Results of a Screening Analysis for Organic Wastewater Contaminants in Treated Wastewater Effluent from Four Wastewater Reclamation Facilities and Two Surface Water Sites on Sweetwater Branch Alachua County, Florida

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Executive Summary

Alachua County Environmental Protection Department (ACEPD) conducted a screening analysis for pharmaceuticals and personal care products (PPCPs), perfluorinated compounds (PFCs), polybrominated diphenyl ethers (PBDE), alkylphenols, trace metals, chlorinated pesticides, and semi-volatile organic compounds (SVOCs) in Sweetwater Branch and in effluent from four wastewater reclamation facilities (WRF) in Alachua County. The goal of the analysis was to assess the types and concentrations of organic wastewater contaminants (OWCs), which include pharmaceutical and personal care products (PPCPs), endocrine disrupting contaminants (EDCs), and perfluorinated compounds (PFCs), in wastewater effluent and in Sweetwater Branch.

The project consisted of a preliminary analysis of Sweetwater Branch downstream of the GRU Main Street Water Reclamation Facility in February 2009 and a second more thorough analysis of wastewater effluent and its possible influence on surface waters. The second phase of this study included analysis of effluent from four WRF and sites upstream and downstream of the treated wastewater effluent discharge point into Sweetwater Branch in September 2009. The four WRFs include those of the City of High Springs, University of Florida, and Gainesville Regional Utilities' (GRU) Main Street and Kanapaha Facilities.

A number of PPCPs and EDCs were detected in Sweetwater Branch at both sampling locations and on both occasions as well as in the effluent from the four WRFs tested. The PPCPs and EDCs detected were atrazine (an herbicide), bisphenol A (a plasticizer), caffeine (a stimulant), N,N-diethyl-meta-toluamide (DEET, an insect repellent), diazepam (a muscle relaxer), diclofenac (an anti-inflammatory), fluoxetine (an antidepressant), iopromide (a medical contrast agent), meprobamate (an anti-anxiety drug), phenytoin (an antiepileptic), sulfamethoxazole (an antibiotic), and salicylic acid (a skin care product). Eleven of these twelve compounds were reported to be present in surface water or groundwater in other studies of OWCs. The distribution, nature, and persistence of the compounds in Sweetwater Branch are similar to those described in other surface waters in the United States and discussed in this report.

Perfluorinated compounds (PFCs) were found in Sweetwater Branch upstream and downstream of the GRU Main Street WRF discharge. In February and September 2009 ten PFCs were detected downstream of the GRU Main Street WRF. Eight PFCs were detected in samples upstream of the facility on Sweetwater Branch. In general, the concentrations of PFCs upstream of the treated effluent entry point were lower, sometimes by almost an order of magnitude, than levels downstream of the discharge. PFCs were detected in all treated wastewater samples. No polybrominated diphenyl ethers (PBDEs) or alkylphenols were detected in the samples from Sweetwater Branch or in effluent from the four WRFs sampled. The absence of detectable PBDEs was most likely due to sorption to sediments or solids. The absence of alkylphenols was likely due in part to the higher laboratory detection and reporting limits for these compounds.

At the present time ACEPD does not plan any additional sampling of OWCs in treated wastewater effluent or surface waters.

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List of Acronyms and Abbreviations

ACEPD	Alachua County Environmental Protection Department
BPA	Bisphenol A
DO	Dissolved Oxygen
EDC	Endocrine disrupting contaminant
FAC	Florida Administrative Code
FDEP	Florida Department of Environmental Protection
GRU	Gainesville Regional Utilities
MDL	Minimum detection limit
MGD	Million gallons per day
µg/L	Microgram per liter
µS/cm	Microsiemens per centimeter (specific conductance reporting unit)
ng/L	Nanogram per liter
OWC	Organic wastewater contaminant
PFC	Perfluorinated compound
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctylsulfonic acid
PPCP	Pharmaceuticals and personal care product
PQL	Practical quantitation limit
SU	Standard Units (pH reporting unit)
SVOC	Semi-volatile organic compound
TCEP or Tris	Tris (1,3-dichloro-2-propyl) phosphate
UF	University of Florida
WRF	Water reclamation facility (wastewater treatment plant)

1.0 Introduction and Purpose

Endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) are increasingly documented in surface water and groundwater in the U.S. and throughout the world. Potential and known EDCs include pesticides, synthetic hormones, plasticizers and detergent metabolites, such as nonylphenols. PPCPs are a broad group of compounds consisting of many types of prescription drugs (e.g. analgesics, lipid regulators, stimulants, synthetic hormones, anti-inflammatories, and antibiotics, both human and veterinary). Additional compounds including antimicrobials, plasticizers, flame retardants, and polymer coatings (e.g. Teflon) fall into the broader category of organic wastewater contaminants (OWCs), which also include EDCs, PPCPs, and perfluorinated compounds (PFCs). Major sources of these OWCs are concentrated animal feeding operations and domestic sewage treatment and disposal (Daughton and Ternes, 1999). In the natural aqueous environment these compounds are often found at microgram or nanogram per liter (µg/ or ng/L) concentrations.

The purpose of this investigation was to identify and quantify OWCs in treated wastewater effluent and in Sweetwater Branch, which receives treated wastewater effluent. This study was expanded following a preliminary evaluation of the OWCs concentrations in Sweetwater Branch downstream of the Gainesville Regional Utilities (GRU) Main Street Water Reclamation Facility (WRF). Based on the identified compounds found in the downstream section of Sweetwater Branch, further sampling plans were developed to evaluate the presence of OWCs in wastewater effluent at local wastewater reclamation facilities and to further evaluate Sweetwater Branch. Preliminary sampling of Sweetwater Branch downstream of the GRU Main Street WRF discharge indicated the presence of 15 EDCs and PPCPs and 10 PFCs. The subsequent sampling was conducted in September 2009 and included analyses of effluent from four WRFs: City of High Springs, University of Florida, GRU Main Street and GRU Kanapaha. Samples were also collected and analyzed from two sites on Sweetwater Branch, one upstream and one downstream of the GRU Main Street WRF.

2.0 Background of Organic Waste Contaminants

Recent literature reports that OWCs have been detected in domestic and agricultural wastewater effluents, surface water (upstream and downstream of known wastewater discharges), groundwater, and drinking water supplies (Daughton and Ternes, 1999; Kolpin *et al.*, 2002; Kolpin *et al.*, 2004; Chen *et al.*, 2006; Conn *et al.*, 2006; Karthikeyan and Meyer, 2006; Benotti *et al.*, 2009). The presence of OWCs in the environment is related to the nature of the compounds, the frequency and amount of use, seasonality, the type of waste treatment process used, and the environmental setting of the discharge (Kolpin *et al.*, 2002; Vieno *et al.*, 2005; Chen *et al.*, 2006; Conn *et al.*, 2006; Gurr and Reinhard, 2006). In the environment degradation rates and pathways, sorption, biological action, and other factors control the overall presence of these compounds. In surface water systems specifically, flow rate, reach length, water depth, temperature, mixing, turbulence, exfiltration, and infiltration are important factors in the fate of OWCs (Gurr and Reinhard, 2006). Some compounds, such as caffeine, lipid regulators, carbamazepine (anti-seizure), and x-ray contrast media, are ubiquitous and can persist in the environment for up to 23 weeks (Daughton and Ternes, 1999; Kolpin *et al.*, 2002; Chen *et al.*, 2006; Conn *et al.*, 2006; Benotti *et al.*, 2009).

Initial studies of OWCs in the environment were focused on surface water and wastewater but now have expanded to groundwater and drinking water sources. Kolpin *et al.* (2002) evaluated concentrations of 95 OWCs in surface waters throughout the U. S. during 1999-2000, finding OWCs in 80% of the streams sampled in the study. There is an increase in detection of these compounds downstream of wastewater discharges as analytical methods are refined and reporting limits lowered (Kolpin *et al.*, 2004; Glassmeyer *et al.*, 2005; Conn *et al.*, 2006; Benotti *et al*., 2009). Detergent metabolites, steroids, and various nonprescription drugs were found in the highest concentrations and with the greatest frequency (Kolpin *et al.*, 2002). Plasticizers and the insect repellant DEET were found at high frequencies (Kolpin *et al.*, 2002).

Septic tank system effluent and shallow groundwater in proximity to drainfields (leach fields) have been found to also contain OWCs (Godfrey *et al.*, 2007). Just as with WRFs, source characteristics and level of septic tank system treatment influenced observed concentrations of OWCs; septic tanks systems with aerobic treatment were reported to have an increased removal efficiency of OWCs (Conn *et al.*, 2006).

Recognized as emerging contaminants in the late 1990s, considerable research has been conducted to assess and evaluate OWCs. These constituents are typically found at concentrations of less than 1 µg/L, with many present at low ng/L levels. Even at ng/L concentrations there are concerns for ecological receptors, including exposing aquatic life to synthetic estrogens, as fish are especially sensitive to this exposure (Daughton and Ternes, 1999; Dorne *et al*, 2007). The antidepressant fluoxetine has been reported to be toxic to some phytoplankton species (Dorne *et al*, 2007). Schwab *et al.* (2005) report that human exposure to active pharmaceutical ingredients in drinking and surface waters is generally classified as "below no effect concentrations" because safe exposure levels are related to therapeutic doses; additionally, many of the compounds tend not to bioaccumulate through fish due to their ionic nature. Schwab *et al*. (2005) report no

"appreciable human health risk" from 26 active pharmaceutical ingredients evaluated in surface and drinking water.

OWCs have also been observed in groundwater and drinking water, usually at much lower concentrations than are seen in wastewater or surface water and elevated concentrations can be used as indicators of wastewater contamination in wells (Johnson *et al.*, 2004; Glassmeyer *et al.*, 2005; Seiler *et al.*, 1999). Drinking water supplies, especially those from surface waters, have been found to contain OWCs (Chen *et al.*, 2006; Benotti *et al.*, 2009). Sample filtration and analytical detection and reporting limits also play a role in the observation of OWCs (Kolpin *et al.*, 2002). Some of the compounds may adsorb to particulates, which are removed through filtration and reduces their concentrations in treated drinking water (Benotti *et al.*, 2009). Benotti *et al.* (2009) reported the eleven most frequently detected OWCs in drinking water supply were atenolol (beta-blocker), atrazine (herbicide), carbamazepine (anti-seizure), estrone (estrogen), gemfibrozil (lipid regulator), meprobamate (anti-anxiety), naproxen (anti-inflammatory), phenytoin (anti-epileptic), sulfamethoxazole (antibiotic), Tris(1,3-dichloro-2-propyl) phosphate (TCEP or "Tris") (flame retardant), and trimethoprim (antibiotic). The majority of these constituents were detected at low concentrations, < 10 ng/L, and the concentrations of OWCs in the finished drinking water was correlated to the type of chemical oxidant used for disinfection (Benotti *et al.*, 2009). As analytical methods improve and reporting limits decrease there has been an increasing variety of OWCs found in surface and groundwater.

Natural attenuation and degradation mechanisms occur in the environment and may potentially reduce concentrations or eliminate the occurrence of OWCs as they move away from source waters. Processes known or believed to be important in reducing OWCs in surface waters include dispersion and dilution, volatilization, sorption (to solids), photolysis, biodegradation, and biotransformation (Loffler *et al.*, 2005; Gurr and Reinhard, 2006). Sorptive processes may include or be influenced by adsorption to suspended sediments, settling velocities, organic carbon content of the sediments, pH, and cation exchange capacities. Tixier *et al.* (2003) report phototransformation as a primary process for elimination of diclofenac (anti-inflammatory) and biodegradation being important for breakdown of ketoprofen and naproxen (both anti-inflammatories). Gurr and Reinhard (2006) described biodegradation and sorption as primary mechanisms for attenuation of estrogenic OWCs. Matamoros *et al.* (2005) evaluated removal efficiency of selected OWCs in wetland systems, and suggested that depth of water was important to the oxidative breakdown of compounds such as ibuprofen. Reductions in carbamazepine concentrations were likely related to sorption to organic material (Matamoros *et al.* 2005). Loffler et al. (2005) also observed that many of the more recalcitrant compounds sorbed to sediments, which is likely a function of the sediment's organic carbon content.

3.0 Sampling Locations and Parameter Coverage

Following preliminary analyses from one site on Sweetwater Branch, four WRFs and two sites on Sweetwater Branch were selected to evaluate OWCs and 22 selected metals (trace metals and major cations), commonly observed in wastewater effluent (Appendices A and B). The WRFs included the City of High Springs, the University of Florida and two municipal facilities operated by GRU, the Main Street and Kanapaha facilities. The WRFs were selected to cover a variety of treatment capacities, treatment types and effluent disposal methods (Table 1). The locations of the WRFs within Alachua County are shown in Figure 1.

Samples were also collected and analyzed from two sites on Sweetwater Branch, one upstream (SWBLF) and one downstream (SWB331) of the GRU Main Street facility (Figure 2). This also allows comparison of the February 2009 and September 2009 data, since the sample site downstream of the GRU Main Street facility was sampled during both events.

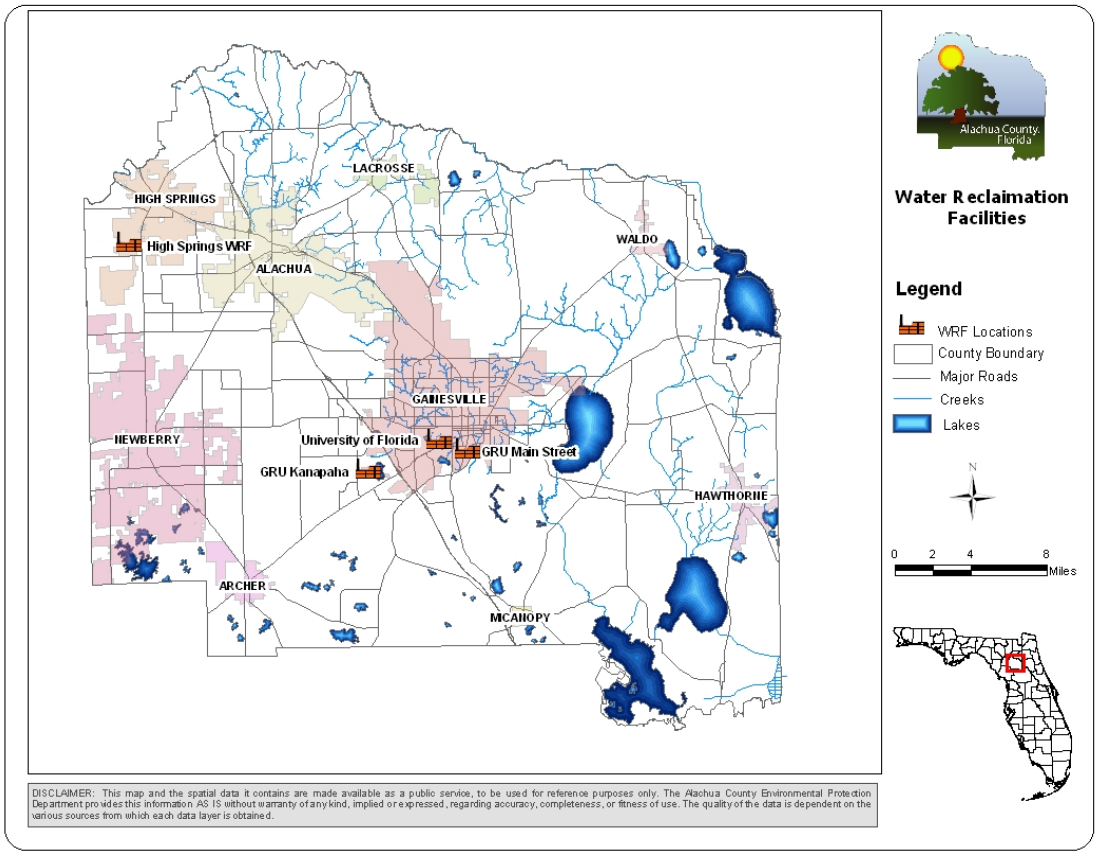

Figure 1. Locations of selected WRFs where effluent samples were collected.

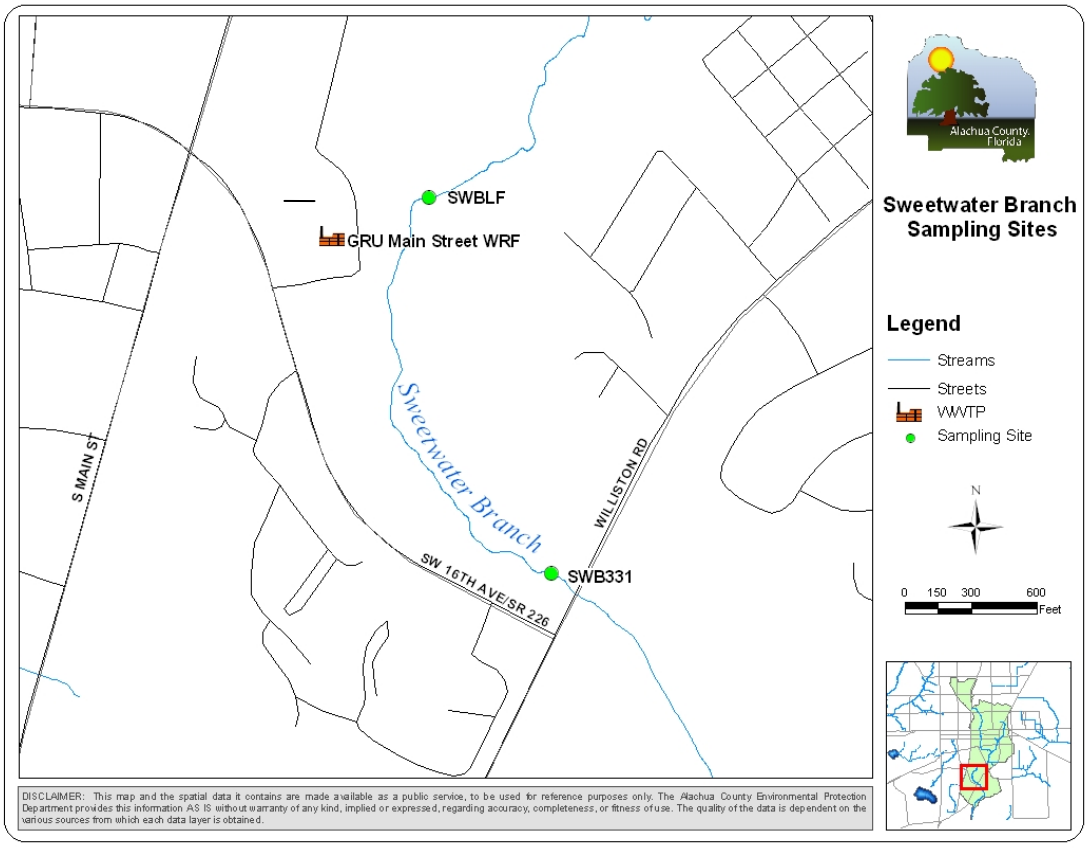

Figure 2. Location of surface water sampling stations on Sweetwater Branch upstream (SWBLF) and downstream (SWB331) of the GRU Main Street facility.

Table 1. WRFs flow and type of wastewater treatment.

WRF	Permitted Average Daily Flow (in MGD)	Type of Treatment	Effluent Disposal
City of High Springs	0.24 MGD	Ludzak-Ettinger activated sludge plant	Land application (spray irrigation)
University of Florida	3.0 MGD	Advanced Wastewater treatment (AWT) plant utilizing Kruger Process (phased isolation oxidation ditch)	3.0 Reuse and underground injection; 0.943 mg reuse reported for 2008
GRU Main Street	7.50 MGD	Advanced secondary wastewater treatment facility	5.5 MGD surface water discharge* (Sweetwater Branch)
GRU Kanapaha	10.00 MGD	Modified Ludzak-Ettinger extended aeration activated sludge treatment process with pre-denitrification biological nitrogen removal	6.890 MGD underground injection and 3.082 MGD reuse reported for 2008

*GRU Main Street Facility was not at 7.5 mgd permitted capacity.

Analyses conducted for both sampling events included field parameters, semi-volatile organic compounds (SVOCs), chlorinated pesticides, metals (total recoverable) and select groups of OWCs (Table 3). Chlorinated pesticides/PCBs, SVOCs, and metals were analyzed by TestAmerica Laboratories, Inc through TestAmerica Tallahassee. A full list of analytes with analytical methods and reporting limits is presented in Appendix A. The OWCs chosen for analyses were those that could be analyzed at µg or ng/L levels by a commercial laboratory using standard methodologies; Columbia Analytical Services, Inc. (CAS) in Kelso, Washington conducted the sample analyses. Five groups of CAS standard analytes were chosen for the trace organic screening analyses, Groups 1 and 2 EDC and PPCPs, Group 3 perfluorinated compounds (fluoropolymer precursors), Group 4 polybrominated diphenyl ethers (PBDEs), and Group 5 alkyphenols (including nonylphenols). A summary of methods is presented in Table 2. A full list of compounds with analytical methods and reporting limits is presented in Appendix B. In the second sampling (September 2009) quality assurance samples were collected, one field duplicated and one field blank. The replicate sample was obtained from the University of Florida wastewater reclamation facility for all constituents analyzed.

Table 2. Analysis analytes grouped by analytical method and type of chemical compound.

Chemical Compound Group	Laboratory Analytical Group	Instrumental Method	Analytical Method	Units/ Reporting Limits
Field Measurements	Not Applicable	Various*	Various*	Various
Semi-volatile Organic Compounds (SVOCs)	Not Applicable	GC/MS	EPA Method 625	µg/L
Organochlorine Pesticides/PCBs	Not Applicable	GC	EPA Method 608	µg/L
Metals	Not Applicable	ICP	EPA 200.7	µg/L
EDC/PPCP	CAS Groups 1 & 2	LC/MS/MS	EPA Method 1694M	ng/L
Perfluorinated Compounds (fluoropolymer precursors)	CAS Group 3	LC/MS/MS	SOC-PFC	ng/L
Polybrominated Diphenyl Ethers (PBDEs)	CAS Group 4	GC/MS/SIM	EPA Method 8270C	ng/L
Alkyphenols	CAS Group 5	GC/MS/SIM	ASTM-D7065-06M	µg/L

* Field measurements collected with YSI 556 multi meter and Hach 2100 P portable turbidimeter following FDEP Standard Operating Procedures set forth in DEP SOP-001/01, 12/3/08.

4.0 Results and Discussion

4.1 Preliminary Samples from Sweetwater Branch February 2009

The sample site that was selected for preliminary screening analysis of OWCs, SWB331, is located on Sweetwater Branch downstream (south) of the GRU Main Street WRF (Figure 2.) and upstream of Williston Road, US Highway 331. The GRU Main Street WRF discharges an average of 5.5 to 6.0 MGD of treated wastewater to Sweetwater Branch (ACEPD, 2007; Hutton, 2008). Analysis of the data from the stream gage at Williston Road, based on median flows, suggests that the GRU Main Street WRF contributes approximately 79% of the total flow to the creek at that site (ACEPD, 2007).

4.1.1 Field Parameters, Metals and Priority Pollutant Organics

Overall water quality for conventional field parameters (temperature, dissolved oxygen (DO), pH, and conductivity) was as expected. Field specific conductance, 740 µS/cm, pH, 7.64 SU, and DO 9.78 mg/L were above background levels for ambient surface waters, in part due to the reclaimed water entering the creek. No SVOCs or organochlorine pesticides were detected in samples collected from downstream the GRU Main Street WRF, site SWB331on Sweetwater Branch. Metals concentrations (trace metals and major cations listed in Appendix A) were generally low, with only calcium, magnesium, potassium, iron, zinc and sodium detected above the analytical method reporting limit.

4.1.2 Organic Wastewater Contaminants (OWCs)

Fifteen compounds in Groups 1 and 2, EDCs and PPCPs, and ten compounds in Group 3, perfluorinated compounds (fluoropolymer precursors), were detected in the samples collected from downstream the GRU Main Street WRF (SWB331) on Sweetwater Branch at ng/L concentrations. Table 3 presents a listing of the compounds in these groups and the concentrations at which they were detected. None of the compounds in Group 4, polybrominated diphenyl ethers (PBDEs), or Group 5, alkylphenols, were detected. This latter group of compounds was analyzed at µg/L concentrations; lower detection limits may have shown these compounds to be present.

Table 3. Results of organic wastewater contaminants analysis for Sweetwater Branch downstream the GRU Main Street WRF (SWB331), February 2009.

Chemical Compound	Use	Sample Result	Units	Group
Atrazine	Herbicide	2.6	ng/L	1 and 2
Bisphenol A	Industrial Chemical – Plasticizer	22	ng/L	1 and 2
Caffeine	Stimulant	41	ng/L	1 and 2
Carbamazepine	Anti-seizure	330	ng/L	1 and 2
DEET	Insect Repellent	110	ng/L	1 and 2
Diazepam	Muscle Relaxer	1.9	ng/L	1 and 2
Fluoxetine	Antidepressant	27	ng/L	1 and 2
Gemfibrozil	Lipid Regulator	36	ng/L	1 and 2
Iopromide	Contrast Enhancer	170	ng/L	1 and 2

Meprobamate	Anti-anxiety	35	ng/L	1 and 2
Phenytoin	Antiepileptic	180	ng/L	1 and 2
Sulfamethoxazole	Antibiotic	110	ng/L	1 and 2
Pentoxifyline (Pentoxifylline)	Improve Blood Flow	2.3	ng/L	1 and 2
Methadone	Opiate	11	ng/L	1 and 2
Salicylic Acid	Skin Care	320	ng/L	1 and 2
Perfluoropentanoic Acid	Fluoropolymer Precursor	4.6	ng/L	3
Perfluorohexanoic Acid	Fluoropolymer Precursor	16	ng/L	3
Perfluoroheptanoic Acid	Fluoropolymer Precursor	5.2	ng/L	3
Perfluorooctanoic Acid (PFOA)	Fluoropolymer Precursor	37	ng/L	3
Perfluorononanoic Acid	Fluoropolymer Precursor	22	ng/L	3
Perfluorodecanoic Acid	Fluoropolymer Precursor	4.7	ng/L	3
Perfluoroundecanoic Acid	Fluoropolymer Precursor	0.89	ng/L	3
Perfluorobutanesulfonic Acid (Perfluorobutane Sulfonate or PFBS)	Fluoropolymer Precursor	5.4	ng/L	3
Perfluorohexylfulfonic Acid (Perfluorohexane Sulfonate or PFHxS)	Fluoropolymer Precursor	240	ng/L	3
Perfluorooctylsulfonic Acid (Perfluorooctane Sulfonate or PFOS) (in Scotchguard)	Fluoropolymer Precursor	170	ng/L	3

EDCs and PPCPs found in the highest concentrations (above 100 ng/L) were carbamazepine, salicylic acid, phenytoin, iopromide, N,N-diethyl-meta-toluamide (DEET), and sulfamethoxazole (Table 3). The detection of these compounds compares favorably with those reported in the literature (Kolpin *et al.*, 2002, Kolpin *et al*., 2004, Benotti *et al.*, 2009, Table 4). Many of the compounds detected in samples from downstream of the GRU Main Street WRF on the Sweetwater Branch were also found in surface waters in other studies including: bisphenol A, caffeine, carbamazepine, fluoxetine, gemfibrozil and sulfamethoxazole (Kolpin *et al.*, 2002, Kolpin *et al*., 2004, Benotti *et al.*, 2009). The plasticizer bisphenol A and the antibiotic sulfamethoxazole were common to Kolpin *et al.* (2002), Kolpin *et al*. (2004) Benotti *et al.* (2009) and the downstream site on Sweetwater Branch from this study (Table 4).

Table 4. Comparison of EDCs and PPCPs (Group 1 and 2) found in the preliminary screening analysis for Sweetwater Branch (February 2009) and those detected in selected other studies.

Chemical Compound	**Alachua County Sweetwater Branch (n=1) February 2009**	**U.S. Streams 139 Stream Sample Sites (n=70 to 85) Kolpin *et al.*, 2002**		**Iowa Streams 23 Stream Sites under Normal and Low Streamflow (n=23) Kolpin *et al.*, 2004**		**U.S. Source Water for Drinking 13 Locations (n=19) Benotti *et al.*, 2009***	
	Single Sample (ng/L)	**Median (ng/L)**	**Max. (ng/L)**	**Normal Flow Max. (ng/L)**	**Low Flow Max. (ng/L)**	**Median (ng/L)**	**Max. (ng/L)**

Atrazine	2.6	NM	NM	NM	NM	32	870
Bisphenol A	22	140	12,000	88	740	6.1	14
Caffeine	41	100	5,700	36	1,390	NM	NM
Carbamazepine	330	NM	NM	8.0	263	4.1	51
DEET	110	NM	NM	NM	NM	85	110
Diazepam	19	NM	NM	NM	NM	0.43	0.47
Fluoxetine	27	12	12	ND	ND	0.8	3
Gemfibrozil	36	48	790	ND	ND	2.2	24
Iopromide	170	NM	NM	NM	NM	NM	NM
Meprobamate	35	NM	NM	NM	NM	8.2	73
Phenytoin	180	NM	NM	NM	NM	5.1	29
Sulfamethoxazole	110	150	710	ND	63	12	100
Pentoxifyline (Pentoxifylline)	2.3	NM	NM	NM	NM	NM	NM
Methadone	11	NM	NM	NM	NM	NM	NM
Salicylic Acid	320	NM	NM	NM	NM	NM	NM

NM = Not Measured
ND = Not Detected
* Twelve surface water sources and one ground water source

The concentrations of EDCs and PPCPs observed in Sweetwater Branch samples were typically within one order of magnitude of the median values in comparison to the studies listed in Table 4. Some concentrations were closer to the maximum values reported in the literature. Data from Kolpin *at el.* (2004) show large variations in concentrations of EDCs and PPCPs with flow; however variations in flow were not examined in this study (Table 4). Wide ranges of concentrations are not unexpected and can be attributed to many factors; for example, Vieno *et al*. (2005) found levels of selected pharmaceuticals in river water were three to five times higher in the winter than in the summer. Carbamazepine, found in Sweetwater Branch samples had a concentration of 330 ng/L which was above the median reported values for similar studies (Kolpin *et al.* 2002; Kolpin *et al*. 2004; Benotti *et al.* 2009), but was similar to the maximum reported under low flow conditions by Kolpin *at el.* (2004). The antidepressant, fluoxetine, and lipid regulator, gemfibrozil, both found in Sweetwater Branch were also reported to be present at similar concentrations in other studies (Kolpin *et al.* 2002, Kolpin *et al*. 2004 Benotti *et al.* 2009, and Table 4). The antimicrobial agent, triclosan, was not detected; this was unexpected because of its ubiquitous nature in hand soaps. Similarly, triclosan was not detected at high or normal flow periods in the Iowa stream study (Kolpin *et al.*, 2004). Another antimicrobial skin care product, salicylic acid, occurred in samples from the Sweetwater Branch site downstream from the GRU Main Street WRF. The presence of a broad range of compounds, including those that persist, is a good indication that these EDC and PPCP data are reliable.

Ten of the eleven PFCs (Group 3) were reported to be present in the water sample from Sweetwater Branch downstream of the GRU Main Street WRF (Table 4). The PFCs in the highest concentration, 170 ng/L, were perfluorooctylsulfonic acid (PFOS); the total concentration of the remaining nine PFCs was 107.79 ng/L. These compounds are common in the human influenced environment; they are used in commercial coatings, fire fighting foams and wetting agents (Andersen *et al.*, 2008). There are Provisional

Health Advisories for drinking water containing PFCs of 400 ng/L for perfluorooctanoic acid (PFOA) and 200 ng/L for perfluorooctysulfonic acid (PFOS) (Lindstrom *et al.*, 2009). PFCs are recalcitrant compounds, reportedly due to the carbon-fluorine bond, with the potential to bioaccumulate (Andersen *et al.*, 2008). None of the PFCs detected in Sweetwater Branch site exceeded applicable drinking water health advisories.

None of the Group 4 polybrominated diphenyl ethers (PBDEs) analyzed were detected in the samples from Sweetwater Branch downstream of the GRU Main Street WRF. These organobromine compounds are used in paints, plastics, foam padding, textiles, carpet, and various other household products as well as flame retardants (Siddiqi *et al.*, 2003). They reportedly have very low water solubility and volatility, leading to accumulation in sediments, soils, and other solids (Siddiqi *et al.*, 2003; Lindstrom *et al*, 2009).

The final groups of OWCs analyzed in the samples from Sweetwater Branch were the alkylphenols (Group 5). This group included 4-tert-octylphenol, grouped nonylphenols, and bisphenol A. Nonylphenols are used in detergents as surfactants and as emulsifiers in cleaning products, paints, and pesticides. Bisphenol A or BPA and 4-tert-octylphenol, although not as common as the nonylphenols, are chemicals used in production of polycarbonate plastics, epoxy resins, and nonionic surfactants (Calafat *et al*. 2008) Although these compounds are thought to be ubiquitous in wastewater; they were not detected at this sampling date, possibly due to the high detection and reporting limit for these compounds. Like PCBs, nonylphenols are closely related and difficult to separate analytically. The CAS method used (ASTM D7065-06M) for the analysis of nonylphenols is generally used for National Pollutant Discharge Elimination System (NPDES) reporting purposes, and was not developed for scientific evaluations of individual nonylphenols (Grindstaff, 2009). To further evaluate the presence of nonylphenols, CAS recommended using a more specific analytical method. This option presents difficulties because one must determine which specific (or individual) nonylphenol should be analyzed. Lee *et al.* (2004) reported the presence of *para*-nonylphenol in the Red River and in finished drinking water. Kolpin *et al*. (2002) reported the presence of five different nonylphenols at frequencies of 23.5 to 50% in U.S. streams with median concentrations between 1 and 0.1µg/L. Without the use of more sophisticated analytical techniques, it is not be possible to evaluate the presence of nonylphenols in reclaimed water or in Sweetwater Branch.

4.2 Effluent from four wastewater reclamation facilities (WRFs) in Alachua County

4.2.1 Field parameters, Selected Metals and Priority Pollutant Organics

No field parameters were measure as part of the WRF sampling. Relatively few priority pollutant organic compounds, chlorinated pesticides or trace metals were detected in the WRFs effluent from any of the four treatment plants. The trace metals and priority pollutant organics detected in the WRFs effluent are reported in Table 5.

Table 5. Detectable metals and priority pollutant organics in four WRFs in Alachua County, September 2009.

Treatment Plant	Chemical Compound(s) Detected	Concentration (µg/L)*	Standard or Criteria (µg/L)
City of High Springs	Barium Dieldrin Heptachlor	0.0058 0.0000045 0.0000031	2.0 µg/L Primary DW Standard** 0.002 µg/L GW Criteria# 0.4 µg/L Primary DW Standard
University of Florida	Barium	0.0096	2.0 µg/L Primary DW Standard
GRU Main Street	Barium Silver	0.011 0.0012	2.0 µg/L Primary DW Standard 100 µg/L Secondary DW Standard##
GRU Kanapaha	Barium Dieldrin	0.0034 0.0000045	2.0 µg/L Primary DW Standard 0.02 µg/L GW Criteria

*All reported concentrations are estimated, between the MDL and PQL
**State of Florida Primary Drinking Water Standard 62-550 FAC (2/16/12)
#State of Florida Groundwater Cleanup Target Levels Chapter 62-777 FAC (4/17/12)
##State of Florida Secondary Drinking water Standard Criteria Chapter 62-550 FAC (2/16/12)

4.2.2 Organic Wastewater Contaminants (OWCs)

Twelve compounds in Groups 1 and 2, EDCs and PPCPs, and 11 compounds in Group 3, PFCs (fluoropolymer precursors), were detected in the WRFs effluent at µg/L concentrations. A listing of the compounds in these groups that were detected is presented in Table 6. Five compounds, N,N-diethyl-meta-toluamide (DEET, an insect repellent), diazepam (a muscle relaxer), fluoxetine (an antidepressant), meprobamate (an anti-anxiety drug), and phenytoin (an antiepileptic), were detected in samples from all WRFs. Effluent from the High Springs WRF had the greatest number of compounds, 11 detected, and the GRU Main Street WRF had the lowest number of compounds, 7 detected.

Table 6. Results of organic wastewater contaminants analysis for four WRFs in Alachua County, September 2009. All units are in ng/L.

Chemical Compound	University of Florida (UF)	UF Field Duplicate	City of High Springs	GRU Main Street	GRU Kanapaha
Atrazine	ND*	ND	4.4	3.2	13
Bisphenol A	ND	11	ND	ND	ND
Caffeine	ND	ND	13	ND	ND
Carbamazepine	ND	ND	51	ND	ND
DEET	250	270	16	180	170
Diazepam	ND	1.4	4.5	1.6	3.3
Diclofenac	ND	26	ND	ND	ND
Fluoxetine	2.8	21	34	8.4	48
Gemfibrozil	ND	ND	4.2	ND	ND
Iopromide	ND	ND	ND	690	ND
Meprobamate	55	91	130	61	190
Phenytoin	220	86	13	310	100
Progesterone	ND	ND	ND	ND	ND
Sulfamethoxazole	ND	ND	110	ND	92

Methadone	ND	ND	11	ND	ND
Salicylic Acid	ND	27	28	ND	14
Perfluorobutanesulfonic Acid	4.8	4.5	17	9.5	10
Perfluorodecanoic Acid	16	16	7.1	4.3	5.6
Perfluorododecanoic Acid	0.61	ND	ND	ND	ND
Perfluoroheptanoic Acid	9.2	9.2	8.9	7.9	3.8
Perfluorohexanoic Acid	36	39	23	21	15
Perfluorohexylsulfonic Acid	1.8	2	2.6	12	3.1
Perfluorononanoic Acid	15	16	7.2	30	5.5
Perfluorooctanoic Acid	110	130	62	38	46
Perfluorooctylsulfonic Acid	6.5	6.1	9.7	110	8.4
Perfluoropentanoic Acid	21	20	27	10	13
Perfluoroundecanoic Acid	1.1	0.87	ND	0.95	ND

*ND =Not Detected

EDCs and PPCPs found in the highest concentrations were N,N-diethyl-meta-toluamide (DEET), meprobamate, phenytoin, and sulfamethoxazole, (Table 6). Many of the compounds detected in samples from the WRFs effluent were also found in surface waters in other studies including: atrazine, bisphenol A, caffeine, carbamazepine, DEET, fluoxetine, gemfibrozil, phenytoin, and sulfamethoxazole. The plasticizer bisphenol A, commonly present in other studies (Table 4) was only reported for one effluent sample at the University of Florida WRF (Table 6). The antibiotic sulfamethoxazole was reportedly found in all studies referenced and in samples from the GRU Kanapaha and the High Springs WRF (Table 6). The presence and or absence of EDCs and PPCPs and other OWCs in WRFs effluent is likely a function the type and duration (retention time) of treatment process, physical conditions, such as temperature, and the persistence of the compound or its ability not to degrade during the treatment process or in the immediate environment.

None of the compounds in Group 4, polybrominated diphenyl ethers (PBDEs), or Group 5, alkylphenols were detected. Due to analytical constraints, as was true with the earlier samples from Sweetwater Branch downstream of the GRU Main Street WRF, the latter group of compounds was analyzed at µg/L concentrations; lower detection limits may have shown these compounds to be present.

4.3 Sweetwater Branch September 2009

4.3.1 Field parameters, Metals and Priority Pollutant Organics

Overall water quality for field parameters (temperature, dissolved oxygen (DO), pH, and conductivity and conventional constituents was similar to that observed in the February sampling in the downstream sampling location. The sampling site in Sweetwater Branch upstream of the GRU WRF discharge had a lower specific conductance, 451 µS/cm, and DO, 7.46 mg/L, and a slightly higher pH, 7.72 SU. No priority pollutant organic compounds, chlorinated pesticides or metals were detected in the September 2009 sample event on Sweetwater Branch upstream and downstream the GRU Main Street WRF.

4.3.2 Organic Wastewater Contaminants (OWCs)

Eleven compounds in Groups 1 and 2, EDCs and PPCPs, and ten compounds in Group 3, PFCs (fluoropolymer precursors), were detected in the samples collected in Sweetwater Branch at ng/L concentrations. Comparison of the compounds detected in Sweetwater Branch upstream and downstream samples (February and September 2009) to the effluent of the GRU Main Street WRF (September 2009) is presented in Table 7. Six compounds including bisphenol A (a plasticizer), caffeine (a stimulant), carbamazepine (an anti-seizure drug), N,N-diethyl-meta-toluamide (DEET, an insect repellent), oxybenzone (a compound contained in sunscreen), and phenytoin (an antiepileptic) were detected in samples from Sweetwater Branch upstream of the discharge from the GRU Main Street WRF (Table 7). Only DEET and phenytoin were found in all of the Sweetwater Branch samples (February and September 2009) and effluent of GRU Main Street WRF (September 2009).

EDCs and PPCPs found in the highest concentrations (> 100 ng/L) in Sweetwater Branch and the effluent from the GRU Main Street WRF were N,N-diethyl-meta-toluamide (DEET), and iopromide (Table 7). Many of the compounds detected in samples from Sweetwater Branch and the GRU Main Street WRF effluent were also found in surface waters in other studies including: atrazine, bisphenol A, caffeine, carbamazepine, DEET, fluoxetine, gemfibrozil, phenytoin, and sulfamethoxazole (Kolpin *et al.* 2002, Kolpin *et al*. 2004; Benotti *et al.* 2009). An OWC called oxybenzone (a sunscreen constituent) was detected in the August 2009 samples from up and downstream sites on the Sweetwater Branch (Table 7). This OWC was not detected in the February 2009 sampling of Sweetwater Branch or the September 2009 samples from the four WRFs. The presence of OWCs in Sweetwater Branch upstream of the GRU Main Street WRF discharge may indicate a source of domestic wastewater entering Sweetwater Branch upstream of the WRF, although none have been identified through outfall reconnaissance work in 2010.

Many of the Group 3 PFCs were found in Sweetwater Branch upstream and downstream of the GRU Main Street WRF discharge (Table 7.). In February and September 2009 ten of the eleven PFCs were detected downstream of the GRU Main Street WRF. Eight of the PFCs were also detected in samples upstream of the GRU Main Street WRF. In general, when PFCs occurred both upstream and downstream of the treated effluent discharge, upstream concentrations were lower, often an order of magnitude lower.

Table 7. Results of organic wastewater contaminants analysis from the GRU Main Street WRF and sites up and downstream of its inflow to Sweetwater Branch February and September 2009. All units are in ng/L.

Chemical Compound	Sweetwater Branch Downstream February 2009	Sweetwater Branch Upstream September 2009	Sweetwater Branch Downstream September 2009	GRU Main Street WRF September 2009
Atrazine	2.6	ND*	2.5	3.2
Bisphenol A	22	41	ND	ND

Caffeine	41	9	ND	ND
Carbamazepine	330	1.8	48	ND
DEET	110	31	130	180
Diazepam	19	ND	1.4	1.6
Diclofenac	ND	ND	17	ND
Fluoxetine	27	ND	17	8.4
Gemfibrozil	36	ND	ND	ND
Iopromide	170	ND	420	690
Meprobamate	35	ND	55	61
Oxybenzone	ND	3.4	2.4	ND
Phenytoin	180	25	90	310
Sulfamethoxazole	110	ND	ND	ND
Pentoxifylline	2.3	ND	ND	ND
Methadone	11	ND	ND	ND
Salicylic Acid	320	ND	11	ND
Perfluoropentanoic Acid	4.6	2.6	8.2	10
Perfluorohexanoic Acid	16	9.5	18	21
Perfluoroheptanoic Acid	5.2	4.7	6.8	7.9
Perfluorooctanoic Acid (PFOA)	37	14	35	38
Perfluorononanoic Acid	22	1.6	26	30
Perfluorodecanoic Acid	4.7	ND	2.8	4.3
Perfluoroundecanoic Acid	0.89	ND	ND	ND
Perfluorobutanesulfonic Acid	5.4	7.6	7.7	9.5
Perfluorohexylsulfonic Acid	12	12	11	12
Perfluorooctylsulfonic Acid	170	19	97	110
Perfluorododecanoic Acid	ND	ND	1.0	0.95

*ND =Not Detected

None of the compounds in Group 4, polybrominated diphenyl ethers (PBDEs), or Group 5, alkylphenols, were detected. The propensity for PBDEs to sorb to sediments or other solids may have contributed to absence in the samples from Sweetwater Branch. Higher detection limits may have been the reason that the alkylphenol compounds were not detected.

5.0 Summary and Conclusions

There are several Group 1 and 2 compounds (PPCPs and EDCs) that were detected in Sweetwater Branch (February and September 2009) as well as in effluent from at least one of the WRFs: the City of High Springs, University of Florida and two municipal facilities operated by GRU, the Main Street and Kanapaha Reclamation Facilities. These OWCs were atrazine (an herbicide), bisphenol A (a plasticizer), caffeine (a stimulant), N,N-diethyl-meta-toluamide (DEET, an insect repellent), diazepam (a muscle relaxer), diclofenac (an anti-inflammatory), fluoxetine (an antidepressant), iopromide (a contrast agent), meprobamate (an anti-anxiety drug), phenytoin (an antiepileptic), sulfamethoxazole (an antibiotic) and salicylic acid (a skin care product). Eleven of these twelve compounds were reportedly present in surface water or groundwater in other studies of OWCs (Kolpin *et al.*, 200; Kolpin *et al.*, 2004; Benotti *et al.*, 2009). This indicates that the use, distribution, nature and persistence of these compounds are similar

in this study as to other studies comparing sites throughout the U.S. Based on the limited data collected in this investigation, it appears that some PFCs are found at lower concentrations in effluent from the GRU Main Street and Kanapaha WRFs, the larger WRFs in this study. This could indicate that their treatment method is more efficient than the UF and High Springs WRFs at degrading PFCs. Possible differences in OWC concentrations may be a result of longer residence time in the larger plants and treatment processes that foster conditions, such as oxidation, which serves to breakdown OWCs. There may also be a difference of inputs to the smaller WRFs that would be difficult to test. A comparison of the September 2009 and February 2009 data indicates the possibility that these classes of OWCs are more persistent in the environment during colder weather, perhaps due to a shorter duration of intense UV radiation and/or decreased microbial activity.

The six compounds, bisphenol A (a plasticizer), caffeine (a stimulant), carbamazepine (a anti-seizure drug), N,N-diethyl-meta-toluamide (DEET, an insect repellent), oxybenzone (a compound used in sunscreen), and phenytoin (an antiepileptic), detected in samples from Sweetwater Branch upstream of the discharge from the GRU Main Street WRF in September 2009 may indicate a source of domestic wastewater entering Sweetwater Branch upstream of that sample location. These findings are consistent with the presence of elevated fecal coliform frequently observed in Sweetwater Branch throughout the stream (ACEPD, 2007).

All samples had detectable levels of eight or more Group 3 PFCs. This gives an indication of how common these compounds are in the environment. The PFCs observed in the highest concentrations, included perfluorooctanoic acid (PFOA) and perfluorooctylsulfonic acid (PFOS). Perfluorinates are persistent compounds that have a potential to bioaccumulate (Andersen *et al.*, 2008). Consequences of bioaccumulation have not yet been tested but as with any bioaccumulation, the organisms higher on the food chain are most susceptible to negative feedbacks. None of the samples collected during this study exceeded the Provisional Health Advisories for drinking water containing perfluorinated compounds of 400 ng/L for perfluorooctanoic acid (PFOA) and 200 ng/L for perfluorooctylsulfonic acid (PFOS).

None of the Group 4 polybrominated diphenyl ethers (PBDEs), a category of organobromine compounds, analyzed were detected in the samples collected for this study. This was not unexpected, as these compounds have low water solubility and volatility, and as with other organohalogen compounds, such as polychlorinated biophenols (PCBs), resist chemical and biochemical transformations. This allows PBDEs to accumulate and persist in the natural environment, where they are frequently found in sediments and soils (Siddiqi *et al.*, 2003; Arnold *et al*, 2008).

None of the alkylphenols (Group 5) were detected in samples from this study. This group included 4-tert-octophenol, selected grouped total nonylphenols, and bisphenol A. Nonylphenols are used in detergents and surfactants and are ubiquitous in wastewater. It is likely that relatively high detection limit and reporting limit (µg/L) for these compounds may be the reason that these compounds were not detected. Nonylphenols

are closely related and difficult to separate analytically, which is part of the reason for the relatively high reporting limit. As analytical techniques advance the detection and reporting limits for these compounds will likely become lower.

In general, analytical methods necessary to detect trace amounts of OWC are still being developed and fine-tuned. The current level of analytical precision has hindered the progression of in-depth data on occurrence of these compounds for this investigation. The full TestAmerica and CAS laboratory analytical reports are available by request to ACEPD. At the present time ACEPD does not plan any additional sampling of OWCs in treated wastewater effluent or surface waters.

6.0 References

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Appendix A. TestAmerica SVOCs, Chlorinated Pesticides and Metal Analytes Grouped by Analytical Method and Type of Compound.

Chemical Compound	Instrumental Method	Analytical Method	Reporting Limit	Units
Semivolatile Organic Compounds				
Acenaphthene	GC/MS	EPA Method 625	1.1	µg/L
2,4-Dichlorophenol	GC/MS	EPA Method 625	1.0	µg/L
2,4-Dimethylphenol	GC/MS	EPA Method 625	1.0	µg/L
4,6-Dinitro-2-methylphenol	GC/MS	EPA Method 625	0.66	µg/L
2,4-Dinitrophenol	GC/MS	EPA Method 625	1.1	µg/L
2-Nitrophenol	GC/MS	EPA Method 625	1.2	µg/L
4-Nitrophenol	GC/MS	EPA Method 625	1.6	µg/L
4-Chloro-3-methylphenol	GC/MS	EPA Method 625	1.1	µg/L
2-Chlorophenol	GC/MS	EPA Method 625	1.1	µg/L
Pentachlorophenol	GC/MS	EPA Method 625	1.1	µg/L
Phenol	GC/MS	EPA Method 625	0.90	µg/L
2,4,6-Trichlorophenol	GC/MS	EPA Method 625	1.0	µg/L
Acenaphthylene	GC/MS	EPA Method 625	1.2	µg/L
Anthracene	GC/MS	EPA Method 625	0.80	µg/L
Benzidine	GC/MS	EPA Method 625	3.0	µg/L
Benzo[a]anthracene	GC/MS	EPA Method 625	0.72	µg/L
Benzo[a]pyrene	GC/MS	EPA Method 625	0.66	µg/L
Benzo[b]fluoranthene	GC/MS	EPA Method 625	1.2	µg/L
Benzo[g,h,i]perylene	GC/MS	EPA Method 625	0.68	µg/L
Benzo[k]fluoranthene	GC/MS	EPA Method 625	0.68	µg/L
Bis(2-chloroethoxy)methane	GC/MS	EPA Method 625	1.1	µg/L
Bis(2-chloroethyl)ether	GC/MS	EPA Method 625	0.28	µg/L
2,2'-oxybis[1-chloropropane]	GC/MS	EPA Method 625	0.79	µg/L
Bis(2-ethylhexyl) phthalate	GC/MS	EPA Method 625	0.89	µg/L
4-Bromophenyl phenyl ether	GC/MS	EPA Method 625	1.2	µg/L
Butyl benzyl phthalate	GC/MS	EPA Method 625	0.60	µg/L
2-Chloronaphthalene	GC/MS	EPA Method 625	1.0	µg/L
4-Chlorophenyl phenyl ether	GC/MS	EPA Method 625	1.3	µg/L
Chrysene	GC/MS	EPA Method 625	0.83	µg/L
Dibenz(a,h)anthracene	GC/MS	EPA Method 625	0.79	µg/L
1,2-Dichlorobenzene	GC/MS	EPA Method 625	0.83	µg/L
1,3-Dichlorobenzene	GC/MS	EPA Method 625	0.63	µg/L
1,4-Dichlorobenzene	GC/MS	EPA Method 625	0.84	µg/L
3,3'-Dichlorobenzidine	GC/MS	EPA Method 625	0.54	µg/L
Diethyl phthalate	GC/MS	EPA Method 625	0.95	µg/L
Dimethyl phthalate	GC/MS	EPA Method 625	1.0	µg/L
Di-n-butyl phthalate	GC/MS	EPA Method 625	0.92	µg/L
2,4-Dinitrotoluene	GC/MS	EPA Method 625	0.84	µg/L
2,6-Dinitrotoluene	GC/MS	EPA Method 625	0.93	µg/L

Di-n-octyl phthalate	GC/MS	EPA Method 625	0.74	µg/L
1,2-Diphenylhydrazine	GC/MS	EPA Method 625	0.70	µg/L
Fluoranthene	GC/MS	EPA Method 625	0.81	µg/L
Fluorene	GC/MS	EPA Method 625	1.1	µg/L
Hexachlorobenzene	GC/MS	EPA Method 625	1.0	µg/L
Hexachlorobutadiene	GC/MS	EPA Method 625	0.79	µg/L
Hexachlorocyclopentadiene	GC/MS	EPA Method 625	0.32	µg/L
Hexachloroethane	GC/MS	EPA Method 625	0.97	µg/L
Indeno[1,2,3-cd]pyrene	GC/MS	EPA Method 625	0.86	µg/L
Isophorone	GC/MS	EPA Method 625	1.1	µg/L
Naphthalene	GC/MS	EPA Method 625	1.0	µg/L
Nitrobenzene	GC/MS	EPA Method 625	0.97	µg/L
N-Nitrosodimethylamine	GC/MS	EPA Method 625	0.45	µg/L
N-Nitrosodi-n-propylamine	GC/MS	EPA Method 625	1.1	µg/L
N-Nitrosodiphenylamine	GC/MS	EPA Method 625	0.94	µg/L
Phenanthrene	GC/MS	EPA Method 625	0.89	µg/L
Pyrene	GC/MS	EPA Method 625	0.79	µg/L
1,2,4-Trichlorobenzene	GC/MS	EPA Method 625	0.87	µg/L
Organochlorine Pesticides/PCB				
Aldrin	GC/ECD	EPA Method 608	0.0069	µg/L
alpha-BHC	GC/ECD	EPA Method 608	0.011	µg/L
beta-BHC	GC/ECD	EPA Method 608	0.01	µg/L
Chlordane (technical)	GC/ECD	EPA Method 608	1.9	µg/L
4,4'-DDD	GC/ECD	EPA Method 608	0.015	µg/L
4,4'-DDE	GC/ECD	EPA Method 608	0.021	µg/L
4,4'-DDT	GC/ECD	EPA Method 608	0.012	µg/L
delta-BHC	GC/ECD	EPA Method 608	0.01	µg/L
Dieldrin	GC/ECD	EPA Method 608	0.0052	µg/L
Endosulfan I	GC/ECD	EPA Method 608	0.013	µg/L
Endosulfan II	GC/ECD	EPA Method 608	0.012	µg/L
Endosulfan sulfate	GC/ECD	EPA Method 608	0.011	µg/L
Endrin	GC/ECD	EPA Method 608	0.012	µg/L
Endrin aldehyde	GC/ECD	EPA Method 608	0.012	µg/L
gamma-BHC (Lindane)	GC/ECD	EPA Method 608	0.0098	µg/L
Heptachlor	GC/ECD	EPA Method 608	0.012	µg/L
Heptachlor epoxide	GC/ECD	EPA Method 608	0.012	µg/L
Methoxychlor	GC/ECD	EPA Method 608	0.019	µg/L
Toxaphene	GC/ECD	EPA Method 608	2.7	µg/L
Metals				
Aluminum	ICP	EPA Method 200.7 Rev 4.4	21	µg/L
Antimony	ICP	EPA Method 200.7 Rev 4.4	4.4	µg/L
Arsenic	ICP	EPA Method 200.7 Rev 4.4	4.2	µg/L
Barium	ICP	EPA Method 200.7 Rev 4.4	0.96	µg/L
Beryllium	ICP	EPA Method 200.7 Rev 4.4	0.49	µg/L
Cadmium	ICP	EPA Method 200.7 Rev 4.4	0.46	µg/L
Calcium	ICP	EPA Method 200.7 Rev 4.4	58	µg/L

Chromium	ICP	EPA Method 200.7 Rev 4.4	1.5	µg/L
Cobalt	ICP	EPA Method 200.7 Rev 4.4	1	µg/L
Copper	ICP	EPA Method 200.7 Rev 4.4	2.4	µg/L
Iron	ICP	EPA Method 200.7 Rev 4.4	4.6	µg/L
Lead	ICP	EPA Method 200.7 Rev 4.4	2	µg/L
Magnesium	ICP	EPA Method 200.7 Rev 4.4	4.8	µg/L
Manganese	ICP	EPA Method 200.7 Rev 4.4	0.72	µg/L
Nickel	ICP	EPA Method 200.7 Rev 4.4	2.2	µg/L
Potassium	ICP	EPA Method 200.7 Rev 4.4	74	µg/L
Selenium	ICP	EPA Method 200.7 Rev 4.4	3.2	µg/L
Silver	ICP	EPA Method 200.7 Rev 4.4	1.1	µg/L
Sodium	ICP	EPA Method 200.7 Rev 4.4	220	µg/L
Thallium	ICP	EPA Method 200.7 Rev 4.4	6.8	µg/L
Vanadium	ICP	EPA Method 200.7 Rev 4.4	1	µg/L
Zinc	ICP	EPA Method 200.7 Rev 4.4	2.6	µg/L

Appendix B. Columbia Analytical Services, Inc. Laboratory Analytes Grouped by Analytical Method and Type of Compound.

Chemical Compound	Instrumental Method	Analytical Method	Reporting Limit	Units
Groups 1 and 2 - EDC/PPCPs				
Androstenedione	LC/MS/MS	EPA Method 1694M	10	ng/L
Atrazine	LC/MS/MS	EPA Method 1694M	1.0	ng/L
Bisphenol A	LC/MS/MS	EPA Method 1694M	10	ng/L
Caffeine	LC/MS/MS	EPA Method 1694M	5.0	ng/L
Carbamazepine	LC/MS/MS	EPA Method 1694M	1.0	ng/L
DEET	LC/MS/MS	EPA Method 1694M	5.0	ng/L
Diazepam	LC/MS/MS	EPA Method 1694M	1.0	ng/L
Diclofenac	LC/MS/MS	EPA Method 1694M	2.0	ng/L
Diethylstillbestrol	LC/MS/MS	EPA Method 1694M	2.0	ng/L
Estradiol (17-beta-estradiol)	LC/MS/MS	EPA Method 1694M	2.0	ng/L
Estriol	LC/MS/MS	EPA Method 1694M	1.0	ng/L
Estrone	LC/MS/MS	EPA Method 1694M	1.0	ng/L
17-alpha-ethynylestradiol (Ethinyl Estradiol)	LC/MS/MS	EPA Method 1694M	2.0	ng/L
Fluoxetine	LC/MS/MS	EPA Method 1694M	1.0	ng/L
Gemfibrozil	LC/MS/MS	EPA Method 1694M	1.0	ng/L
Hydrocodone	LC/MS/MS	EPA Method 1694M	1.0	ng/L
Ibuprofen	LC/MS/MS	EPA Method 1694M	10	ng/L
Iopromide	LC/MS/MS	EPA Method 1694M	10	ng/L
Meprobamate	LC/MS/MS	EPA Method 1694M	5.0	ng/L
Naproxen	LC/MS/MS	EPA Method 1694M	1.0	ng/L
Oxybenzone	LC/MS/MS	EPA Method 1694M	2.0	ng/L
Phenytoin	LC/MS/MS	EPA Method 1694M	5.0	ng/L
Progesterone	LC/MS/MS	EPA Method 1694M	10	ng/L

Sulfamethoxazole	LC/MS/MS	EPA Method 1694M	1.0	ng/L
Testosterone	LC/MS/MS	EPA Method 1694M	10	ng/L
Trimethoprim	LC/MS/MS	EPA Method 1694M	5.0	ng/L
17-alpha-estradiol	LC/MS/MS	EPA Method 1694M	1.0	ng/L
Pentoxifyline (Pentoxifylline)	LC/MS/MS	EPA Method 1694M	1.0	ng/L
Methadone	LC/MS/MS	EPA Method 1694M	5.0	ng/L
Acetaminophen	LC/MS/MS	EPA Method 1694M	1.0	ng/L
Salicylic Acid	LC/MS/MS	EPA Method 1694M	100	ng/L
Triclosan	LC/MS/MS	EPA Method 1694M	10	ng/L
Group 3 - Perfluorinated Compounds (PFC)				
Perfluoropentanoic Acid (PFHeA)	LC/MS/MS	SOC-PFC	0.5	ng/L
Perfluorohexanoic Acid (PFHxA)	LC/MS/MS	SOC-PFC	0.5	ng/L
Perfluoroheptanoic Acid (PFHpA)	LC/MS/MS	SOC-PFC	0.5	ng/L
Perfluorooctanoic Acid (PFOA)	LC/MS/MS	SOC-PFC	0.5	ng/L
Perfluorononanoic Acid (PFNA)	LC/MS/MS	SOC-PFC	0.5	ng/L
Perfluorodecanoic Acid (PFDA)	LC/MS/MS	SOC-PFC	0.5	ng/L
Perfluoroundecanoic Acid (PFUnA)	LC/MS/MS	SOC-PFC	0.5	ng/L
Perfluorododecanoic Acid (PFDoA)	LC/MS/MS	SOC-PFC	0.5	ng/L
Perfluorobutane Sulfonate (PFBS)	LC/MS/MS	SOC-PFC	0.5	ng/L
Perfluorohexane Sulfonate (PFHxS)	LC/MS/MS	SOC-PFC	0.5	ng/L
Perfluorooctane Sulfonate (PFOS) (in Scotchguard)	LC/MS/MS	SOC-PFC	0.5	ng/L
Group 4 - Polybrominated Diphenyl Ethers (PBDE)				
PBDE-17	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-28	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-47	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-66	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-71	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-85	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-99	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-100	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-128	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-138	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-153	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-154	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-183	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-190	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-203	GC/MS/SIM	EPA Method 8270C	0.9	ng/L
PBDE-206	GC/MS/SIM	EPA Method 8270C	9.9	ng/L
PBDE-209	GC/MS/SIM	EPA Method 8270C	9.9	ng/L
Group 5 – Alkylphenols				
Total Nonylphenols	GC/MS/SIM	ASTM-D7065-06M	2	µg/L
Total Nonylphenol	GC/MS/SIM	ASTM-D7065-06M	4	µg/L

Monoethoxylates				
Total Nonylphenol Diethoxylates	GC/MS/SIM	ASTM-D7065-06M	8	µg/L
4-tert-Octylphenol	GC/MS/SIM	ASTM-D7065-06M	0.40	µg/L
Bisphenol A (monomer in the production of polycarbonate)	GC/MS/SIM	ASTM-D7065-06M	0.40	µg/L