

**Septage Indicator Monitoring in Grand Lake Using Organic
Indicators of Wastewater**

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Project Information:
FY 2006 319(h), EPA Grant # C9-996100-13, Project 9 - *Honey Creek Watershed
Implementation Project*
Septage Indicator Monitoring (Output 9.5.3), Addendum

ABSTRACT

The objective of this study was to investigate septage, partially treated effluent from a septic system, as a contaminant in Grand Lake. Our approach was to identify septage and wastewater contamination by measuring the presence of organic wastewater contaminants (OWCs). Passive samplers were deployed throughout Grand Lake in the fall of 2008 and over the July 4th holiday 2009 in order to contrast the levels of contamination that may occur seasonally as the population around the lake varies. Samplers were deployed in coves that are highly populated, coves that are sparsely populated, in both major tributaries (Elk and Neosho Rivers), and at a location within the lake and outside of the lake that have known input of human sewage. The results of the present study agree with previous reports that have found elevated levels of organic wastewater contaminants in aquatic systems receiving input from municipal wastewater treatment plants. As the population of the lake increased during the July 4th holiday, the concentration of OWCs originating from a municipal sewage input also increased. However, OWC concentrations in developed coves, where septage contamination was of concern, were not different from those detected in undeveloped coves and were much lower than concentrations at sites receiving known inputs of municipal sewage. As such, based on the analytes measured in this study, there was no clear indication of increased septage input in the developed coves of Grand Lake.

INTRODUCTION

The Pensacola Hydroelectric Project impounds the Neosho and Spring Rivers in northeastern Oklahoma to form Grand Lake O' the Cherokees (Grand Lake). This lake covers 18,818 hectares, holds 2.06×10^9 M³ of water, and is the third largest reservoir in Oklahoma with 2,092 km of shoreline (OSE 2004). Lake depth averages 11m with a greatest depth of approximately 50m. The lake spans a total of four Oklahoma counties including Ottawa, Mayes, Delaware, and Craig, while the entire drainage area of the lake covers over 2.5 million hectares and extends across state borders into Arkansas, Kansas, and Missouri (OSU and OWRB 1995). The fact that this watershed spans across state lines results in several different government jurisdictions and United States Environmental Protection Agency (USEPA) regions coordinating issues related to environmental impacts or restoration.

Grand Lake is an extremely valuable natural resource and has fostered considerable economic growth in northeastern Oklahoma. This area is one of the most popular and fastest growing retirement locations in the United States (OSE 2004). During Memorial Day, 4th of July, and Labor Day, the Grand Lake community grows to the third largest in Oklahoma followed only by Oklahoma City and Tulsa (Alberty 2005). While communities surrounding the lake have enjoyed both physical and economic growth due to the popularity of the lake, this popularity has led to extensive development of property close to the shoreline over the entire lake. Grand Lake is one of the few in Oklahoma that allow homes on the waterfront and where nearshore development is considered a factor in the lake's current state of cultural eutrophication (OSE 2004). The objective of this study was to investigate septage, partially treated effluent from a septic system, as a contaminant in Grand Lake. Our approach was to identify septage and wastewater contamination by measuring the presence of organic wastewater contaminants (OWCs).

Organic Wastewater Contaminants (OWCs)

Recent research has demonstrated the occurrence of OWCs such as hormones, pharmaceuticals, and personal care products in wastewater, and in turn, in surface water throughout the country (Kolpin et al. 2002; Heberer 2002, Galloway et al. 2004, Ramirez et al. 2009). OWCs are important to study for a variety of reasons including the potential

to directly cause toxic effects. OWCs such as natural estrogens, synthetic estrogens, and some estrogen-mimicking compounds can cause endocrine disruption in fish and other aquatic organisms. The estrogenicity of sewage effluent has been widely documented (White et al. 1994, Silvia et al. 2002, Fent et al. 2006). For a regional example, male fish collected downstream from the discharge of Stillwater, Oklahoma's municipal sewage treatment plant were found to have high levels of an egg-yolk protein called vitellogenin that should only occur in female fish (Porter and Janz, 2003). This is a strong indicator of feminization of the male fish associated with exposure to estrogens or estrogen-mimicking chemicals. The effects of most pharmaceuticals and personal care products on fish and other organisms are relatively unknown, but recent reports indicating these compounds may accumulate in organisms are troubling (Ramirez et al. 2009). Although only a few examples of toxicity occurring at environmentally-relevant concentrations have been reported thus far, studies aimed at known biological targets of the contaminant are nearly nonexistent (Fent et al. 2006).

Other OWCs, such as caffeine, nicotine, and musks (fragrances) are not likely to occur at levels that will result in toxicity, but are useful indicators that human sewage has entered a water body (Seiler et al. 1999, Buerge et al. 2003). While microbial and nutrient analyses can indicate contamination, the source of the contamination is not conclusive. The presence of OWC indicators in an aquatic system provides a strong line of evidence that sewage is present. By testing for a variety of OWCs that have different potential for transport, it may be possible to fingerprint sources. For example, if a compound does not move well through soil, it may contaminate a water system when released from municipal sewage, but not from septic systems. Furthermore, the presence of indicator OWCs likely indicates that other OWCs that are more likely to cause an environmental effect are present. One of the lessons learned to date on OWC toxicity is that the proximity to sewage and the dilution of the sewage into the receiving water are major determinants of observed effects (Sumpter and Johnson, 2005). By using an indicator list, we can efficiently obtain a relative measure of sewage contamination.

Determining the Presence of OWCs

Although analytical techniques for the measurement of OWCs are available, few laboratories conduct the analyses. (No standardized USEPA methods are currently available for most analytes.) Frequently, scientists attempt to analyze for as many compounds as possible at the lowest detection limits possible, which require the use of several techniques. For example, Kolpin et al. (2002) measured 95 compounds and used three techniques. Cost for just the analytical chemistry involved in this approach is around \$3,000 per sample which can significantly reduce the number of sites that can be sampled.

As an alternative approach, more ubiquitous OWCs such as caffeine or cotinine (a breakdown product of nicotine) can be used as indicators of sewage OWC contamination (Buerge et al. 2003, Glassmeyer et al. 2005). The advantage of this approach is that caffeine and cotinine are present at higher levels than most OWCs and can be analyzed using techniques and protocols that are commonly used for USEPA methods such as gas chromatography / mass spectrometry (for example USEPA 8270). Thus, more laboratories can conduct the analysis on less expensive instrumentation resulting in lower cost per sample. Although this approach has promise, an individual compound is not likely to be representative of all systems. For example, both caffeine and cotinine can biodegrade in biological treatment systems or within streams. Thus, their presence indicates contamination but their absence does not indicate the lack of contamination (Bradley et al. 2007).

The approach developed for this study is a hybrid technique. We have a highly targeted list of 12 analytes that are likely to be present in municipal effluent and septage (Table 1). The compounds also have different mobility and persistence in the environment (Heberer 2002, Galloway et al. 2004, Seiler et al. 1999, Halden and Paull 2005). Thus, some analytes like caffeine will be likely to move larger distances from the source as compared to less mobile analytes like the musk fragrance tonalide. Eight of our compounds are in the top 12 of those most frequently detected in previous surveys for OWCs (Kolpin et al. 2002). Each of the compounds frequently occurs at relative high levels in sewage effluent (>40 ng/L), are amenable to GC analysis, and are likely to occur in effluent from both municipal and on-site sewage treatment systems.

Table 1. List of indicator organic wastewater contaminants used in this study.

Class	Compound	CAS #	Use
Indicators with Expected High Mobility	Caffeine	95789-13-2	Stimulant
	Cotinine	486-56-6	Nicotine Metabolite
	Bisphenol-A	80-05-7	Leaches from Plastics
	Acetaminophen	8055-08-1	Pain/fever relief
	TDCPP [Tri(2,3-dichloropropyl) phosphate]	78-43-3	Flame Retardant
	TCEP [Tris(2-chloroethyl) phosphate]	115-96-8	Flame Retardant
Indicators with Expected Moderate to Low Mobility	Triclosan	3380-34-5	Antimicrobial common in soaps
	Methyltriclosan	4640-01-1	Triclosan metabolite
	Galaxolide [HHCb]	1222-05-5	Musk Fragrance
	Tonalide [ATHN]	1506-02-1	Musk Fragrance
	Estrone	53-16-7	Naturally occurring estrogen
General Fecal Indicator	Cholesterol	57-88-5	Naturally occurring compound

Passive Sampling

The most commonly used method for collection and analysis of water is grab sampling, which only provides data for the moment of sampling. This is less than ideal for compounds that have fluctuating concentrations in the environment due to rain events or periodic releases from a sewage treatment system. In these cases, grab sampling could under- or over-estimate exposure concentrations. Passive integrated samplers, e.g. polar organic chemical integrative samplers (POCIS) used in this study, accumulate contaminants continuously during the exposure period, while allowing little desorption (Alvarez et al. 2004). The continuous sampling process allows detection and identification of chemicals in an integrated manner, providing time-weighted average concentrations, and detection of chemicals that rapidly dissipate or degrade in the environment (Alvarez et al. 2004; Alvarez et al. 2005; Mazella et al. 2008). POCIS samplers have been shown to sample a wide variety of organic compounds with differing chemical properties; thus, they are ideal for many OWCs.

Previous Research on Grand Lake

During the summer of 2007, Oklahoma State University, the Oklahoma Conservation Commission, and the Grand River Dam Authority conducted a screening study in which Polar Organic Integrative Samplers (POCIS) were deployed to detect the presence of organic wastewater contaminants at Grand Lake. A total of 15 POCIS samplers were deployed in Dripping Springs, Hickory Cove, an undeveloped cove, two sites on the main lake body, and at the outfall of the City of Grove municipal waste water treatment plant. Ten organic compounds were initially targeted in this study. The compounds detected included cholesterol (most common analyte found), phenol, Tri (2-chloroethyl) phosphate, coprostanol and nonyl-phenol. The highest number of compounds was detected near the outfall of the Grove WWTP and a similar number of compounds were detected at developed and undeveloped sites. While the overall number of compounds detected was low, these results indicated the presence of some common wastewater contaminants in Grand Lake. The study described in this report builds upon that study by deploying more samplers and reworking the analyte list and techniques to optimize sensitivity and selectivity to human wastewater.

Approach

POCIS samplers were deployed throughout Grand Lake in the fall of 2008 and over the July 4th holiday 2009 in order to contrast the levels of contamination that may occur seasonally as the population around the lake varies. Samplers were deployed in three coves that are highly populated. In addition, samplers were deployed in one cove that is sparsely populated, in both major tributaries (Elk and Neosho Rivers), and at a location within the lake and outside of the lake that have known input of human sewage. This sampling regime provides a measure of OWC concentrations in areas unlikely to be contaminated and in areas known to be contaminated. This provides a reference for the concentrations found within the developed coves, which are the primary focal points for the study.

METHODS

Materials

Neat standards (>98%) of all analytes in Table 1 were purchased from Sigma-Aldrich (St. Louis, MO). All solvents were pesticide or GC/MS grade (Burdick and Jackson, Muskegon, MI, USA)

Passive Samplers

Sampling devices were built using a similar design as previously published (Alvarez et al. 2004, Petty et al. 2004). Samplers are commercially available from Environmental Sampling Technologies (St. Joseph, MO). Briefly, two stainless steel washers sandwich polyethersulfone membranes (Pall Gilman Sciences, Ann Arbor, MI) containing 200 mg HLB packing (Waters Corporation, Milford, NH). Contact to water is available from both sides of the sampler allowing 41 cm² surface area. Samplers were used individually in the calibration study described further below. For field collection, four samplers were deployed as one unit to increase sensitivity and decrease variability. All four samplers were housed in a stainless steel mesh protective container (provided in-kind by the Grand River Dam Authority). Each four-sampler unit was treated as an experimental unit.

Calibration of passive samplers

As part of this project, we calibrated the samplers for all analytes (Table 1) which is necessary to determine water concentrations (Alvarez et al. 2004, Petty et al. 2004, Tagola and Budzinski, 2007, MacCloud et al. 2007). Since water movement, temperature, pH, and ionic strength can all influence the uptake of analytes onto the sampler, we calibrated the samplers based on conditions found in Grand Lake. Water from Grand Lake was transported to the laboratory (insuring pH, ionic strength, and dissolved carbon are similar to lake conditions) and average lake temperatures of the last testing season (July) were used (26°C). Water was exposed to ultraviolet light to reduce microbial populations and decrease biodegradation of analytes prior to use. Additionally, a parallel study using moderately hard laboratory water was performed to allow comparison to literature calibration values (USEPA, 1994).

Two samplers built as described above were placed in 20-L glass aquaria containing 6 L of either Grand Lake or laboratory water. The water was fortified with all

reagents to a concentration of 1000 ng/L using 0.12 ml of methanol as a carrier. Three replicate tanks were used for each water type. In order to match planned field conditions, the samplers were maintained in the aquaria for 28 d. Every third day, a 50% renewal of the test water was conducted in order to maintain chemical concentrations. Twice during the experiment, analyte levels in the exposure water were determined prior to and immediately after a water exchange. We chose to conduct the calibration studies under mixing conditions since none of the sampling sites were deemed to be primarily static. To provide mixing, a stir plate was installed under the aquarium with a 3 cm stir bar within the aquarium and the plate was set to the slowest speed that would result in stable spinning of the stir bar.

Sampling rates were determined as follows:

$$R_s = \frac{\text{Total Mass of Analyte Recovered, ng}}{\text{Concentration in Water, ng/L} \times \text{Time Deployed, d}} \quad \text{Equation 1}$$

To determine the concentration of analytes in water from the concentration in the sampler, the equation can be rearranged as follows:

$$\text{Concentration in Water, ng/L} = \frac{\text{Total Mass of Analyte Recovered, ng}}{R_s \times \text{Time Deployed, d}} \quad \text{Equation 2}$$

Field Deployment

Sites were selected using the concepts described in the Approach section (Table 2). Specific site locations were identified as part of previous work on the lake, which included extensive scouting from the lake and the shore to identify coves that may have septage contamination problems (Burgess, 2008). Samplers were deployed from June 29 – July 27 in the summer of 2009 to capture the July 4th holiday. Samplers were also deployed from September 10th to October 8th 2008. Deployment involved placing the samplers into the protective stainless steel cages and then either chaining these cages to clay chimney tiles which were placed under water or chaining the cages to navigation buoys. Samplers remained in the field for 28 days, except for a few from the Fall 2008 deployment that remained in the field for 50 days (past September 10th) due to problems

with recovery during a period of high water in the lake. All samples that remained longer than 28 days had minimal detections and thus no adjustments were made to the concentration of OWCs found in these samples to account for the additional exposure time. The samplers were retrieved by cutting the cages from the anchor tiles or buoys, removing the samplers from the cages and placing them in sealed steel paint cans on ice for transport back to the laboratory at Oklahoma State University, Stillwater. Samples were stored frozen for up to 90 days before extraction.

Table 2. Sampling sites and number of sampling units per site.

Sample Type	Sites	Number of sampling units deployed and recovered and their placement	
		Fall 2008	Summer 2009
Undeveloped Control	Undeveloped Cove on upper end of lake	Four; one at mouth and 3 at sites inside the cove	Three units; one at the mouth and two at sites within the cove
Known Sewage Input	City of Grove Municipal Sewage Effluent	Duplicate units very near effluent pipe	Duplicate units very near effluent pipe and one 4 m toward center of lake
	Jay Creek	None	One unit downstream from known sewage effluent (City of Jay)
Main Lake	Main body of lake	Two units at different locations	None
River Input	Elk	One unit	One unit
	Neosho	None	One unit
Developed Coves	Hickory Cove	Three units inside cove	Four units; one at mouth and three at sites inside the cove
	Dripping Springs	Three units at sites inside the cove and one site duplicated	Four units; one at mouth and three at sites inside the cove
	Cedar Cove	Four units; one at mouth and three at sites inside the cove	Four units; one at mouth and three at sites inside the cove

Analysis of Passive Samplers and Water

POCIS samplers were disassembled and the HLB resin was gently washed into a vial with methanol. Additional methanol was added to the vial to bring the volume to 10ml. The vials were placed in a sonicator bath for 20 minutes and then allowed to further extract for at least 48 h. The methanol was then filtered to remove the HLB and the extract was evaporated to 1 ml and frozen (-4° C) prior to analysis. Water samples from the calibration study were extracted by solid phase extraction. Briefly, a 200-ml

aliquot of water was passed through a preconditioned HLB extraction cartridge (6 ml canister, 500 mg sorbent; Waters Corporation, Milford, NH). Analytes were eluted from the cartridge using 10 ml of methanol: ethyl ether 1:1. The extract was evaporated to 1 ml and frozen (-4° C) prior to analysis.

In order to adequately measure the selected indicators, two different analysis techniques were needed. Method 1 was used for analytes that are readily analyzed on the GC, while Method 2 targeted analytes that had inadequate volatility or break down on the inlet of the GC. In Method 1, 0.20 ml of extract was evaporated to near dryness and reconstituted in 0.20 ml ethyl acetate. The ethyl acetate was then analyzed using an Agilent 6850 GC coupled with a 5975C MSD detector. Basic parameters that were similar for both methods are listed below. Specifically for Method 1, the ethyl acetate was directly injected into the inlet and caffeine-13C₃ was added to each extract during the extraction process as a surrogate providing a measure of accuracy for each sample. In Method 2, 0.20 ml of extract was evaporated to dryness. In order to create a trimethylsilyl derivative, 0.100 ml pyridine and 0.100 ml of derivatization agent (BFTSA:TMSI, Sigma Aldrich, St. Louis, MO) was added and the mixture was heated to 60°C for 60 minutes. The extract was cooled, evaporated to dryness under a stream of dry nitrogen gas, and reconstituted in 0.400 ml of hexane. This final solution was analyzed via GC/MS. Biphenol A-D6 was added during the extraction process as a surrogate.

For both methods, a standard GC/MS configuration was used: GC inlet 250°C; column- HP-5MS, 30 meters long, 0.25 mm diameter, and 0.25µm film thickness; carrier- 1 ml/minute flow helium; electron ionization (EI); 150°C MS quad; 230°C MS source. Internal calibration for both methods used EPA 8270 standard (PAHs) including anthracene D10, phenanthrene D10, chrysene D10, perylene D10. Internal standards were paired to analytes based on nearest retention time. Analysis was performed using select ion monitoring to improve sensitivity. In order for a concentration to be reported, the quantification ion and two qualifier ions had to be present in the sample and the ratios had to be within 25% of that observed in the standards. The quantitative and qualitative ions are listed in Table 3. Reporting limits were set at a level that was greater than 3x the method detection limit in a clean matrix, within the linear portion of the calibration curve,

and based on the judgment of an experienced analyst to resolve qualitative ions within the environmental matrix found in Grand Lake.

Table 3. Method, ions used for mass spectrometry analysis, and the sampling rate for all analytes. Sampling rate for cotinine could not be determined.

Analyte	Method	Quantitation: Qualitative Ions	POCIS Sampling Rate, ml / d	
			Lab Water	Grand Lake Water
Caffeine	1	194: 109, 82	11 (3)	11 (2)
Cotinine	1	176: 147, 98	--	--
Bisphenol-A	2	357: 358, 372	95 (17)	116 (9)
Acetaminophen	2	223: 181, 166	3.6 (1.5)	3.1 (0.7)
TDCPP	1	381: 383, 191	90 (16)	86 (6)
TCEP	1	249: 250, 205	65 (9)	68 (7)
Triclosan	2	362:347,345	90 (18)	112 (7)
Methyltriclosan	1	302:304, 252	29 (4)	34 (8)
HHCB	1	243: 258, 213	17 (1)	24 (4)
ATHN	1	243: 258, 159	35 (1)	51 (6)
Estrone	2	342: 257, 218	140 (37)	145 (25)
Cholesterol	2	458: 368, 329	5.4 (1.4)	17 (9)

Quality Control

For all analyses, initial calibration curves (r^2 values greater than 0.98), and continuing calibration verification ran at a frequency of 10%, not to exceed 20% deviation from nominal, were monitored to insure quality data. Extraction and procedural efficiency were measured using surrogates in each sample and were always between 50-125%. Procedural blanks (laboratory derived) and trip blanks (field derived) did not have analytes exceeding reporting limits. Laboratory spikes demonstrated precision and accuracy as all fell within the limits of 50-125% of nominal.

RESULTS AND DISCUSSION

Ten of the twelve analytes were measured in the passive samples from at least one field site. Only cotinine and acetaminophen were not present in any samples. The lack of measurement of these compounds is likely tied to poor uptake into the passive sampler or stability in the extract. Although cotinine was stable during quality control procedures, it was rapidly lost during the POCIS calibration study (Table 3) and water

Table 4. Mass of analyte recovered and estimated water concentration based on sampling rates for the fall 2008 sampling event.
 RL=Laboratory reporting limit, WWTP= lake site influenced by direct input from the Grove municipal wastewater treatment plant.

	RL		WWTP		Undeveloped Sites (maximum)		Main Lake		Tributaries (maximum)		Developed (maximum)		Developed (Median)	
	ng	ng/L	ng	ng/L	ng	ng/L	ng	ng/L	ng	ng/L	ng	ng/L	ng	ng/L
Caffeine	20	16	<20	<16	<20	<16	<20	<16	<20	<16	<20	<16	<20	<16
BPA	10	0.80	12	0.92	29	2.2	20	1.5	<10	<0.80	540	41	61	4.7
TDCPP	20	2.1	170	17	33	3.4	22	2.3	<20	<2.1	57	5.9	<20	<2.1
TCEP	20	2.6	220	28	18	2.4	<20	<2.6	<20	<2.6	40	5.2	<20	<2.6
Triclos.	10	0.8	230	18	74	5.9	<20	<2.1	87	6.9	85	6.8	<20	<2.1
MTriclos.	10	2.6	<10	<2.6	<10	<2.6	<10	<2.6	<10	<2.6	<10	<2.6	<20	<2.6
AHTN	10	1.8	35	6	<10	<1.8	<10	<1.8	<10	<1.8	13	2.2	<10	<1.8
Estrone	10	0.60	12	0.74	<10	<0.60	<10	<0.60	<10	<0.60	<10	<0.60	<20	<2.6
Cholest.	30	16	72	37	1300	660	130	66	460	240	660	350	160	86

Table 5. Mass of analyte recovered and estimated water concentration based on sampling rates for the summer 2009 sampling event. RL=Laboratory reporting limit, WWTP= lake site influenced by direct input from the Grove municipal wastewater treatment plant.

	RL		Jay Creek		WWTP		WWTP 4 m Downstream		Undeveloped Sites (maximum)		Tributaries (maximum)		Developed (maximum)		Developed (Median)	
	ng	ng/L	ng	ng/L	ng	ng/L	ng	ng/L	ng	ng/L	ng	ng/L	ng	ng/L	ng	ng/L
Caffeine	20	16	190	150	<20	<16	<20	<16	<20	<16	<20	<16	<20	<16	<20	<16
BPA	10	0.80	54	4.2	16	1.2	<10	<0.77	<10	<0.77	<10	<0.77	19	1.5	12	0.9
TDCPP	20	2.1	450	47	2000	210	650	68	18	1.9	34	3.5	38	3.9	19	2.0
TCEP	20	2.6	104 0	140	1210	160	410	54	14	1.8	17	2.2	70	9.2	14.	1.8
Triclos.	10	0.8	120	9.6	130	10	38	3.0	<10	<0.80	<10	<0.80	14	1.1	11	0.9
MTriclos.	10	2.6	21	5.5	<10	<2.6	<10	<2.6	<10	<2.6	<10	<2.6	<10	<2.6	<10	<2.6
HHCB	10	3.7	960	360	10200	3800	3200	1200	22	8.2	31	12	40	15	24	8.9
AHTN	10	1.8	90	16	760	130	210	36	<10	<1.8	<10	<1.8	<10	<1.8	<10	<1.8
Estrone	20	1.2	<20	<1.2	80	4.9	<20	<1.2	<20	<1.2	<20	<1.2	<20	<1.2	<20	<1.2
Cholest.	30	16	600	320	2500	1300	440	230	2600	1400	320	170	7900	4100	680	360

concentrations were not stable enough to allow for calculations. An overview of the mass of OWCs recovered from the samplers deployed in the field and the estimated water concentrations based on sampling rates is provided in Tables 4 and 5.

Sampling Efficiency

Sampling rates ranged from 11-145 mL/day, with the exception of acetaminophen and cholesterol, which tended to have lower rates (Table 3). The sampling rates are similar in range to those previously reported in the literature. For example, Arditoglou and Voutsas (2008) reported sampling rates of estrone and bisphenol A of 129 and 88 ml/day. We calculated rates of 145 and 116 ml/day for these analytes, respectively (Table 3). In general, sampling rates did not vary between Grand Lake and laboratory water sources, with the exception of higher rates for the two musk fragrances and cholesterol in Grand Lake water. Interestingly, these are three of the least polar analytes (Table 3).

Seasonal Differences

The summer 2009 sampling resulted in much higher concentrations of OWCs in the lake water near the Grove municipal wastewater effluent (Figure 1). This trend was not unexpected as the population of Grove is known to greatly increase over the July 4th holiday (Alberty 2005). It is unclear whether the increase is due to simple increased outflow from the system and thus less dilution by the lake water, an overload of the treatment system resulting in reduced treatment conditions, or a combination. The trend was not as clear for the developed coves as a few sites in fall 2008 had higher concentrations of bisphenol A. However, analytes such as the flame retardants TCEP and TDCPP that are common within the lake and present at high concentration in the WWTP influenced sites were present at similar or higher levels in the summer of 2009. Based on these results and the assumption that as the population of the lake increases, septage contamination is likely to increase, we will base our interpretation of the data primarily on the summer 2009 results.

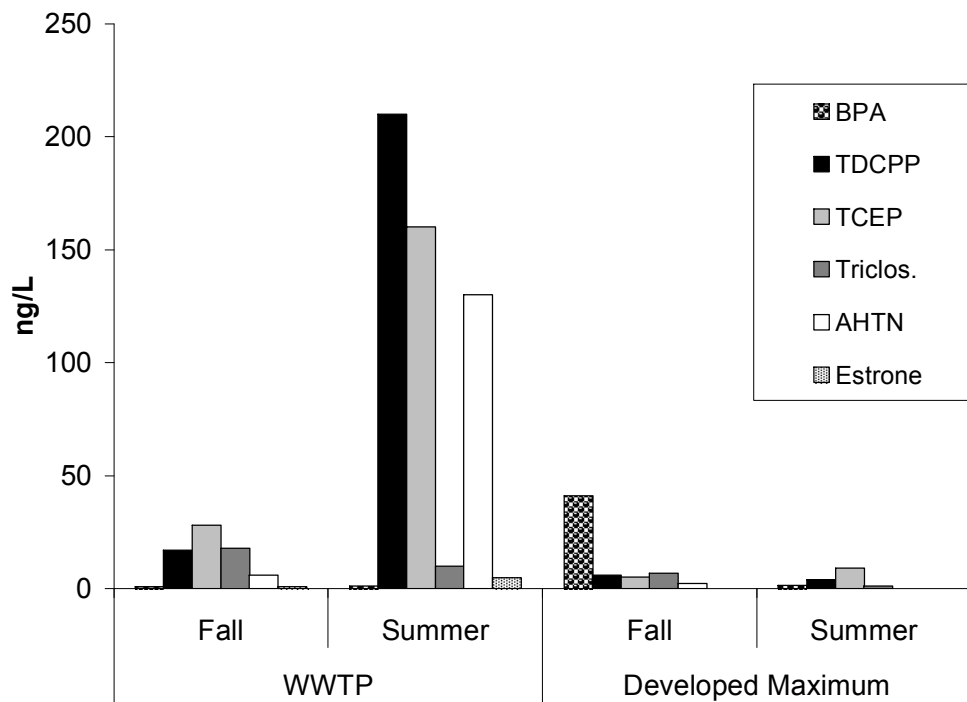


Figure 1. Concentration of OWCs in Grand Lake near the Grove municipal treatment plant and the maximum concentration found in developed coves within the lake by season. WWTP= lake site influenced by direct input from the Grove municipal wastewater treatment plant.

Best Indicators

The greater goal of the project was to compare OWC concentrations in the “positive control” sites (Jay Creek and Grove WWTP) and the “negative control” sites (undeveloped coves) to the concentrations within the developed coves in order to obtain a measure of the level of contamination that is occurring. For this to be successful, a large contrast between concentrations at the positive control sites and negative control site or between the positive control site and the reporting limits is necessary. As shown in Figure 2, the four best analytes in this regard are the two musks HHCb and ATHN and the two flame retardants TDCPP and TCEP. Each was measured at the positive control sites at concentrations more than 50x the concentration found in the undeveloped site or the reporting limit if the compound wasn’t detected. Thus, if septage contamination is entering the lake, significant dilution would be necessary prior to these OWCs being

undetectable or below background levels. For other compounds, such as estrone, even a small amount of dilution would result in a concentration that was below reporting limits. Cholesterol was present at high concentrations in the positive control sites, but was also found in high concentrations in the undeveloped site resulting in little contrast.

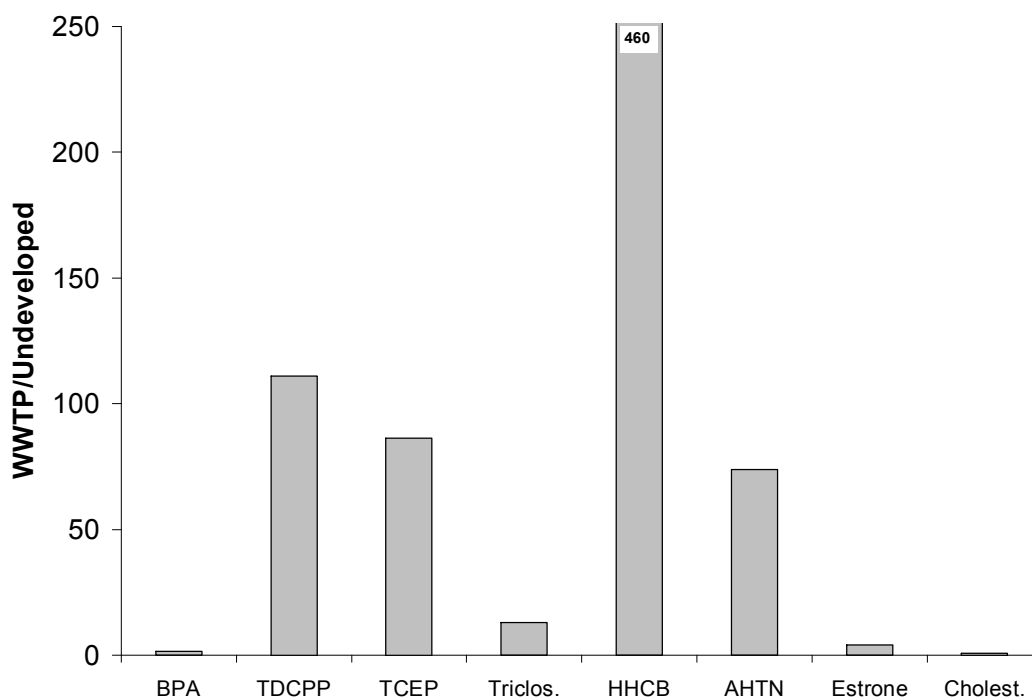


Figure 2. The concentration of lake water near the sewage treatment plant divided by the concentration in water from an undeveloped portion of the lake (or reporting limit). The ratio illustrates the degree of contrast in OWC concentrations between sites serving as positive and negative controls. The greater the ratio, the better the indicator is for discriminating contamination in conditions where dilution is likely.

Comparison of “Developed Coves” to Controls

Based on the prevalence of the four “best indicators”, it is clear that the concentrations in the water within the developed coves is much more similar to the concentrations found in undeveloped coves as compared to the known sources of contamination (Figure 3). The analyte that has the best response in the developed coves is TCEP. It is a flame retardant that is commonly used on furniture, carpet, and children’s pajamas. However, it also used in foams and may be incorporated to materials

used for boats, docks, and life jackets. Thus, its lone presence at low concentrations is not adequate demonstration of sewage contamination. It has also been found in remote regions and may have some input from atmospheric deposition (Regnery and Püttmann 2010).

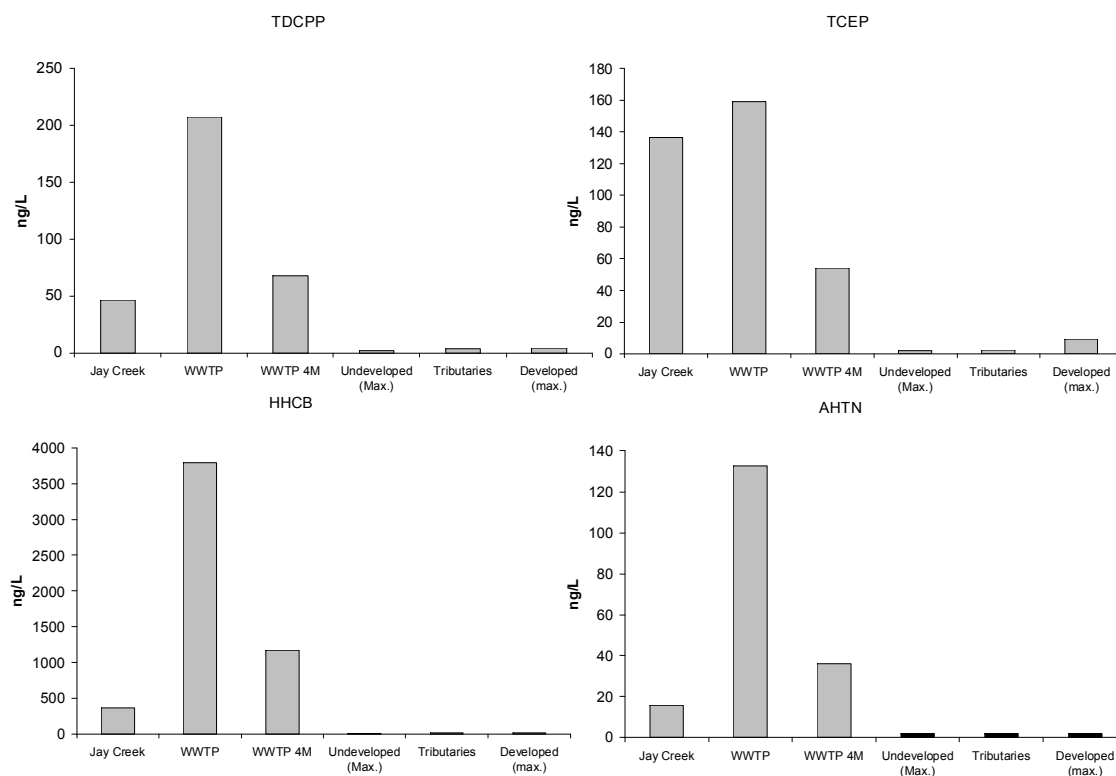


Figure 3. Concentration of four of the most prevalent OWCs at sites that have known sewage contamination (Jay Creek, WWTP, and WWTP 4m down lake), sites that are unlikely to have sewage contamination (undeveloped), and sites that were being tested for the presence of sewage contamination (tributaries and developed coves). The maximum concentration for all samples was reported for the undeveloped, tributary and developed sites to contrast the differences between these sites and the sites that were influenced by WWTP.

CONCLUSIONS

The results of the present study agree with previous reports that have found elevated levels of organic wastewater contaminants in aquatic systems receiving input

from municipal wastewater treatment plants (e.g. Kolpin et al. 2002; Galloway et al. 2004). Elevated summertime OWC levels associated with the Grove WWTP as compared to fall sampling was also observed and indicates a seasonal trend most likely due to a higher population at the lake in the summer months. The present results also highlight the ubiquity of the analytes targeted since detectable levels of most of the chemicals were found in at least one of the sites monitored, including the undeveloped lake sites. Flame retardants and musk fragrances were the most prevalent of the compounds measured. Overall, OWC levels in developed coves were not different from those detected in undeveloped coves. As such, based on the analytes measured in this study, there was no clear indication of increased septage input in the developed coves of Grand Lake. These results agree with those of Burgess (2008) who similarly observed no clear patterns of septic contamination in developed coves of the lake. Some of the chemicals targeted in this study can enter aquatic systems in association with precipitation and/or are components of materials commonly found in the lake (e.g. styrofoam) and these sources are probably more important determinants of whether the chemicals were present than was septic input. In addition, no clear longitudinal trends in OWC levels were observed along the length of Grand Lake, indicating the Neosho and Spring Rivers do not represent major sources of OWCs. This contrasts previous work since Burgess (2008) observed longitudinal trends in nutrient levels and other water quality parameters that indicated a clear influence by these major tributaries of the lake. Higher levels of trace metal contaminants have also been observed in the upper portion of Grand Lake (near the confluence of the Neosho and Spring Rivers) as compared to near the dam which has been attributed to input from the rivers that is derived from the Tar Creek Superfund site (OWRB 1995).

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