The Effect of Increased Flows on the Treatability of Emerging Contaminants at a Wastewater Treatment Plant during Rain Events

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ABSTRACT

A large number of pharmaceuticals and personal care products (PPCPs) have been found in U.S. surface waters. These compounds are part of a growing class of pollutants known as emerging contaminants, chemical compounds or organism only recently found in significant proportion in surface and groundwaters. Research has shown that these compounds can enter the environment, disperse and persist to a greater extent than first anticipated (Kolpin et al. 2002, 1202-1211).Wastewater treatment plants are a common source of emerging contaminants in waterways because some emerging contaminants are difficult to remove in conventional wastewater treatment systems. Stormwater runoff is known to carry some of these emerging contaminants, such as pesticides and PAHs from non-point sources, plus pharmaceuticals from pet wastes, and possibly other PPCPs. In most areas, some runoff enters sanitary sewer lines through inflow or infiltration and consequently enters the wastewater treatment system. This additional stormwater increases the volumes and flow rates and changes the characteristics of the influent to the wastewater treatment plant, factors that may detrimentally affect treatment plant performance. This EPA-funded research is focusing on wet weather flow contributions of emerging contaminants, including their treatment, at municipal wastewater treatment plants during wet weather when the flows are substantially greater than during normal dry weather conditions.

KEYWORDS: Emerging contaminants, Wastewater treatment, Stormwater infiltration, Pharmaceuticals and Personal Care Products, PAHs, Pesticides

INTRODUCTION

Emerging contaminants are defined by the USGS as “any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects.” They are a concern because many of them are frequently used and are ubiquitous in the environment. Some emerging contaminants are persistent in the environment for many years exposing aquatic wildlife to potential adverse effects. Persistent organic pollutants (POPs) tend to have low water and high fat solubility, stability during degradation processes, low vapor pressure and are persistent in the environment (Katsoyiannis and Samara 2004, 2685-2698). Compounds such as human and veterinary medicines, lotions, perfumes, pesticides, surfactants and plasticizers can adversely affect the environment and its ecology. These contaminants do not need to be persistent in the environment to cause negative effects, since their high transformation and removal rates can be offset by their continuous introduction into the environment (Petrovic, Gonzalez, and Barceló 2003, 685-696)Pharmaceuticals were first reported in U.S. surface waters during the investigations in the 1970s, although they are not regulated as legacy pollutants such as PCBs and DDTs (Snyder et al. 2006). The USGS conducted the first nationwide reconnaissance of the occurrence of pharmaceuticals, hormones, and other organic wastewater contaminants (OWCs) in water resources (Kolpin et al. 2002, 1202-1211). One or more of the targeted OWCs were found in 80% of the 139 streams sampled during the USGS reconnaissance study (Kolpin et al. 2002, 1202-1211). Pollutants can be discharged into the wastewater matrix as unchanged parent compounds or through elimination from the human body as metabolites, which can be more toxic.

To reduce emerging contaminants in wastewater, scientists and researchers must determine the fate and transport of the contaminant in the wastewater treatment facilities. Sources of targeted emerging contaminants include urban and agricultural non-point discharges and point sources charges such as sanitary sewer and septic tanks. Some of the main sources of emerging contaminants are untreated urban wastewaters and WWTP effluents (Petrovic, Gonzalez, and Barceló 2003, 685-696) Wastewater treatment plants are important point sources, because many of the emerging contaminants that enter the plant are not adequately treated. A variety of these compounds enter wastewater treatment plants, from surfactants to pharmaceuticals; all of them having different chemical properties. A large portion of the emerging compounds and their metabolites escape elimination in WWTPs and enter the aquatic environment via sewage effluents (Petrovic, Gonzalez, and Barceló 2003, 685-696).

Stormwater runoff is known to carry pollutants of concern such as pesticides from urban landscaping activities and PAHs from automobile and power plant emissions. Infiltration of stormwater into the sanitary sewer line increases the volume and the flow rate of influent in the wastewater system and changes the concentrations. These concentration changes and decreased residence times during wet weather may reduce a wastewater system's effectiveness in treating emerging contaminants. In our study, we are comparing wastewater samples collected during wet weather and wastewater samples collected during dry weather conditions at several locations within a wastewater treatment plant to identify if changes occur and which unit processes are most effective under a range of flow conditions. This comparison will help to determine if stormwater significantly affects treatment of emerging contaminants, if stormwater is a contributor of emerging contaminants in the wastewater, and if wet weather significantly affects the treatment plant's treatability of emerging contaminants. This treatability information will also be used to estimate which stormwater unit treatment processes may be effective for emerging contaminant treatment of separate stormwater. This EPA-funded research is focusing on wet weather flow contributions of emerging contaminants, including their treatment, at municipal wastewater treatment plants during wet weather when the flows are substantially greater than during normal dry weather conditions. Selected separate stormwater sheetflow samples are also being analyzed for these emerging contaminants to verify increased loads to the wastewater treatment plant during periods of wet weather and higher flows.

Theoretical removal of the emerging contaminants based on their physical and chemical properties will also be compared to the observed removals during the different unit treatment processes. Some contaminant removals will likely be accurately predicted and new separate stormwater treatment methods can be proposed. However, other emerging contaminant removals are not well predicted from the theoretical treatment characteristics due to interfering factors, or other reasons.

Samples were taken from the treatment plant in Tuscaloosa (having separate sanitary and stormwater drainage systems) during normal weather and wet weather from different sampling locations after major unit processes. The Tuscaloosa wastewater treatment plant is a standard conventional activated sludge treatment plant with standard pre-treatment, primary treatment and UV disinfection.

Description of Targeted Analytes

To predict the process of treatability, there has to be knowledge concerning the constituent that enters the treatment plant and their theoretical behavior. 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 ($\log_{10} K_{ow}$).

Pharmaceuticals and personal care products with low $\log_{10} K_{ow}$ values less than 3 tend to be less hydrophobic and generally are soluble in water, whereas higher $\log_{10} K_{ow}$ values above 3 indicate a higher affinity to sorb to particles in the water-sediment matrix. PPCPs that are problematic (resistant to conventional sedimentation treatment) are those that are highly soluble in water and typically do not sorb to particles.

Table 1. Physical and Chemical Properties of Pharmaceuticals

Chemical Name (Pharmaceutical)	Molecular Weight (g/mol)	Log Octanol-water coefficient ($\log_{10} K_{ow}$	Solubility (mg/L)	Dissociation constant (pka)
Carbamazepine	236.1	2.45	17.7	13.9 *
Fluoxetine	309.3	4.05	38.4	9.5 ***
Gemfibrozil	250.12	4.78	5.0	4.5 ****
Ibuprofen	206	3.5-4.0	41.5	4.91 ***
Sulfamethoxazole	253	0.9	600	pka1=1.7, pka2=5.6
Triclosan	289.5	4.8-5.4	2-4.6	8.0 ****
Trimethoprim	290.32	0.79	400	6.6 *

(Goodson et al. 2012) *****(Beausse 2004) ****** (Chen et al. 2011) ******* (Lindqvist 2005) ******** (Rossner 2009)

Of the pharmaceuticals that are targeted for this study, sulfamethoxazole and trimethoprim show the lowest $\log_{10} K_{ow}$ values and both tend to be ionic when the pH is over 5. At pH levels above 5.7, the sulfamethoxazole remains as anionic species, neutral at pH values between 1.7 and 5.7, and positive at pH levels below 1.7 (Nghiem, Schäfer, and Elimelech 2005, 7698-7705). In wastewater, sulfamethoxazole theoretically will remain aqueous in solution and can only be removed by a secondary treatment (biochemical) process. Trimethoprim has a disassociation constant (pka) of 7.2, but under acidic conditions, it is completely ionized (Mikes and Trapp 2010, 1-6). Under neutral conditions, it has a log K_{ow} of 0.79 but can range from -1.7 to 0.79 from acidic pH to neutral pH (Mikes and Trapp 2010, 1-6).

Fluoxetine, gemfibrozil, ibuprofen and triclosan have high $\log_{10} K_{ow}$ and correspondingly very low water solubility values. Triclosan has a pka of 8.1 in which pH of wastewater between 7 and 9 would have a significant influence on its speciation (Singer et al. 2002, 4998-5004). Triclosan has a water solubility of about 2000-4600 µg/L at 25˚C and a high octanol/water partition coefficient ($\log_{10} K_{ow}$) of 4.8-5.4 (Singer et al. 2002, 4998-5004; Heidler and Halden 2007, 362-369). Fluoxetine has a high $\log_{10} K_{ow}$ and its pka is 9.5, outside normal pH for wastewater. Carbamazepine has low solubility and low sorption. This compound is highly resistant to biodegradation and has shown very little removal during the monitoring at the treatment plant. Gemfibrozil and ibuprofen have high $\log_{10} K_{ow}$ values and dissociation pkas of 4.5 and 4.91, respectively.

Theoretically, primary sedimentation should remove non aqueous pollutants such as flouxetine, gemfibrozil and ibuprofen. Biodegradation is the mechanism to remove pollutants in aqueous form, however it is more difficult. Other factors also affect treatability, including the retention time available.

Table 2. Physical and Chemical Properties of PAHs

Chemical Name (PAH)	**Molecular Weight (g/mol)**	**Solubility (mg/L)**	**log octanol-water coefficient ($\log_{10} K_{ow}$**
naphthalene	128.2	31.5	3.37
acenaphthylene	152.2	3.80	3.89
acenaphthene	154.2	16.1	4.02
fluorene	166.2	1.90	4.12
anthracene	178.2	0.045	4.53
phenanthrene	178.2	1.12	4.48
pyrene	202.2	0.132	5.12
fluoranthene	202.2	0.260	5.14
benzo[a]anthracene	228.3	0.011	5.61
chrysene	228.3	1.6×10^{-3}	5.71

(Goodson et al. 2012)

A number of 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 (fewer rings in their structure) have increased solubilities in water. The 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 degradation and associated changes in their physical and chemical structure, resulting in daughter products having different characteristics.

Some wastewater treatment systems treat wastewaters which can contain pesticides. Pesticide contaminants can enter wastewater treatment plants by surface runoff from locations treated by pesticides, from contaminated rinses during cleaning of pesticide applicators and containers, and/or from disposal of unused pesticides. 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 therefore persistent in the environment.

Table 3. Chemical and Physical Properties of Pesticides

Chemical Name (Pesticides)	**Molecular Weight (g/mol)**	**Solubility in water (mg/L)**	**Log octanol-water coefficient $\log_{10} K_{ow}$**
Methoxychlor	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	373.32	0.056	6.10
Heptachlor-epoxide	389.40	not found	5.40

(Goodson et al. 2012)

LOCATION AND DESCRIPTION OF SITE

The Hilliard K. Fletcher wastewater treatment plant serves the sanitary sewer area for the entire area of Tuscaloosa and some surrounding areas in Tuscaloosa County. The current permitted treatment flow rate is 30 million gallons per day and is undergoing expansion to add 15 MGD in 2013 for a 45 MGD total capacity flow. Most wastewater treatment plants in the US are typical secondary treatment systems with a pretreatment phase, a primary clarifier, an aeration tank, a secondary clarifier and disinfection system. Tuscaloosa's wastewater treatment uses ultraviolet disinfection instead of chlorine. An anaerobic digester is used for treatment of the sludge. Frequent monitoring of performance focusses on conventional pollutants (BOD_5, $CBOD_5$, NH_3-N, TKN, pH, and TSS).

Figure 1. Hilliard K. Fletcher Wastewater Treatment Plant

Before sample collection and data analyses were performed, preliminary performance data were obtained from the wastewater treatment plant to determine its treatability for conventional parameters. Influent and effluent concentrations for each parameter were obtained. Probability plots of BOD and TSS show a reduction of two to two and one half logs, or 90+% removals.

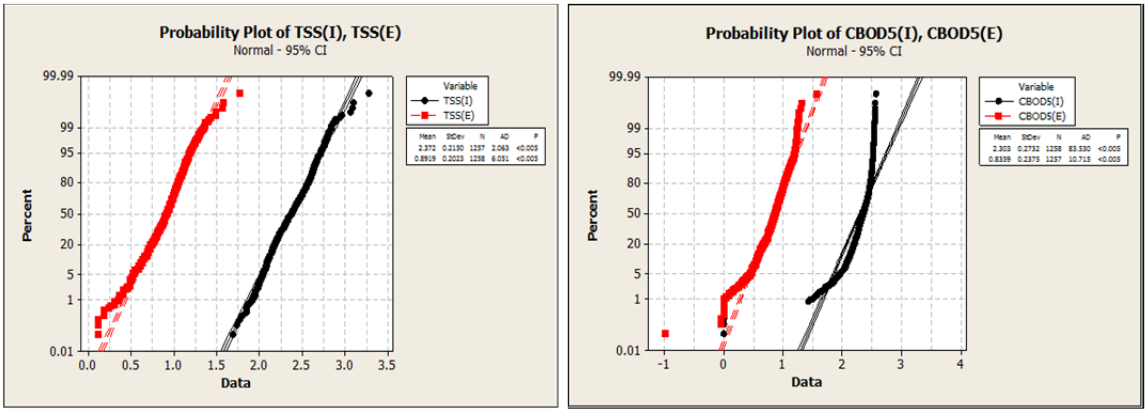

Figure 2. Data from 2005-2008 of daily monitoring

The pH of wastewater may affect the ionization of certain pharmaceuticals, therefore affecting treatability. The pH of wastewater for the influent and effluent remained neutral, ranging from 6.5 to 7.4. Sulfamethoxazole, trimethoprim and triclosan tend to be ionic in solutions with pH ranging between 5.6 and 8.1. It is anticipated than some of these compounds will be aqueous in the influent and/or the effluent, affecting their treatability.

Table 4. pH concentrations for sample dates

Wet weather date	Influent pH	Effluent pH
01/16/10	7.23	6.80
03/02/10	7.42	6.79
04/24/10	6.94	6.61
06/25/10	6.93	6.62
10/24/10	7.02	6.72
11/02/10	6.92	6.48
03/09/11	7.24	6.64
09/20/11	7.09	7.04

Rainfall data from 2005 to 2008 was compared to the flow rates at the treatment facility and the concentration of each parameter to determine if there were any correlations. There was only a weak correlation between elevated rainfall data and flow rates, possibly indicating an increasing flow after about 1 inch of rain, but a large variation is noted. The correlations for the concentrations of the total suspended solids and the BOD with flow were also insignificant.

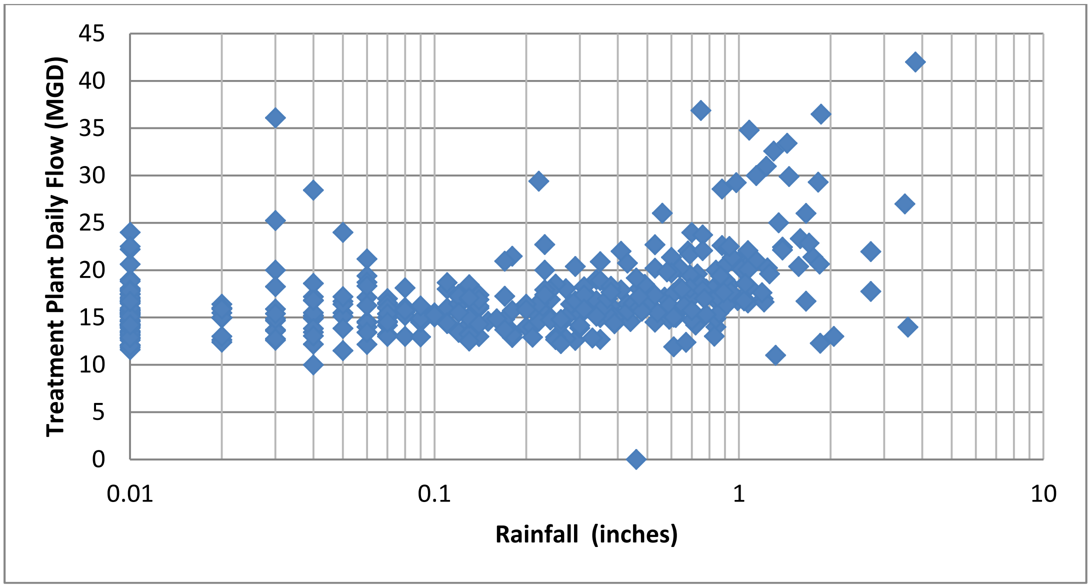

Figure 3. Comparison of rainfall and flow rates at the Tuscaloosa Wastewater Treatment Plant (2005-2008 data)

SAMPLING AND ANALYSIS

Sampling method

During each sampled event, samples of wastewater were manually collected from four locations at the wastewater treatment 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.

Analyses

The acidic pharmaceuticals were extracted using solid phase extraction (SPE) (EPA method 1694) after being acidified to pH 2.0 ± 0.1 using hydrochloric acid. Sodium ethylenediaminetetraacetic acid (Na-EDTA) was added for chelation of any heavy metals that might be present. The SPE cartridges were conditioned by eluting them with methanol and pH 2.0 reagent water before extraction. Samples for basic pharmaceutical analyses were adjusted to a pH of 10 ± 0.1 using ammonium hydroxide before the extraction. SPE cartridges for basic analyses were conditioned by eluting them first with methanol and dionized water. Polycyclic aromatic hydrocarbons (PAHs) were extracted using separation funnels and concentrated using Kuderna Danish (KD) procedures. Samples for pesticides were sent to Penn State Harrisburg for analyses, where they were extracted with separation funnels and KD sample concentrations. The analyses were conducted using HPLC for the ECs, GC-ECD for the pesticides and GC-MS for the PAHs.

RESULTS

Long-term rainfall data were collected from the Tuscaloosa Oliver Dam NOAA website for each of the days wet weather samples were collected. Flow rates were significantly higher for the wastewater treatment plant for rain events that exceeding two inches. Some of the rain events did not increase the flow rates, possibly due to rain only affecting a small fraction of the service area, or the rain depth was insufficient to trigger inflow or infiltration. For April 2010, the flow rate was relatively lower than the flow rates for two of the rain events that showed no rainfall data from the Tuscaloosa Oliver Dam website.

Table 5. Rainfall and flow rates during sampling events

	Rainfall (in)	*Flow rate (MGD)*
01/16/10	0.55	18.2
03/02/10	0.68	23.3
04/24/10	1.01	16.5
06/25/10	trace	20.7
10/24/10	trace	15.7
11/02/10	trace	20.5
03/09/11	2.7	42.2
09/20/11	2.2	26.5

The pharmaceuticals yielded variable results. Carbamazepine had detectable concentrations for both wet weather events, while dry weather samples yielded concentrations below the detection limits, as shown on Figure 4. Carbamazepine showed potential increases in concentration during the wet weathers, possibly due to matrix interference for the dirtier samples at the front end of the treatment facility. Sulfamethoxazole s is shown on Figure 5. Large reductions occurred in the primary sedimentation process while the secondary treatment showed some reductions for some of the monitored events.

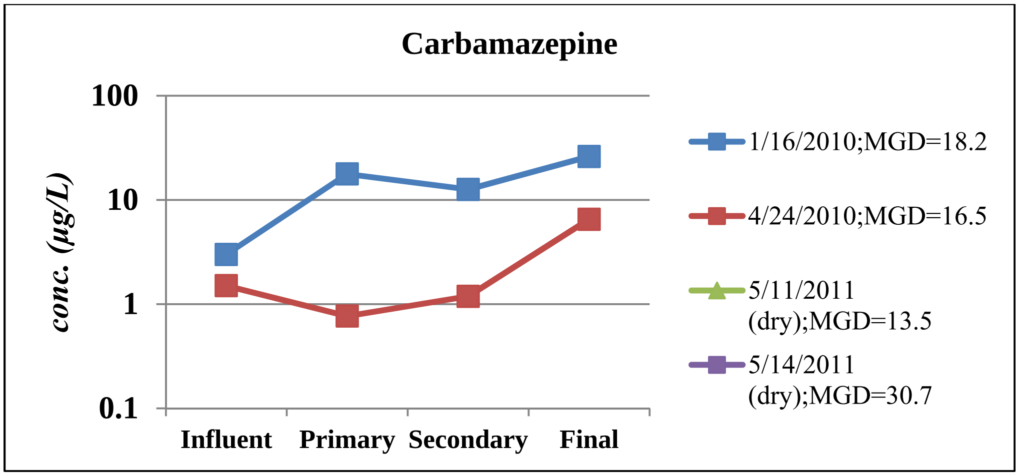

Figure 4. Comparison of wet and dry weather samples for pharmaceutical carbamazepine

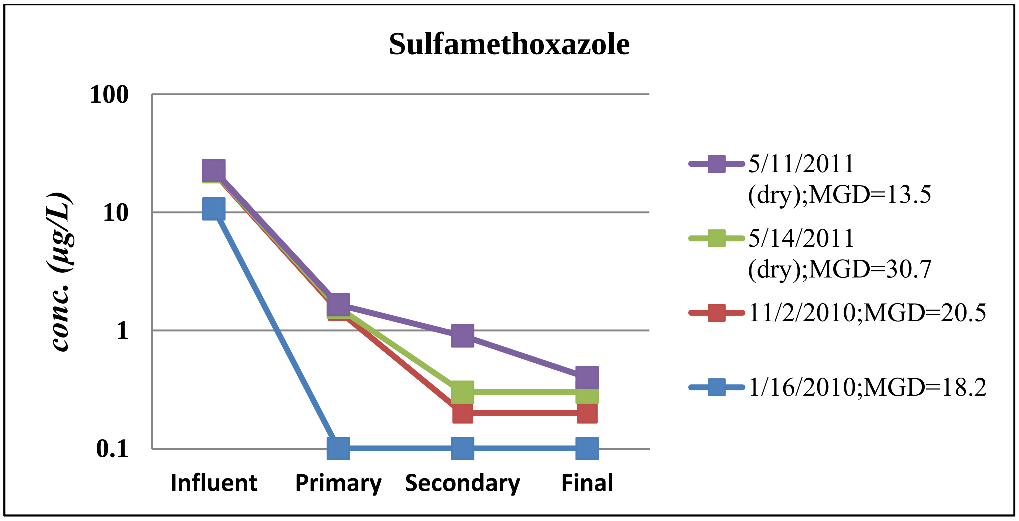

Figure 5. Comparison of wet and dry weather concentrations for pharmaceutical sulfamethoxazole

For anthracene, all four of the available samples showed no treatability, but periodic non-detectable values. Although the concentrations are not reduced, all of the events are below the lower limit of quantification of 20 μg/L.

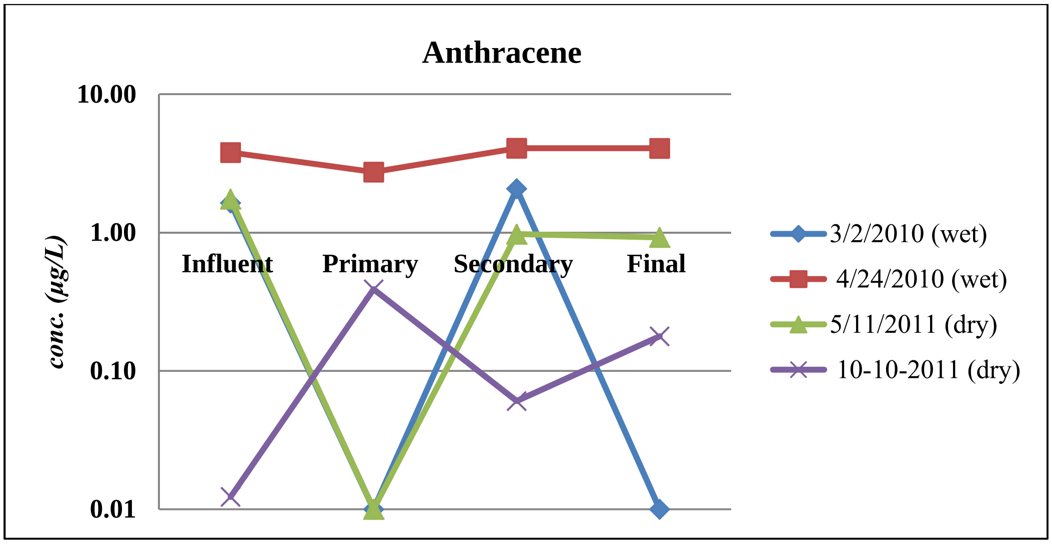

Figure 6. Comparison of wet and dry weather samples for PAH anthracene

Flouranthene shows reductions for three of the four data sets available. All of the concentrations for flouranthene were also below the lower limit of quantification.

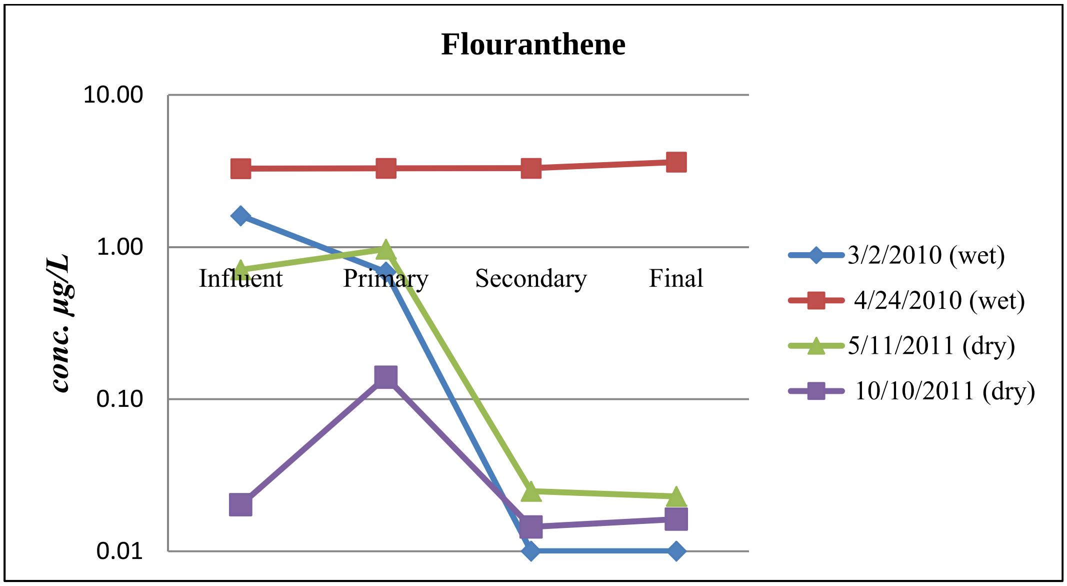

Figure 7. Comparison of wet and dry weather samples for PAH fluoranthene

Mass loadings are based on the flow rate of the treatment plant and the observed concentrations. Mass loads for influent samples were calculated to determine if there is an increase in pollutants entering into the treatment during wet weather. Table 6 summarizes mass loads for two close events. The mass loads for PAHs were all higher for the wet weather events, except for phenanthrene. Phenanthrene was nondetected during wet weather. The rainfall records indicated over an inch of rain occurred on April 24, 2010, but no increase in flow rate at the treatment facility was observed.

Table 6. Mass loads for PAHs

PAHs	Wet weather; 04/24/10 MGD=16.5	Dry weather; 05/14/10 MGD=30.7
	Grams/day	Grams/day
Acenaphthylene	290	14
Acenaphthene	260	120
Phenanthrene	0.0	260
Fluorene	204	190
Anthracene	250	95
Flouranthene	220	61
Pyrene	170	71

CONCLUSIONS

Stormwater only affects the flow rate at the treatment facility during large rainfall events (>1.5 inches). However, the preliminary data shows stormwater infiltration does contribute to the mass load of ECs to the wastewater treatment plant: there were increases in masses for both PAHs and pharmaceuticals during some of the rain events. The PAHs showed higher masses in the influent during wet weather, and were consistent in showing significant reductions during both wet and dry weather. Therefore, the stormwater contributions did not appear to affect treatability of these compounds.

There was more variability in treatment for each pharmaceutical during wet weather. Sulfamethoxazole showed a steady reduction in concentrations, whereas carbamazepine showed no treatment. The difference in treatability may be caused by pharmaceuticals being active in wastewater by conjugation and deconjugation of metabolites, which may increase concentrations in the effluents. Overall, it appears that pharmaceuticals were better removed in the secondary treatment process compared to the other processes.

Seven wet weather samples will be compared to seven dry weather samples at the treatment plant obtained from four locations to separate the benefits of the different unit processes. Final conclusions will be based on the complete data set, but these preliminary data indicate performance as expected, with minimal wet weather effects, although wet weather is shown to be a significant source of some of the ECs.

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