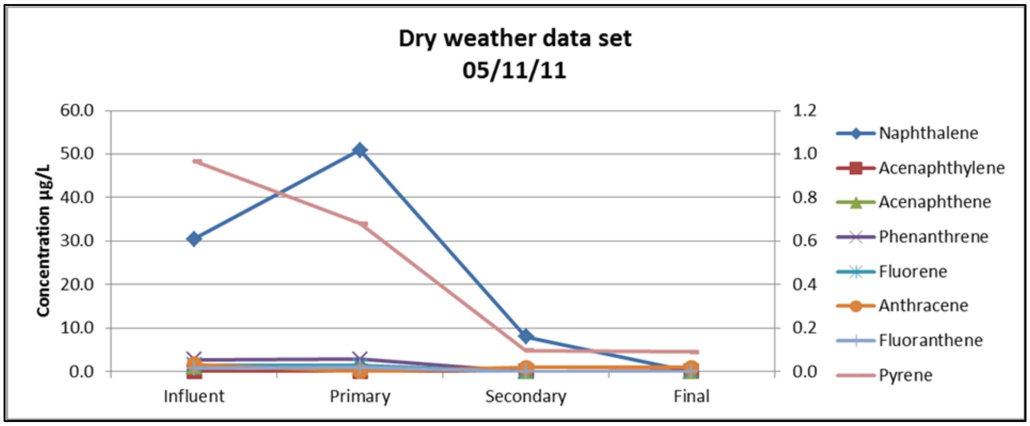
Samples for basic pharmaceutical analyses were adjusted to a pH of 10 ± 0.1 using ammonium hydroxide. SPE cartridges for base analysis were eluted using methanol and dionized water. Polyaromatic hydrocarbons (PAHs) were extracted using separation funnels with KD concentration. Samples for pesticides were sent to Penn State Harrisburg for analysis. The analyses were conducted using HPLC for the ECs, GC-ECD for the pesticides and GC-MS for the PAHs.

Results and discussion

PAHs

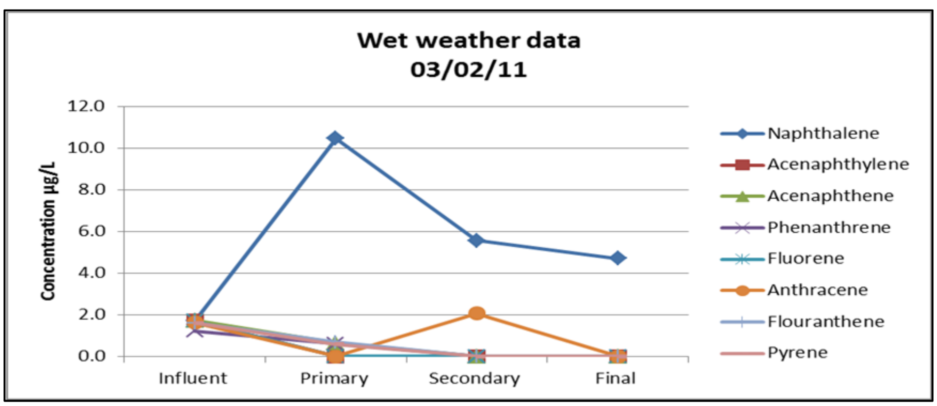
The concentrations for some of the emerging contaminants have been now analyzed and compared in wet weather and dry weather samples. There was consistency in each of the constituents evaluated for the dry weather samples. Some of the samples showed an increase in the concentrations in the primary effluent from the influent before being reduced significantly in the secondary treatment process.

This is likely due to matrix interferences by the very high organic solids concentrations in the influent that was reduced by the primary treatment process. Pyrene was the only pollutant that reduced in concentration after the primary effluent.



,There was significantly variability in each of the constituents for the wet weather samples. Some showed an increase in concentrations after the primary treatment, with some indicated a decrease with primary treatment. All had reductions in the final effluent, except for naphthalene. These variations were also thought to be associated with matrix interferences during the sample analyses, and because many of the constituents were only found at very low concentrations.

Mass discharges and loadings per day were calculated and compared to indicate the likely stormwater contributions to the treatment plant. The flow rate for May 11th was 13.3 MGD, while the flow rate for March 2nd was 23.3 MGD.



All of the PAHs in the influent samples had a higher mass value during the wet weather period than during the dry weather period, expect for naphthalene (again, likely due to matrix interferences). During the wet weather period, the high mass loadings decreased throughout the treatment system for most of the constituents.

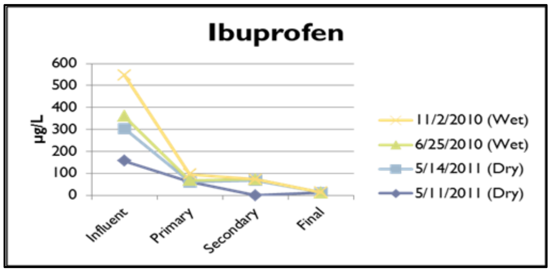
MGD=23.3	grams/day			
03/02/10	**Influent**	**Primary**	**Secondary**	**Final**
Naphthalene	151	921	490	414
Acenaphthylene	150	0.0	0.0	0.0
Acenaphthene	152	56.7	0.0	0.0
Phenanthrene	108	53.3	0.0	0.0
Fluorene	150	0.0	0.0	0.0
Anthracene	144	0.0	183	0.0
Flouranthene	141	60.3	0.0	0.0
Pyrene	142	52.5	0.0	0.0
Benzo(a)pyrene	133	150	0.0	0.0

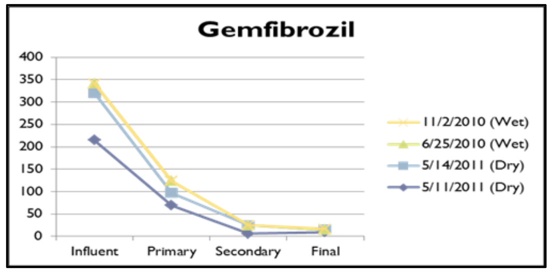
For dry weather, each analyte is varied in mass from 3.0 grams per day to 1.5 kg per day. There is a steady reduction throughout the treatment plant, but there is more of a reduction in the secondary treatment process than in the primary treatment system. Anthracene showed the least amount of reduction in the final effluent, but was reduced by approximately 50% from the influent.

MGD=13.3	grams/day			
5/11/2011	**Influent**	**Primary**	**Secondary**	**Final**
Naphthalene	1,530	2,560	405	0.7
Acenaphthylene	3.0	3.8	2.6	4.5
Acenaphthene	52.4	47.4	0.0	0.0
Phenanthrene	138	142	0.0	0.0
Fluorene	73.9	68.7	0.0	0.0
Anthracene	87.8	0.0	49.0	46.3
Flouranthene	35.6	48.7	1.2	1.2
Pyrene	48.6	34.2	4.9	4.6

Pharmaceuticals

For pharmaceuticals, wet and dry weather samples were compared for ibuprofen and gemfibrozil. Each contaminant shows a steady decrease from influent to final effluent. For these chemicals, the wet weather had no significant effect on the treatability of the pharmaceuticals.





For the pharmaceuticals, ibuprofen and triclosan showed higher mass loadings at the treatment plant during wet weather conditions than during dry weather. Gemfibrozil shows a higher mass entering the treatment system during dry weather than during wet weather. Overall, there are still significant reductions in concentration and mass from the influent to the final effluent.

grams/day	MGD	20.6		
11/2/2010	Influent	Primary	Secondary	Final
Ibuprofen	14,500	2,150	8.3	102
Gemfibrozil	0.0	0.0	0.0	114
Triclosan	3,680	2,440	27.8	0.0

grams/day	MGD	13.5		
5/11/2010	Influent	Primary	Secondary	Final
Ibuprofen	7,970	3,110	0	610
Gemfibrozil	10,960	3,540	316	468
Triclosan	0	0	0	0

Pesticides

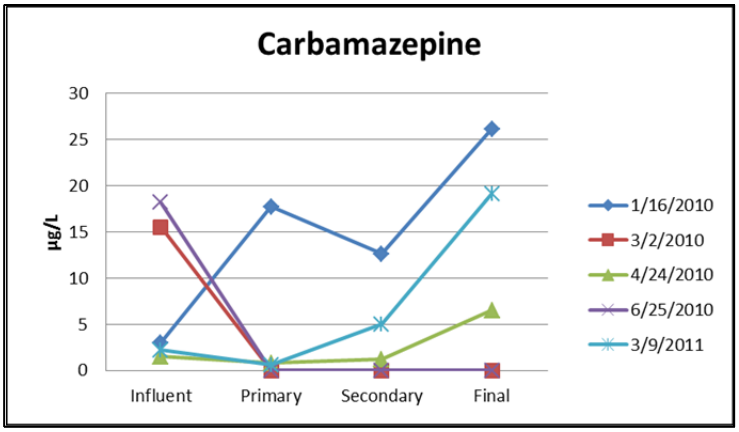
Samples for pesticides have been obtained, but the analyses have not been completed yet. It is expected that the pesticide data will be available for the final presentation.

Conclusions

The purpose of this research is to determine if the treatability of emerging contaminants at wastewater treatment facilities is significantly reduced during higher flow periods associated with wet weather. The targeted pollutants have a variety of chemical characteristics are expected to affect their treatability. Data from several sets of samples are presented in this paper as an example of the observed performance.

The data indicate that during wet weather, there is an increase in the flow rate at the treatment plant, and that higher concentration and masses of most of the pharmaceuticals and PAHs occur.

Overall, while there are increases in pollutant loadings entering the treatment plant during wet weather for both pharmaceuticals and PAHs, these increases did not adversely affect the treatability of pollutants at the treatment plant. Most of the analytes are treated consistently during secondary treatment. However, carbamazepine was not treated in the treatment system, which is consistent with literature observations.



Wet weather

Future work

For future work, pesticides will be analyzed and presented for the conference. To gain a better understanding of the treatment plant, hydraulic retention times and hourly flow rates will be gathered and calculated for each event.

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