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Occurrence of Pharmaceutical and Personal Care Products (PPCPs) in Source Water of the New York City Water Supply

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Ashokan Reservoir

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I. ABSTRACT

In response to the issue of emerging contaminants in drinking water, including those classified as pharmaceuticals and personal care products (PPCPs), the New York City Department of Environmental Protection (DEP) conducted a one-year occurrence study to document the presence or absence of a target group of PPCPs in the source waters of the New York City Water Supply. Although there are currently no state or federal mandatory testing or reporting requirements for PPCPs, DEP is being proactive in PPCP data collection and research in an effort to better understand the occurrence and potential human health consequences of PPCPs in our waterways; to better educate the public; and in anticipation of potential future regulation of these compounds.

The PPCP Monitoring Program was a one-year study initiated in January 2009 with water samples collected quarterly from the Catskill, Delaware, and Croton untreated source waters. Two samples (a sample and a duplicate) were collected by DEP from each of the three source waters for each quarterly event. The samples were analyzed by two contract laboratories using newly developed and highly sensitive analytical methods to look for a target group of 78 analytes that are representative of PPCPs in surface and groundwater sources, as well as effluent from wastewater treatment plants. Several industrial chemicals were also included in the target group of analytes. Due to the extremely low detection levels required for this study, DEP implemented strict quality control requirements for field sampling and laboratory analysis.

The results indicate that some PPCPs are present in very low concentrations (low parts-per-trillion range) in the source waters of New York City with a greater frequency of detection in the Croton source water compared to the Catskill/Delaware source waters. A screening level risk assessment conducted by DEP suggests that the concentrations of the detected PPCPs are well below levels that would pose a risk to the health of consumers of NYC's drinking water. A total of 16 individual PPCP compounds were detected in at least one sampling event during the pilot study. The PPCP compounds detected most frequently, in at least three of the four sampling periods, included the following nine compounds: butalbital, sulfamethoxazole, carbamazepine, caffeine, cotinine, diazepam, gemfibrozil, and cis-testosterone. Perfluorooctane Sulfonate (PFOS), an industrial chemical was also detected frequently. The measured concentrations of the target analytes at all three keypoints were all well below the New York State generic standards for individual unspecified organic contaminants (UOCs) or principal organic contaminants (POCs) of 50,000 nanograms per liter (ng/L) and 5,000 ng/L, respectively. Due to the limited scope of this study, the potential sources of PPCP inputs into the Croton and Catskill/Delaware Watersheds were not investigated. The results of this study will be used to help assess the need for continued monitoring for emerging contaminants and to develop a more targeted program for subsequent years, as necessary.

II. Background

In recent years, the issue of Pharmaceuticals and Personal Care Products (PPCPs) and other emerging contaminants as potential drinking water pollutants has received increasing national and international attention and media coverage. Several national studies have confirmed the presence of trace concentrations (low parts-per-trillion) of PPCPs in surface water, groundwater and finished drinking water. While PPCPs can originate from numerous sources, effluents from wastewater treatment plants (WWTPs) have been identified as a significant source to surface waters. PPCPs can enter WWTPs when people excrete pharmaceutical products or their metabolites, or flush unused medications down a drain or other sewer system input.

The pharmaceutical drugs that have been detected nationally comprise a large range of emerging drinking water contaminants, including prescription and over-the-counter drugs, antibiotics, tranquilizers, antidepressants, and other organic chemicals which are not completely removed by wastewater treatment plants. The personal care products that have been detected include but are not limited to: fragrances, disinfectants, sunscreen, preservatives, and surfactants or their metabolites (Kolpin et al., 2002). These and other emerging contaminants are not yet regulated under the Safe Drinking Water Act, however they are regulated in New York State by the unspecified organic contaminants (UOCs) and principal organic contaminants (POCs) standards[1].

PPCPs have previously been detected in the New York City (NYC) watershed by the United States Geological Survey (USGS) (Kolpin et al., 2002) as well as the New York State Department of Health (NYSDOH) (Wilson et al., 2006). The NYSDOH study reported that samples from the effluent of four WWTPs consistently showed traces of pharmaceutical contaminants including atenolol, caffeine, carbamazepine, ibuprofen, and trimethoprim. Estrogen was also found in one sample. NYSDOH also looked at PPCPs in several reservoirs on the east and west side of the Hudson River. Two compounds, caffeine and ibuprofen, were found infrequently in the low nanograms per liter (ng/L) range in several East-of-Hudson reservoir samples, but their presence was not confirmed in the corresponding duplicates. NYSDOH concluded that the measured concentrations were well below those that may be expected to have any effect on human health.

The human health risks associated with PPCPs in the aquatic environment are largely unknown; however, the risks are likely to be very low, especially for water supplies with protected watersheds such as New York City's. Most current drinking water standards for regulated organic chemicals are in the low ranges (<5 to 0.2 parts per billion (ppb)), and in New York State, the generic standard for any UOC is 50 micrograms per liter (µg/L) equal to 50,000 ng/L (10 NYCRR Part 5 – Public Water Systems) and for any POC it is 5 µg/L (5,000 ng/L). Furthermore, the NYSDOH standard for Total POCs and UOCs is 100 µg/L (100,000 ng/L). The levels found in the various occurrence studies tend to be in the low

[1] POCs are generally halogenated alkanes, ethers, benzenes, and some other classes of compounds as defined in the State Sanitary Code http://www.health.state.ny.us/regulations/nycrr/title_10/part_5/subpart_5-1_tables.htm. UOCs refer to any organic chemical not otherwise specified in the State Sanitary Code. **Table 10** of this report lists the applicable NYS standards for the compounds detected.

ng/L range in surface water and are generally some 500-10,000-fold below these limits. Drinking water treatment and disinfection may potentially reduce these already low levels of PPCPs found in streams to even lower levels.

Based on several screening level assessments of pharmaceuticals in source and drinking water, the human health risks are likely to be *de minimis*. As summarized by American Water Works Association Research Foundation (AWWARF), "screening level risk assessments conducted to date have not indicated that the trace concentrations of pharmaceuticals detected in drinking water pose a risk to consumers" (Snyder et al., 2008). This was also the conclusion of the NYSDOH, in the final report of their NYC Watershed study which looked at eleven PPCPs. Even though very sensitive analytical methods were used…"the few observed detections were not found in consecutive samples at any location, and were at levels well below those that would be considered to present a potential health concern from long-term exposure" (Wilson et al., 2006).

Currently, there is no state or federal mandatory testing or reporting requirements for PPCPs. The New York City Department of Environmental Protection (DEP) is being proactive in its sampling and analysis of PPCPs to better understand any potential impacts, to educate the public, and in anticipation of possible future regulations of these compounds. This occurrence study contains DEP's initial findings regarding the New York City water supply.

III. Purpose

DEP conducted a one-year occurrence study to document the potential presence or absence of a target group of PPCPs in the source waters of the New York City Water Supply, just prior to the first point of disinfection. The study was developed as a pilot study because of the need to test new advanced and highly sensitive analytical methods to determine whether DEP could reliably detect PPCPs at very low levels (parts-per-trillion), as well as the need to utilize new sampling methods to prevent cross-contamination of samples. At the time the study was initiated, USEPA had recently published analytical method 1694 (PPCPs in environmental samples) (USEPA, 2007a) and method 1698 (steroids and hormones in environmental samples) (USEPA, 2007b), but DEP did not have the necessary instrumentation or experience to perform the analytical work using in-house laboratory resources. Additionally, there were and still are few commercial environmental laboratories with demonstrated capabilities in producing reliable results for PPCP analysis of water samples with detection limits in the ng/L (parts-per-trillion) range. DEP retained Montgomery Watson Harza Laboratories (MWH) and its subcontractor Underwriters Laboratories (UL) to analyze samples collected by DEP personnel for the pilot study. The study was designed to examine whether any of approximately 78 constituents[2] are present in New York City source waters, and to ascertain a general range

[2] Most of the 78 constituents that DEP tested for can be classified as either a pharmaceutical or personal care. The laboratory methods provided by MWH and UL laboratories included several constituents that are classified as industrial chemicals. Only one of these, perfluorooctane sulfonate (PFOS), was detected in the study and is reported here separately from the PPCPs.

of concentrations found during each of the four seasons through quarterly monitoring. The target analytes list was chosen to include many of the analytes or classes of compounds that have been detected in national and regional occurrence studies conducted by USGS and NYSDOH, as well as additional compounds associated with the contract laboratories' proprietary analytical methods. The results of this pilot study are being used to help assess the need for a continued program on emerging contaminants and to develop a more targeted program for subsequent years, as necessary.

IV. Site Selection and Sampling

Study Design: DEP initiated the PPCP Monitoring Program in 2009, with samples collected on a quarterly basis (every three months) starting in January, for a total of four sampling events (January, April, July, October). For each quarterly sampling event, samples were collected in duplicate from DEP's three source water keypoints (**Table 1**). These keypoints are locations where representative raw water samples can be collected at locations just prior to the point where chlorine is added for disinfection.

Table 1: PPCP Monitoring Program Sampling Locations

Site Code	Site Description
CATLEFF	Catskill Aqueduct, Lower Effluent Chamber, untreated Catskill source water, Kensico Reservoir
DEL18	Delaware Aqueduct, Shaft 18, untreated Delaware source water, Kensico Reservoir
CRO1T [3]	Croton Gatehouse 1, untreated Croton source water, New Croton Reservoir

Quality Control (QC) Samples: In addition to the sample, for each quarterly sampling event, the following QC samples were collected:

- Sample Duplicate. For each analytical method used, a sample and sample duplicate were collected by filling one bottle immediately after the other. The purpose of the sample duplicate is to test the overall precision of the analytical and sampling methods. Three samples and three duplicates were collected for each round of sampling.

[3] CROGH, the primary site for Croton raw water effluent from the New Croton Reservoir, could not be used as the source water keypoint for the Croton System because the Croton System was offline during the study. Instead, the sample was collected at Gate House 1 where there is a sample tap — the CRO1T site.

- Field Blank. A field blank was collected with each round of sampling. The purpose of the field blank is to test for potential cross-contamination in sample handling and with sampling equipment. Field blanks were generated by pouring analyte-free water supplied by the contract laboratories into sample bottles in the field, utilizing the same equipment and processes as used to collect the water samples.
- Trip blank. A trip blank was collected with each round of sampling. The purpose of the trip blank is to test for potential cross-contamination during the transport and storage of the water samples. Trip blanks were prepared by the contract laboratories using analyte-free water in the appropriate sample containers with the proper preservative. Trip blanks are taken out into the field and then returned to the contract lab for analysis without being opened.
- Laboratory Fortified Matrix (LFM) and Laboratory Fortified Matrix Duplicate (LFMD). These are water samples collected by DEP at one of the three sampling sites in a manner identical to the procedures used to collect the samples. The LFM and LFMD samples are used by the laboratories to spike known concentrations of target analytes or surrogate compounds. The LFM sample helps to assess analytical preparation and analysis bias using a raw water sample rather than distilled or laboratory water. Similarly, the LFMD is used to test analytical bias and precision with an actual raw water sample rather than with laboratory water.

As summarized in **Table 2** below**,** ten samples (including QC samples) were collected for each quarterly round of sampling. Alternating locations were selected each quarter from which to draw or collect samples for QC purposes. In one quarter, the QC samples were collected from CRO1T, the next quarter from CATLEFF, and so on.

Table 2: Samples Collected

	Sample	Sample Dup	Trip Blank	Field Blank	LFM	LFMD
CRO1T	X	X	X*	X*	X*	X*
CATLEFF	X	X				
DEL18	X	X				

* At alternating locations for each quarterly sampling event.

V. Field Methods

Since PPCPs are a class of emerging contaminants that are currently unregulated by USEPA, there is no required sample collection or analytical procedures. However, since the desired detection levels of the pilot program are generally in the ng/L (parts-per-trillion) range, all three keypoints were sampled using the *"clean hands"* method (USEPA, 1996), as guidance to reduce the potential for contamination of the samples from exogenous sources (e.g. sampling personnel). These sources could include airborne dust, dirt, and lint, as well as transference from human contact with the samples (e.g., dandruff, skin oils, sweat). Upon arrival at the sampling site, one member of the two-person sampling team was designated as *"dirty hands";* the second member was designated as

"clean hands." All operations involving contact with the sample bottle and with transfer of the sample from the sample collection device to the sample bottle were handled by the individual designated as *"clean hands." "Dirty hands"* was responsible for all activities that did not involve direct contact with the sample. This is depicted in **Figure 1** below.

Figure 1: *"Dirty hands"* (right) assisting *"clean hands"* (left) with sample collection

VI. Description of Analytical Methods

The samples were analyzed by MWH and UL laboratories using proprietary High Pressure Liquid Chromatography and Dual Mass Spectroscopy (LC/MS/MS) methods to analyze the untreated water samples. The difference between the methods resulted in a variation in the range, sensitivity, and performance of the methods when searching for 78 target analytes with varying physical-chemical properties. Each laboratory established minimum reporting levels (MRL) for their LC/MS/MS methods. The MRL is the minimum level (concentration) that the laboratory can report accurately. Anything below the MRL is considered to be not detected. In several instances, the laboratories had different MRLs for the same target compounds.

Compounds Analyzed: MWH utilized their Method EDC2SCR (a peer-reviewed isotope dilution based solid phase extraction (SPE) LC-MS-MS method using a sensitive API4000 instrument) to analyze and quantify 21 compounds. The list included Perfluorooctane Sulfonate (PFOS), which is an industrial compound that has been detected at trace levels in surface waters in New York State (Sinclair, 2006), and elsewhere, as well as butalbital,

which has been found in wastewater effluent (Phillips et al., 2007). Under a subcontract to MWH, UL provided additional analytical services utilizing their related proprietary Methods UL200, UL211, UL220, and UL221 to cover a broader range of PPCPs than provided by MWH Method EDC2SCR. In total, the target analytes list included 78 individual compounds. **Table 3** and **Table 4** provides the general classes of compounds and analytes for which tests were performed utilizing the five different laboratory methods, and the MRL for each analyte. There was some overlap between the various methods; therefore some analytes were measured using more than one method (e.g. sulfamethoxazole).

Table 3: Selected PPCP Analysis Methods (MWH)

MWH Method	Compounds Analyzed (21 total) **	MRL ng/L
EDC2SCR	Atenolol	5
	Carbamazepine	5
	Estrone	1
	Estradiol	1
	Ethinyl Estradiol - 17 alpha	5
	Progesterone	1
	Testosterone	1
	Bisphenol A (BPA)	10
	Butalbital	5
	Gemfibrozil	1
	Ibuprofen	1
	Iopromide	10
	Perfluorooctane Sulfonate - PFOS	0.2
	Triclosan	5
	Acetaminophen	1
	Caffeine	3
	Cotinine	1
	Diazepam	1
	Fluoxetine	5
	Sulfamethoxazole	1
	Trimethoprim	1

** Some overlap of compounds analyzed by both labs and methods

Table 4: Selected PPCP Analysis Methods (UL)

UL Method	Compounds Analyzed (85 total) **	MRL ng/L
UL200	Bisphenol A (BPA)	100
	Nonylphenol, Isomer mix	500
	4-n-Octylphenol	500
	4-tert-Octylphenol	500
	Pentachlorophenol	100

UL Method	Compounds Analyzed (85 total) **	MRL ng/L
	Phenylphenol	100
	Tetrabromobisphenol A	100
	2,4,6 - Trichlorophenol	100
UL211	Diethylstilbestrol (DES)	0.5
	17alpha-estradiol	0.5
	17beta-estradiol	0.5
	Estriol	0.5
	Estrone	0.5
	17alpha-Ethynyl estradiol	0.5
	Progesterone	0.1
	cis-Testosterone	0.1
	trans-Testosterone	0.1
UL221	Bezafibrate	0.5
	Chloramphenicol	5
	Chlorotetracycline	50
	Clofibric Acid	0.5
	Diclofenac	0.5
	Dilantin	2
	Doxycycline	50
	Gemfibrozil	0.5
	Ibuprofen	50
	Levothyroxine (Synthroid)	2
	Naproxen	2
	Oxytetracycline	500
	Penicillin G	2
	Penicillin V	2
	Prednisone	2
	Salinomycin	2
	Sulfachloropyridazine	50
	Sulfadiazine	50
	Sulfadimethoxine	5
	Sulfamerazine	500
	Sulfamethazine	500
	Sulfamethizole	5
	Sulfamethoxazole	2
	Sulfathiazole	50
	Theophylline	5
	Triclosan	5
	Tylosin	50
	Virginiamycin M1	0.5
UL220	Acetaminophen	5
	Antipyrine	1
	Azithromycin	1
	Bacitracin	100
	Caffeine	50
	Carbadox	50

UL Method	Compounds Analyzed (85 total) **	MRL ng/L
	Carbamazepine	1
	Ciprofloxacin	50
	Cotinine	1
	DEET	5
	Dilantin	50
	Diltiazem	1
	Enrofloxacin	500
	Erythromycin	1
	Fluoxetine	1
	Lasalocid	1
	Levothyroxine	50
	Lincomycin	0.1
	Monensin	1
	Narasin	0.1
	Nicotine	5
	Norfloxacin	500
	Oleandomycin	1
	Paraxanthine	5
	Prednisone	5
	Roxithromycin	1
	Salinomycin	0.1
	Simvastatin	1
	Sulfachloropyridazine	5
	Sulfadiazine	5
	Sulfadimethoxine	0.1
	Sulfamerazine	5
	Sulfamethazine	1
	Sulfamethizole	5
	Sulfamethoxazole	5
	Sulfathiazole	5
	Theobromine	50
	Trimethoprim	1
	Tylosin	1
	Virginiamycin M1	1

** Some overlap of compounds analyzed by both labs and methods

VII. Quality Control Issues

Quality Controls: The laboratories analyzed Quality Controls with every batch of samples. The results document the accuracy and precision at the time of the actual testing and to show that any compounds present in the samples, came only from the water being tested, and not from some other sources, such as trace contamination from sampling and analysis procedures.

Sample Duplicates: Sample duplicates were collected and processed in the same batches as the corresponding samples. The analytical results for sample duplicates were compared using the relative percent difference (RPD) between the sample duplicate and the sample. A relative percent difference of 20% or less for MWH, and 30% or less for UL, between the sample and its field duplicate was used as an indication of good overall precision.

Trip/Field Blanks: One set of trip blanks and field blanks was collected for each analytical method at one sampling location per sampling event, alternating locations at each subsequent quarterly sampling event. There was no detection of any measured analytes in any of the trip blanks indicating that no external contamination from bottle handling, transportation or storage had occurred. There were only two field blank detections during the study period. During the second quarter, one field blank collected at Del 18 was positive for ibuprofen at 1.5 ng/L. During the fourth quarter sampling at CRO1T, one field blank was also positive for bisphenol A (BPA), a plasticizer, at a concentration of 100 ng/L. BPA was not detected in any of the samples. These two positive field blank detections indicate that sampling procedures may have resulted in limited cross-contamination. However, DEP field personnel implemented a strict *"clean hands"* sampling procedure which was designed to preclude sample contamination during collection, storage, and delivery. Overall, there were very few to no positive detections of target analytes in the field and trip blanks indicating that cross-contamination was adequately prevented.

Table 5: Compounds Measured with More Than One Method

Compounds Analyzed	MWH MRL (ng/L)	UL MRL (ng/L)
Carbamazepine	5	1
Estrone	1	0.5
Ethinyl Estradiol - 17 alpha	5	0.5
Progesterone	1	0.1
Testosterone	1	0.1
Bisphenol A (BPA)	10	100
Gemfibrozil	1	0.5
Ibuprofen	1	50
Triclosan	5	5
Acetaminophen	1	5
Caffeine	3	50
Cotinine	1	1
Fluoxetine	5	1
Sulfamethoxazole	1	5
Trimethoprim	1	1

Minimum Reporting Levels: **Table 5** shows the compounds which were measured using more than one analytical method, and their associated MRLs. Method UL211 exhibited

very low MRLs for all of the steroid hormones, which were undetected by EDC2SCR. For analytes targeted by both laboratories, and where there were comparable MRLs, the results were similar, providing additional confidence in the quality of the data for those analytes.

VIII. Results and Discussion

Two samples (a sample and a duplicate) were collected from each of the three source water keypoints (CATLEFF, DEL18, CRO1T) for each quarterly event. This resulted in a total of 24 samples being analyzed during 2009 plus the associated QC samples. As indicated in **Table 6**, sixteen PPCP compounds were detected in at least one sampling event during the pilot study as well as one industrial chemical.

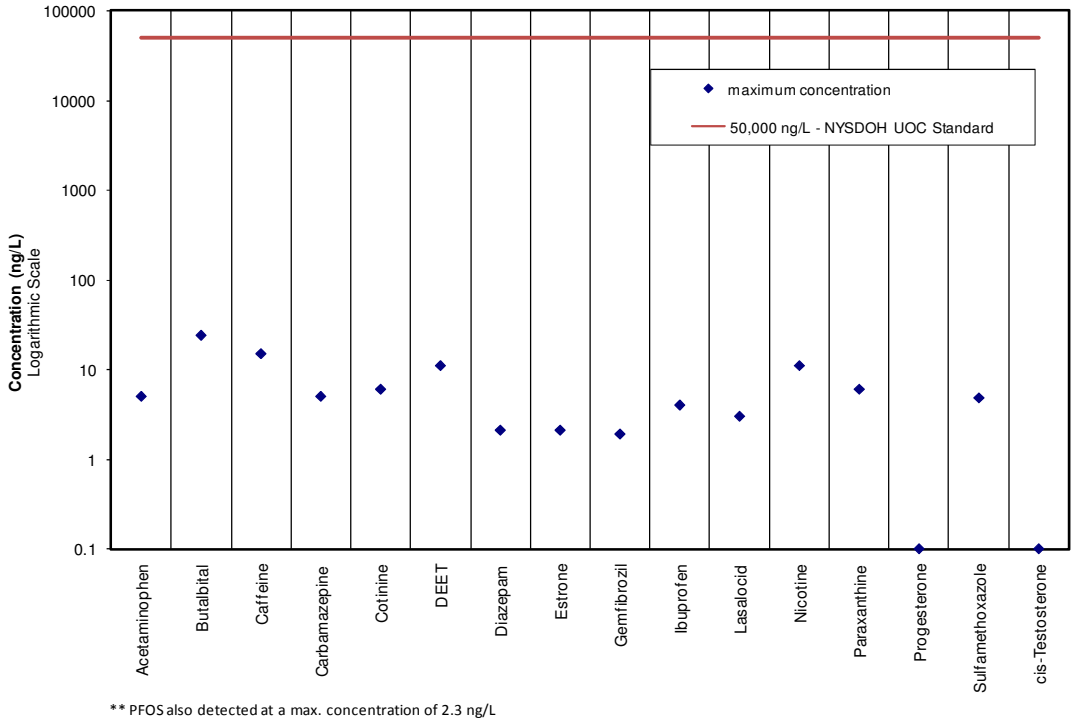
Measured concentrations were generally in the low parts-per-trillion range, with most concentrations below 10 ng/L and all concentrations falling well below the New York State generic standard for UOCs of 50,000 ng/L and for principal organic compounds (POCs) of 5,000 ng/L (**Figure 2**). Many of the compounds that were detected were very close to or just above the minimum reporting limits for the method.

Table 6: Detected PPCP Compounds and General Use Category

Compound**	Type of Compound
Acetaminophen	antipyretic, nonprescription drug
Butalbital	barbiturate, pain reliever, prescription drug
Caffeine	Stimulant
Carbamazepine	anticonvulsant, prescription drug
cis-Testosterone	reproductive hormone
Cotinine	nicotine metabolite
DEET	insect repellent
Diazepam	antianxiety/insomnia, prescription drug
Estrone	reproductive hormone
Gemfibrozil	antihyperlipidemic, prescription drug
Ibuprofen	anti-inflammatory, nonprescription drug
Lasalocid	Antibiotic
Nicotine	stimulant, alkaloid
Paraxanthine	stimulant, caffeine metabolite
Progesterone	reproductive hormone
Sulfamethoxazole	Antibiotic

**PFOS, a flurosurfactant, was also detected

Figure 2: Maximum Concentrations of Detected PPCP Compounds



Summaries of the positive detections of PPCPs found in the samples from CROIT, DEL18, and CATLEFF are provided in **Table 7**, **Table 8**, and **Table 9,** respectively. As indicated in these tables, the frequency of occurrence was greater in the Croton System than in the Catskill/Delaware System. For example, six PPCP compounds[4] were detected in every sample at CRO1T (either by MWH or UL), including the four prescription drugs butalbital, sulfamethoxazole, carbamazepine, and gemfibrozil, as well as caffeine, and cotinine. Cotinine is a metabolic byproduct of nicotine.

Most PPCPs were detected at concentrations below 10 ng/L (10 parts-per-trillion); however, two compounds were detected at CRO1T in each quarter, at concentrations somewhat greater than 10 ng/L. This included butalbital, with a maximum detected concentration of 24 ng/L, and caffeine at a maximum concentration of 15 ng/L. Diazepam, gemfibrozil, and cis-testosterone were also detected frequently in at least three of four quarters of sampling. The first two compounds were found in three of four quarters at CRO1T; cis-testosterone was detected in three of the four quarters at CATLEFF, at levels just above the reporting limit of 0.1 ng/L. Of the compounds detected in at least three of the four sampling periods in both the Croton and Catskill/Delaware Systems, the average concentrations, although well below the NYSDOH UOC or POC standards, were slightly higher in Croton than Catskill/Delaware.

[4] PFOS was also detected at all three keypoints, though at trace levels in the low parts-per-trillion (ng/L) range in the Croton system and below 1 part-per-trillion in the Catskill/Delaware System.

Table 7: Summary of Positive PPCP Detections at the Croton Water Supply System Source Water Testing Point (CRO1T)

Compound**	MRL (ng/L)	1st Quarter		2nd Quarter		3rd Quarter		4th Quarter	
		CROGH	CROGH-DUP	CROGH	CROGH-DUP	CROGH	CROGH-DUP	CROGH	CROGH-DUP
Acetaminophen (1)	1							1.7	2.5
Acetaminophen (2)	5						5		
Butalbital	5	24	21	15	15	13	12	12	14
Caffeine	3	13	14	14	15	14	15	13	13
Carbamazepine	1	4	4	3	2	5	4	5	5
cis-Testosterone	0.1			0.1	0.1				
Cotinine (1)	1	2.9	2.1	2.8	3	1.9	2.9	5.6	6
Cotinine (2)	1	3	3	2	2	3	3	5	6
DEET	5	6						10	11
Diazepam	1	1.7	1.8	2	2.1	1.5	1.6		
Gemfibrozil (1)	1	1.7	1.5	1.8	1.9	1.2	1.2		
Gemfibrozil (2)	0.5	0.8	1	1.3	1.6	1.5	1.3	0.7	0.5
Ibuprofen	1	2.5	2.6	3.9	4				
Lasalocid	1							3	3
Nicotine	5	7	11					11	11
Paraxanthine	5					6	5	6	5
Sulfamethoxazole	1	4.5	3.7	4.1	4	4.8	4.8	3.1	3.4

All concentrations listed in ng/L (parts-per-trillion)

**PFOS was also detected in all samples at CRO1T in a range of 0.61-2.3 ng/L

(1) - MWH Method EDC2SCR

(2) - UL Method UL220 or UL221

Table 8: Summary of Positive PPCP Detections at the Delaware Water Supply Source Water Testing Point (DEL18)

Compound**	MRL (ng/L)	1st Quarter		2nd Quarter		3rd Quarter		4th Quarter	
		DEL18	DEL18-DUP	DEL18	DEL18-DUP	DEL18	DEL18-DUP	DEL18	DEL18-DUP
Acetaminophen	5					5			
cis-Testosterone	0.1			0.1	0.1	0.1	0.1		
Cotinine	1	3	2						
Estrone	0.5	1.1	2.1						
Ibuprofen	1			2.2	2.2			2.5	2.1
Nicotine	5							7	
Progesterone	0.1					0.1	0.1		

All concentrations listed in ng/L (parts-per-trillion)

**PFOS was also detected in all samples at Del 18 in a range of 0.21-0.71 ng/L

Table 9: Summary of Positive PPCP Detections at the Catskill Water Supply Source Water Testing Point (CATLEFF)

Compound**	MRL (ng/L)	1st Quarter		2nd Quarter		3rd Quarter		4th Quarter	
		CATLEFF	CATLEFF-DUP	CATLEFF	CATLEFF-DUP	CATLEFF	CATLEFF-DUP	CATLEFF	CATLEFF-DUP
Caffeine	3	ND						3.4	4
cis-Testosterone	0.1			0.1	0.2	0.1	0.1	0.2	0.2
Cotinine	1	2	2						
Estrone	0.5	0.5							
Ibuprofen	1	1.6	1.4	2.3	1.8			3.2	2.8
Nicotine	5							6	6

All concentrations listed in ng/L

**PFOS was also detected in a range of ND- 0.73 ng/L

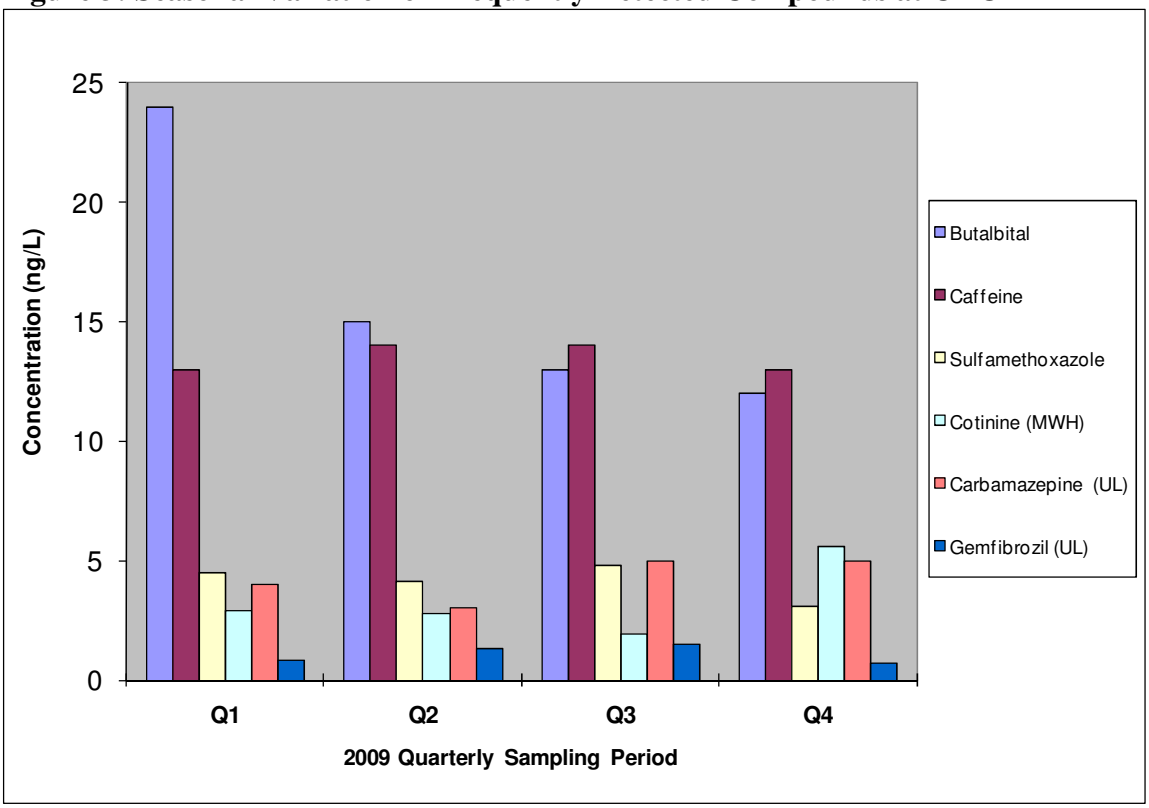
Butalbital was detected at a higher concentration than any of the other compounds detected in the pilot study, though it was detected only in the Croton System, in all Croton samples at concentrations ranging from 12-24 ng/L. From 2003 to 2006, the United States Geological Survey conducted a nationwide study to assess the occurrence and concentrations of organic wastewater compounds, and detected butalbital in approximately 50% of all samples, with a maximum concentration in wastewater effluent as high as 500 ng/L (Phillips et al., 2007).

The occurrence and concentrations of other frequently detected PPCP compounds in this study such as gemfibrozil, carbamazepine, caffeine, cotinine, and sulfamethoxazole are consistent with the results from other investigations within New York State/New Jersey, and the New York City Watershed, (Wilson et al., 2006; Benotti et al., 2006; Stackleberg et al., 2007; Palmer et al., 2008) as well as other national studies (Kolpin et al., 2002; Benotti et al., 2009).

Although the data are limited, at CRO1T, the concentrations of butalbital were observed to be higher in winter (24 ng/L) than in summer (12 ng/L). Concentrations of cotinine were lowest in the warmer temperatures of the third quarter (July 2009). At CATLEFF and DEL18, cotinine was only detected in the first quarter sampling event (January 2009) during colder temperatures. Carbamazepine did not exhibit the same type of seasonal trend as it was detected at consistent levels at CRO1T during each sampling event. A 2006 study of effluent concentrations also found that carbamazepine is consistently present throughout the year at consistent levels (Brun, 2006).

Concentrations of gemfibrozil and caffeine at CRO1T did not exhibit any significant seasonal variation in concentration. Both compounds were present at consistent levels for each sampling event (**Figure 3**). Additional seasonal sampling would be required to determine whether these observations are reproducible.

Figure 3: Seasonal Variation of Frequently Detected Compounds at CRO1T



IX. Health Implications

Although the human health risks associated with the presence of PPCPs in drinking water have not yet been thoroughly studied, several screening level risk assessments have concluded that no appreciable human health risk exists for the trace levels of PPCPs detected in this and other comparable studies (Snyder et al., 2008; Wilson et al., 2006; Schwab et al., 2005; Schulman et al., 2002). USEPA has summarized the different approaches that have been used to screen for human health risk from pharmaceuticals in drinking water (USEPA, 2008). In general, these approaches utilize existing toxicological data on acceptable therapeutic doses, or toxicological thresholds such as Acceptable Daily Intakes (ADIs), or Lowest or No Adverse Effect Levels (LOAELs or NOAELs), to establish some type of reference dose or point of departure to compare with screening level exposure estimates. In some cases, uncertainty factors are added to the "acceptable" toxicological reference value to account for intra- and inter-species differences in toxicity, as well as for gender, age or individual differences in susceptibility to toxicants. These numbers are then used to calculate screening level health risk metrics such as a Margin of Exposure (MOE). Simply put, the MOE is the ratio of the no-observed adverse-effect-level (or other toxicological threshold such as an Acceptable Daily Intake) to the estimated exposure dose.

Table 10 provides DEP's application of this methodology. Specifically, we utilized a screening level approach similar to that used by Snyder (Snyder, Trenholm, et. al., 2008).

This MOE approach compares the number of glasses of water that would have to be consumed to exceed a drinking water guideline (DWG) value derived by the authors from Acceptable Daily Intake values and other toxicological information. In most instances, the DWG is based on either the lowest therapeutic dose or the ADI.

The MOE for caffeine provides some perspective on the minute quantities of PPCPs found in the study. For example, it indicates that it would take over 200 million 8-oz. cups of water at the maximum concentration of caffeine detected in this study of 15 ng/L to exceed a drinking water guideline value represented by the amount of caffeine in one 8-oz. cup of coffee. For the remaining compounds, the number of glasses of water required to exceed an acceptable daily intake, the MOE, is well over 1000, often by several orders of magnitude. Consistent with the conclusions of other screening level risk assessments, these large MOEs suggest that the risks to the health of New York City consumers, if any, are likely to be *de minimis.*

Table 10: Number of Glasses of Water Required to Exceed Derived Drinking Water Guideline

Detected Compound	NYS Standard$^{\Omega}$ (ng/L)	Max Conc. (ng/L)	Toxicity Threshold	Units	Basis	DWG (ng/L)	# of 8 oz. glasses of water/day to exceed DWG	Reference
Acetaminophen*	5,000	5	50	µg/kg/day	ADI	175,000	296,100	fn 5
Butalbital	50,000	24	5,000	µg/kg/day	MRTD	175,000,000	61,687,500	fn 6
Caffeine	50,000	15	100	mg/(8-oz-cup)		423,000,000	238,572,000	fn 7
Carbamazepine	50,000	5	200	mg/day	LTD	100,000	169,200	fn 5
Cotinine	50,000	6	20	mg/day	LTD	10,000	14,100	fn 5
DEET*	5,000	11	0.1	mg/kg/day	ADI	3,500,000	2,691,818	fn 8
Diazepam	50,000	2.1	5	mg/day	LTD	2,500	10,071	fn 5
Estrone*	50,000	2.1	0.013	µg/kg/day	ADI	460	1,853	fn 9
Gemfibrozil	50,000	1.9	1,200	mg/day	LTD	600,000	2,671,579	fn 5
Ibuprofen	50,000	4	800	mg/day	LTD	400,000	846,000	fn 5
Lasalocid*	50,000	3	NI					
Nicotine	50,000	11	NI					
Paraxanthine	50,000	6	NI					
Progesterone*	50,000	0.1	30	µg/kg/day	ADI	105,000	8,883,000	fn 5
Sulfamethoxazole	5,000	4.8	10	µg/kg/day	ADI	10,000	17,625	fn 5
cis-Testosterone	50,000	0.1	2	µg/kg/day	ADI	7,000	592,200	fn 5

* Found in fewer than 50% of samples.
Ω NYS standard for UOCs = 50,000 ng/L and POCs = 5,000 ng/L
8 oz glasses/day = [DWG (ng/L)* 2 (L/d)*4.23 8oz glasses]/L/ (max water conc. (ng/L))

ADI = Acceptable **Daily Intake**. Maximum amount of a substance to which an individual can be exposed on a daily basis over his or her life span, without causing any harmful effects.
DWG = Drinking **Water Guideline**. Health-based guideline values representing minimum requirements for drinking water safety.
LTD = Lowest **Therapeutic Dose**. The LTD which produces the desired clinical effect.
MRTD = Maximum **Recommended Therapeutic Dose**. The recommended maximum amount of a drug to be given to a patient without causing adverse health effects.
NI = No Information

[5] *Australian Guidelines for Water Recycling*, Augmentation of Drinking Water Supplies, May 2008, Environment Protection and Heritage Council, National Health and Medical Research Council, Natural Resource Management Ministerial Council.
[6] U.S. Food and Drug Administration (FDA), Maximum Recommended Therapeutic Dose (MRTD) Database. http://www.fda.gov/aboutfda/centersoffices/cder/ucm092199.htm.
[7] Gilbert SG. *A Small Dose of Toxicology – The Health Effects of Common Chemicals*. CRC Press, Boca Raton, February 2004.
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X. Conclusions

The results of this one-year occurrence study indicate that PPCPs are present in very low concentrations (low parts-per-trillion range) in the New York City Watershed, with a greater frequency of detection in the Croton Water Supply's source water, compared to the Catskill/Delaware's source water. As indicated in **Table 6**, a total of 16 individual PPCP compounds were detected in at least one sampling event during the pilot study. The compounds detected most frequently, in at least three of the four sampling periods, included the following 8 compounds: butalbital, sulfamethoxazole, carbamazepine, caffeine, cotinine, diazepam, gemfibrozil, and cis-testosterone. The concentrations of these compounds at all locations were well below the New York State generic standards for UOCs or POCs of 50,000 ng/L and 5,000 ng/L, respectively. A screening level risk assessment conducted by DEP suggests that the concentrations of the detected PPCPs are well below levels that would pose a risk to the health of consumers of NYC's drinking water.

Positive detections of sulfamethoxazole, gemfibrozil, carbamazepine, caffeine, ibuprofen, cotinine, and diazepam at CRO1T are similar to results seen in other studies of wastewater compounds in surface waters (Kolpin et al., 2002; Benotti et al., 2009; Stackleberg et al., 2007; Heberer et al., 2001). Other studies have identified wastewater treatment plants as a point source of pharmaceutical and organic compound pollution into receiving waters (Benotti et al., 2006; Phillips et al., 2007). Wastewater treatment plants in the Croton and Catskill/Delaware Watersheds may be potential sources of pharmaceutical and personal care product compounds in surface waters (Palmer et al., 2008); however, due to the limited scope of this study, the potential sources of PPCP inputs into the Croton and Catskill/Delaware Watersheds were not investigated.

In addition to the PPCPs that were detected, PFOS, an industrial chemical was also detected year-round at all three sampling locations. As with the PPCPs, the maximum concentration of PFOS (2.3 ng/L) was well below the New York State generic standards for UOCs of 50,000 ng/L as well as below USEPA's Provisional Health Advisory level of 200 ng/L in drinking water (USEPA, 2009).[10]

DEP believes that the overall quality of the data provided by the contract labs was acceptable, and that the quality of the data improved as the laboratories became more familiar with the methods and optimized the methods as part of this study. For analytes targeted by both laboratories, and where there were comparable MRLs, the results were similar, providing additional confidence in the quality of the data for those analytes. DEP field personnel implemented a strict "clean hands" sampling procedure which was designed to preclude sample contamination during collection, storage, and delivery. Almost all field and trip blanks were non-detect, indicating that cross-contamination was adequately prevented.

[10] PFOS is an industrial compound that is a widespread, global pollutant. The discharge of wastewater from treatment plants has been demonstrated to be a major input of PFOS into aquatic environments (Becker et al., 2008). PFOS is one of the most prevalent of the perfluorinated compounds (PFCs) in the natural environment, and used to be used in various applications such as surface-treatments of fabric for soil/stain resistance (CMWG, 2003), lubricants, paints, and fire fighting foam. It has been detected at similar if not higher concentrations in surface waters of New York State (Sinclair, 2006). In 2009, USEPA's Office of Water developed Provisional Health Advisory values for PFOS to assess potential exposure risks. The Public Health Advisory value set for PFOS is 0.2 µg/L (200 ng/L). This value reflects health-based hazard concentrations above which action should be taken to reduce exposure in drinking water (USEPA, 2009b).

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