NYC Department of Environmental Protection 2019 Emerging Contaminant Monitoring Project Report September 2020

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Abstract

Emerging contaminants have long been a challenge for government regulators, scientists, engineers, and members of the public we serve. The term "emerging contaminants" is used to reference a class of compounds that is potentially harmful to human health, but for which there has not been substantial scientific analysis to understand the concentrations at which they might cause harm. Analysis of these contaminants in drinking water has become an avenue for assessing this potential risk. Because some these compounds are relatively new, they are not all subject to state and federal regulations that set limits for other contaminants after they have been studied for decades.

As part of our mission to protect public health, DEP periodically tests for emerging contaminants to determine whether they are present in our reservoir system. This proactive monitoring in the watershed allows us to gather information on these contaminants as early as possible if they are present in the system. In our most recent effort, DEP developed and conducted a one-year study of its untreated source water supply. The study included quarterly sampling and any positive results were compared to existing federal and state drinking water quality standards.

Fifteen sample sites were selected based on their identification as a source water, potential source water, or a perennial stream in the Kensico watershed. Representative sites included a total of four source water keypoints from Kensico and New Croton reservoirs, three upstate keypoints from West Branch, Rondout and Ashokan reservoirs; and eight streams from the Kensico basin. Samples were analyzed using ultra-low level, highly sensitive detection methodologies developed by either the contract laboratory via an in-house proprietary method, or by the U.S. Environmental Protection Agency (USEPA) when available. Strict quality control procedures were adhered to when collecting and analyzing the samples, which is important for testing analytes at ultra-low levels of detection.

Analytes selected included those from the $3rd$ and $4th$ Unregulated Contaminant Monitoring Rule (UCMR), pharmaceutical and personal care protection products (PPCPs), and a radionuclide suite. Overall, samples were analyzed for 148 compounds and were negative for 106 (72%) of those tested. Forty-two contaminants were detected among all sites. While Kensico streams were positive for perfluoroalkyl substances (PFAS), the outflow of the reservoir was not positive. Only one source water keypoint, New Croton Reservoir, had PFAS detections. Two of the four UCMR metals (manganese and strontium) were detected often, while hexavalent chromium and vanadium were detected less frequently. Most of the UCMR 4 compounds were not detected, with a maximum of 12 out of 124 compounds (9.7%) detected at one of the stream sites. Within the PPCP suite of analytes, the majority of the stream detections were composed of herbicides, pharmaceuticals, sugar substitutes and stimulant-related compounds such as caffeine. Only two of six radionuclides were detected, and these were indicative of ambient background levels naturally occurring in bedrock. Only keypoint sites were tested for algal toxins, and they were all negative.

The measured concentrations of the detected contaminants were all well below any regulated USEPA health reference concentration for drinking water, and New York State generic standards for individual unspecified organic contaminants (UOCs) or principal organic contaminants (POCs) of 50 μ gL⁻¹ and 5 μ gL⁻¹ respectively. Compliance with regulations is a moving target that DEP proactively evaluates on a continuing basis.

Introduction

An emerging contaminant is defined by the United States Environmental Protection Agency (USEPA) as "a chemical or material that is characterized by a perceived, potential, or real threat to human health or the environment, or by a lack of published health standards" (USEPA, 2014). Emerging contaminants have been regulated since 2001 (USEPA, 2016) under the umbrella of the Safe Drinking Water Act (SDWA). The SDWA process for selection of such contaminants begins first with the Contaminant Candidate List (CCL). Under the SDWA, a CCL must be published every five years. Various scientific organizations such as the World Health Organization, National Toxicology Program, and the Agency for Toxic Substance Disease Registry are but a few scientific sources for selecting substances for the CCL. These substances are not limited to inorganic or organic compounds, but also include items such as algal toxins, and microbes, such as *Cryptosporidium*. The CCL is then published in the Federal Register for public review and comment. Once a CCL is determined, the SDWA requires the USEPA to determine whether or not to regulate no fewer than five contaminants from the CCL in a process called regulatory determination. The endpoint of this regulatory determination is a National Primary Drinking Water Regulation (NPDWR), and a publication of an enforceable Maximum Contaminant Level (MCL) for these contaminants.

The CCL is considered the primary source of contaminants considered for the Unregulated Contaminant Monitoring Rule (UCMR). The UCMR program provides the USEPA with nationally representative data on the occurrence of particular contaminants in drinking water.

The USEPA has developed a PFAS Action Plan (USEPA, 2019) and a recent update (USEPA, 2020) detailing steps to contend with the growing concern over PFAS compounds within the United States. The action plan highlights the regulatory background of PFAS compounds and recommendations for short and long-term actions such as mitigation, public outreach, regulatory considerations, and research. The USEPA has recently reached the stage of a regulatory determination for contaminants within the $4th UCMR$ (USEPA, 2020); perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are part of this determination. Moreover, the NYSDOH recently promulgated MCLs for PFOS, PFOA and 1,4 dioxane.

Concern for the potential detection of emerging contaminants such as PFOS and PFOA in public drinking water supplies throughout the country prompted the DEP to determine if these compounds were present in its source waters.

Purpose

DEP completed the required monitoring for the UCMR4 within its distribution system; however, UCMR monitoring is not required within reservoir source waters. DEP designed this source water study to supplement the information gathered from the distribution system sampling. This monitoring also represents a follow-up to the 2009-2010 DEP study on the occurrence of pharmaceuticals and personal care products (PPCP) within the NYC Water Supply (NYCDEP, 2011), and the 2014 DEP UCMR3 watershed investigation (NYCDEP, 2014). This study broadens the analyte list to include both UCMR3 and UCMR4 contaminants, as well as radionuclides.

Specifically, this 2019 Emerging Contaminant Monitoring Project (ECMP) was designed to assess the spatial distribution of emerging contaminants at ultra-low levels over a calendar year. The goal of the study was to determine the occurrence of these compounds during each season. By proactively monitoring the upstate watershed, DEP can discover identifiable sources and ensure responsible parties mitigate those sources to protect the water supply. This is consistent with Bureau of Water Supply's goals to provide the highest quality water to NYC.

Site Selection and Sampling

The NYC watershed covers approximately 1,900 square miles in the lower Hudson Valley and Catskills. The watershed consists of three surface water sources: the Croton watershed, and the combined Catskill and Delaware (CAT/DEL) watershed system. Site selection was primarily designed to characterize Kensico Reservoir and its tributaries, as it is the terminal reservoir for the CAT/DEL system (Figure 1), and represents approximately 90% of the water supply. The outflows of New Croton and West Branch reservoirs (Figure 1) as well as the Rondout and Ashokan reservoirs (Figure 2) were also sampled. Kensico and New Croton samples were collected quarterly, while Rondout, Ashokan and West Branch outflows were added mid-year resulting in two samples each: one in the summer and one in autumn.

Figure 1. East-of-Hudson sites for the Emerging Contaminant Monitoring Project, 2019

Figure 2. West-of-Hudson sites for the Emerging Contaminant Monitoring Project, 2019.

Sites selected for ECMP sampling are all existing sample collection points for DEP and represent source water and upstate keypoints, as well as the eight perennial streams at Kensico Reservoir (Table 1).

Site Names	Watershed	Description	Drainage Area (km ²)		
Keypoints (source waters)					
DEL18DT	CAT/DEL, Kensico	Delaware Shaft 18, the	4209.7		
		outflow of Kensico			
		Reservoir.			
DEL17	Delaware, Kensico	Delaware Shaft 17, the	2733.18		
		inflow from the Delaware			
		Reservoir System.			
CATALUM	Catskill, Kensico	Catskill Alum Plant, the	1476.52		
		inflow from the Catskill			
		Reservoir System.			
CROGH/CROIT/CRO1B	New Croton	Croton Gatehouse and	969.92		
(CROGH was not online for		other Croton keypoints,			
the $2nd - 4th$ rounds of sampling,		outflow of New Croton			
so other representative sites		Reservoir			
were selected.)					
Upstate Keypoints					
EARCM	Catskill, Ashokan	Outflow of Ashokan	1476.52		
		Reservoir			
RDRRCM	Delaware, Rondout	Outflow of Rondout	2624.03		
		Reservoir			

Table 1. Source water and upstate keypoint sampling sites and descriptions for 2019.

Samples were collected between January 29 and October 31, 2019. All samples were collected on the same day with the exception of the first quarter, when sampling was spread over two days. After collection, samples were shipped the same day for overnight delivery to the contract laboratory (Eurofins-Eaton Analytical, LLC).

All sites were sampled during each sample round, with the following exceptions: 1) resampling was needed related to an issue with the contract laboratory, 2) bottle breakage during sampling or shipping and 3) Rondout, Ashokan and West Branch sites were added mid-year and sampled only twice.

For quality control purposes, field reagent blanks (FRB) and field duplicates (DUP) were collected at one site per sampling run. The location of the duplicate sample was changed for each round of quarterly sampling (Table 2).

Table 2. Locations of field reagent blanks and duplicate samples collected throughout the study.

x – Upstate reservoir keypoints were added to the study for the third and fourth quarter sampling.

Field Methods

Samples were collected as grab samples using protocols established for each individual method as developed by Eurofins-Eaton Analytical, LLC (2019 NYCDEP ECMP Project Plan). Some methods with ultra-low levels of detection were selected (ng L^{-1} = parts per trillion compared to $\mu g L^{-1}$ = parts per billion). Sampling was performed with extreme care throughout the collection process. This included precautions such as avoiding the handling of food packaging and certain foods and beverages before sampling, and wearing powderless nitrile gloves while filling and sealing the sample bottles to avoid contamination.

After collection, samples were packed in coolers and shipped the same day with overnight delivery to the Eurofins-Eaton Analytical, LLC in California.

Figure 3. DEP staff sampling for PFAS compounds per instructions from Eurofins-Eaton Analytical LLC.

Analytical Methods

Samples were analyzed for 148 different compounds. They included 19 chemicals from the UCMR3 list: three metals, one volatile organic compound, one salt of chloric acid, and 14 perfluorinated compounds; and chemicals from the UCMR4 list: two metals, nine pesticides, three semi-volatile compounds, three alcohols, nine algal toxins; and 97 PPCPs. DEP also included a suite of six radionuclides for this study.

Eurofins-Eaton Analytical, LLC established a minimum reporting level (MRL) for each method. The MRL is the minimum level (concentration) that the laboratory can report accurately for each analyte. MRLs were established based on the capability of the analytical method as determined by the USEPA and not based on a level considered "significant" or "harmful" (USEPA, 2018). Units for reporting MRLs can vary due to differences in method sensitivity. For consistency, MRLs and other data in this report, are recorded as micrograms per liter ($\mu g L^{-1}$) which is equivalent to parts per billion.

MRLs are often below current "health reference concentrations" (HRC) to the extent that HRCs have been established (USEPA, 2017, 2018) (Tables 3 and 4). HRCs are health-based and provide context for the detection of a contaminant. They do not represent regulatory standards or action levels and should not be interpreted as an indication that the USEPA intends to establish a future drinking water regulation (USEPA, 2018). The HRC may also be altered in the future as new data become available. Appendix 1 contains PPCP contaminants and radionuclides examined in this study that were not associated with UCMR3 (Table 3) or UCMR4 (Table 4).

Table 3. Summary of UCMR3 compounds, methods, MRLs and the HRCs (USEPA, 2017). (Units are $\mu g L^{-1}$)

NA- not applicable (USEPA, 2017)

¹ The contaminant is on the Integrated Risk Information System (IRIS) Agenda for either a new assessment or update assessment (USEPA, 2017)

² Reference concentration range is based on cancer risk of 10^{-6} to 10^{-4} ; 10^{-6} cancer risk $\lt MRL < 10^{-4}$ cancer risk *(USEPA, 2017)*

³ The analytical methodology and the derivation of an MRL of the hormones listed in Table 3 were not generated by a USEPA methodology, but by a proprietary Eurofins-Eaton Analytical, LLC methodology (EEA 9609). EEA 9609 is part of the UCMR4 suite of compounds, and is cross referenced in Table 4.Method EEA-9609 is reported as ng/L; however, MRLs and USEPA HRCs are reported here in µg/L for consistency.

Table 4. Summary of UCMR4 compounds, methods, MRLs and HRCs (USEPA, 2018). (Units are μ gL⁻¹)

¹*Reference concentration is based on cancer risk of 10-6 to 10-4 ; 10-6 cancer risk<MRL<10-4 cancer risk (USEPA, 2017)*

² *Cross-Referenced to Table 3.*

³*The Algal Toxins analytical methodology and the derivation of an MRL were not generated by a USEPA methodology, but by a proprietary Eurofins-Eaton Analytical, LLC methodology (Algal – Low 9).*

Quality Control

Eurofins-Eaton Analytical, LLC analyzed quality controls (QC) with each group of samples sent. The results document the accuracy and precision at the time of the actual testing, and are meant to indicate that any compounds present in the samples came only from the water being tested. Field duplicates were collected as part of the QC procedure to prepare laboratory fortified sample matrix and laboratory fortified matrix duplicate QC samples (USEPA, 2019).

Field (Sample) Duplicates: Field duplicates are separate samples collected at the same time and sampling location as a companion sample, and are shipped and stored under identical conditions (USEPA, 2019). Method precision, including the contribution from sample collection procedures, is estimated using the field duplicates. DEP collected two sample duplicates each sampling quarter for each analyte, with the exception of algal toxins, which was one duplicate per quarter.

Field Reagent Blanks: Reagent water is placed in a sample bottle by Eurofins-Eaton Analytical, LLC and treated as a sample in all respects including the following:

- Shipping to the DEP
- Exposure to sampling site conditions
- Storage
- Shipping back to Eurofins-Eaton Analytical, LLC
- All analytical procedures

A field reagent blank for PFAS compounds (537.1) is slightly different than a field blank. Instead of pouring DI water into bottles containing the preservative, the DI water is mixed with the preservative at the lab and the preserved DI water is poured into an empty 250 mL plastic bottle in the field. (Eurofins-Eaton Analytical, LLC, 2019).

Origin of Detected Compounds

This section provides some background on the detected compounds and describes potential sources (Tables 5 and 6).

UCMR 3 Analytes

PFAS compounds are anthropogenic in origin (State of California, 2017). These compounds are used to make products that are non-stick, resistant to stains, and waterproof. Examples include: non-stick cookware, furniture, carpets, mattresses, clothing, and food packaging. Additional uses include fire suppression and friction modifiers for the aerospace, automotive, construction and electronic industries.

Of the 14 PFAS compounds investigated, five were not detected at any stream site studied, and will not be discussed further due to lack of detection.

PFAS not detected in this study:

- N-ethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA)
- N-methyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA)
- Perfluorododecanoic acid (PFDoA)
- Perfluorotetradecanoic acid (PFTA)
- Perfluorotridecanoic acid (PFTrDA)

PFAS compounds detected at least once during this study:

- Perfluoroundecanoic acid (PFUnA)
- Perfluoroheptanoic acid (PFHpA)
- Perfluorononanoic acid (PFNA)
- Perfluorobutanesulfonic acid (PFBS)
- Perfluorooctanic acid (PFOA)
- Perfluorooctanesulfonic acid (PFOS)
- Perfluorohexanesulfonic acid (PFHxS)
- Perfluorohexanoic acid (PFHxA)
- Perfluorodecanoic acid (PFDA)

PFOA and PFOS are the only two PFAS compounds within the UCMR3 with HRCs – both at $0.07 \mu gL^{-1}$, and a recently promulgated New York State Department of Health (NYSDOH) Maximum Contaminant Level (MCL) of 0.01 µgL-1 for *drinking water*. The other PFAS compounds within the UCMR3 spectrum (PFBS, PFHpA, PFHxS and PFNA) and others within USEPA 537 that are not within UCMR3 (PFDA, PFUnA, PFHxA) have a NYSDOH Unregulated Organic Contaminant (UOC) MCL of 50 μgL^{-1} .

Strontium is a natural and commonly occurring element (ATSDR, 2004b). Rocks, soil, dust, coal, oil, surface and underground water, air, plants, and animals all contain varying

amounts of strontium. Stable strontium that is dissolved in water comes from running over and through rocks and soil. Only a very small portion of the strontium found in water is from the settling of strontium dust out of the air. Strontium compounds, such as strontium carbonate, are used in making ceramics and glass products, pyrotechnics, paint pigments, fluorescent lights, medicines, and other products.

Vanadium occurs naturally in soil, water, and air. Natural sources of atmospheric vanadium include continental dust, marine aerosol, and volcanic emissions (ATSDR, 2012d). Releases of vanadium to the environment are mainly associated with industrial sources, especially oil refineries and power plants using vanadium rich fuel oil and coal. Global humanmade atmospheric releases of vanadium have been estimated to be greater than vanadium releases due to natural sources. Natural releases to water and soil are far greater overall than human-made releases to the atmosphere. Vanadium concentrations in surface water can range from approximately 0.04 to 220 μ gL⁻¹ depending on geographical location (ATSDR, 2012d).

Chromium can be found in air, soil, and water after release from the manufacture, use, and disposal of chromium-based products (ATSDR, 2012a). Chromium does not usually remain in the atmosphere, but is deposited into the soil and water. Specifically, hexavalent chromium is used for chrome plating, dyes and pigments, leather tanning, and wood preserving. It has been noted in other water quality monitoring programs that widespread occurrence at generally low levels suggests that these concentrations represent natural background levels and are not necessarily from a specific source of pollution (CDPH, 2011). Possible background sources in drinking water are from chromium dissolving from soil and bedrock, which is a natural part of the earth's crust. It should also be noted that chromium compounds are very persistent in the aquatic environment, mostly bound to sediments and soil.

Chlorate sources commonly originate from the degradation of hypochlorite solutions, the on-site generation of hypochlorite, and the production and degradation of chlorine dioxide (Alfredo, K, et al., 2015). Sources may be from finished drinking water or other sources of chlorinated water within a sub-basin.

1,4-Dioxane is a clear liquid that easily dissolves in water (ATSDR, 2012b). It is used primarily as a solvent in the manufacture of chemicals and as a laboratory reagent. 1,4-Dioxane is a trace contaminant of some chemicals used in cosmetics, detergents, and shampoos. However, manufacturers now reduce 1,4-dioxane from raw materials to low levels before these chemicals are made into products used in the home. 1,4-Dioxane can be released into the air, water, and soil at places where it is produced or used as a solvent. In water, 1,4-dioxane is stable and does not break down. In soil, 1,4-dioxane does not adsorb to soil particles, so it can move from soil into groundwater. NYSDOH recently promulgated a drinking water MCL of 1 μgL^{-1} for 1,4-dioxane.

Table 5. Detected UCMR3 analytes and potential sources.

UCMR 4 Analytes

Manganese is a natural component of the environment (of soil and rock) and is contained in groundwater, drinking water, and soil at low levels (ATSDR, 2012c). Having both natural and anthropogenic sources (ATSDR, 2012c), manganese can be transferred to streams and reservoirs via runoff. From a potable drinking water standpoint, the World Health Organization (2017) does not consider manganese a health concern as related to drinking water quality.

Tebuconazole, the only pesticide detected during this study, is a systemic fungicide used for control of fungi and diseases on ornamental plants and turf (e.g., golf courses) (Albaugh, LLC, 2019)

The Eurofins-Eaton Analytical, LLC proprietary method for PPCPs, EEA-9609, contains 97 compounds of various sorts including pesticides, pharmaceuticals, insect repellants, stimulants and metabolites of the aforementioned products. A total of 73 of these 97 compounds were not detected and will not be discussed. Herbicides were the primary class of pesticide detected. Due to their overall low soil absorption (K_{∞}) value, they tend to be found in runoff, and have a higher surface water leaching potential than other classes of pesticides. K_{oc} is defined as a measure of a chemical's tendency to bind to soil organic carbon (Pesticide Research Institute, 2020). Values vary based on, for example, soil pH and soil type. A higher K_{oc} value indicates the chemical has lower mobility and less likelihood of leaching in soil; a lower K_{oc} value indicates higher mobility greater likelihood of leaching in soil.

Two compounds were detected only once in streams, therefore there was no consistency in detection. These compounds will be mentioned briefly in the "Other Detections" section later in this document.

Table 6. Detected UCMR4 analytes and potential sources.

Results and Discussion

Results are presented by site, beginning with reservoir keypoints (Kensico, New Croton, Rondout, Ashokan and West Branch) followed by the eight Kensico perennial streams. As mentioned previously, while some compounds were analyzed with ultra-low level sensitivity $(ngL^{-1}$ = parts per trillion), for consistency, all results are reported in μgL^{-1} , which is parts per billion.

Keypoint Results – Kensico Reservoir

The results of this keypoint section of the report are presented by reservoir with subsections for: Perfluorinated Compounds, Other Compounds, Algal Toxins, and Radionuclides. At the end of the section there is a Keypoint Summary.

Perfluorinated Compounds

No PFAS compounds were detected at the Kensico Reservoir inflows or outflow (CATALUM, DEL17, or DEL18DT).

Other Compounds

Of the 148 compounds tested in this study, only a few were detected at the aqueduct inflows of Kensico Reservoir. Four compounds were detected at CATALUM, and seven at DEL17 (Table 7a). Strontium, hexavalent chromium, and manganese were the most commonly detected and found in samples from all four quarters at both aqueduct inflows. Caffeine, metformin, tris (1-chloro-2- propyl) phosphate (TCPP), and theobromine were also detected at the Delaware inflow, each occurring once in either the spring or summer sampling events. The Catskill inflow had one other detection and that was metformin during the summer quarter.

Table 7a. Detected compounds at Kensico Reservoir aqueduct inflows, 2019.

** First quarter hexavalent chromium data resulted from USEPA Method 218.6, the other quarters with USEPA Method 218.7.*

The Kensico Reservoir outflow (DEL18DT) was positive for seven of the 148 compounds tested in 2019 (Table 7b). Five of the seven compounds were the same as those detected at the aqueduct inflows and occurred at similar concentrations. As with the inflows, strontium, hexavalent chromium and manganese were the most commonly detected and were positive all quarters of testing. Metformin was similarly detected once in the summer, as it was at the Catskill and Delaware aqueduct inflows. TCPP was detected twice at DEL18DT, in the summer and autumn, while it was detected once at the Delaware inflow in the summer. There were two compounds detected at DEL18DT that did not appear in the aqueduct inflow samples, and those were lidocaine and quinoline. These compounds were each identified once during the spring sampling.

Table 7b. Detected compounds at the Kensico Reservoir outflow, 2019.

** First quarter hexavalent chromium data resulted from USEPA Method 218.6, the other quarters with USEPA Method 218.7.*

As an observation, the amount of strontium measured in drinking water in different parts of the United States by the USEPA is on average less than $1000 \mu gL^{-1}$ (ATSDR, 2004a). Reservoir inflow and outfall concentrations are well below this range.

Levels of hexavalent chromium detected in keypoints were lower than the majority of samples collected from drinking water sources across the USA between 1998 and 2005: in those samples total chromium levels were 0.02 -100 μ gL⁻¹ (Seidel, et al, 2013). Currently the USEPA measures chromium as total chromium, which includes the +6 valence state (U.S. Water Systems, 2019).

Manganese was found at all keypoints during 2019. This is not unusual, as it is a very common and ubiquitous element in the environment occurring in the majority of all soils (ATSDR, 2012c). In a study conducted within five states over a four-year period with greater than 37,000 results, the median manganese concentration was $10 \mu gL^{-1}$ with the 99th percentile being 720 μ gL⁻¹. Concentrations found at keypoints ranged from a low of 7.7 μ gL⁻¹ at CATALUM and DEL18DT in April, to a high of 82 μgL^{-1} at CROGH in July.

Algal Toxins

There were no detections of algal toxins at the Kensico Reservoir inflows or outflow during this study.

Radionuclides

There were no detections of uranium, radium 226, radium 228 or gross alpha or gross beta at Kensico Reservoir inflows or outflow during this study.

Keypoint Results – New Croton Reservoir

Perfluorinated Compounds

Three of the 14 PFAS compounds included in this study were detected at the outflow of New Croton Reservoir (CROGH or alternate site) in each of the sampling quarters (Table 7c). PFHxA, PFOA and PFOS concentrations were just slightly above the ultra-low MRL of 0.0020 μ gL⁻¹ and all results were below the USEPA HRC and below the NYSDOH MCL for PFOS and PFOA.

** First quarter hexavalent chromium data resulted from USEPA Method 218.6, the other quarters with USEPA Method 218.7.*

Other Compounds

The New Croton Reservoir outflow samples were positive for 13 of the nonperfluorinated compounds tested in 2019 (Table 7c). Five of these were the same as some found in the Kensico outflow, with strontium and manganese also positive in each quarter of sampling, and hexavalent chromium positive three of the quarters. Metformin was positive once, in the autumn, and quinoline was positive in the spring and summer quarters.

Compounds identified at the New Croton outflow that were not identified at Kensico Reservoir include: 1,7-dimethylxanthine, caffeine, 2,4-D, acesulfame-K, iohexol, sucralose,

theophylline and one winter sample was positive for Gross Beta. Of these, caffeine, acesulfame-K, iohexol and sucralose were positive every quarter.

Algal Toxins

There were no detections of cyanotoxins at the New Croton Reservoir outflow during this study.

Radionuclides

There were no detections of uranium, radium 226, radium 228 or gross alpha at the New Croton Reservoir outflow during this study. Gross beta was detected in the first quarter winter sample, at 3.4 pCiL $^{-1}$.

Keypoint Results – Additional Reservoirs

Perfluorinated Compounds

No PFAS compounds were detected at upstate reservoir keypoints (Rondout - RDRRCM, Ashokan - EARCM or West Branch - CWB 1.5).

Other Compounds

As mentioned, the Rondout, Ashokan and West Branch reservoir outflow samples were added midway through the study, and as such were sampled only in the summer and autumn quarters (Table 8). These reservoirs were selected as they have the potential to become terminal reservoirs under certain operational configurations. Seven compounds were detected among these three reservoirs. Strontium, hexavalent chromium and manganese were positive at all three sites in both quarters sampled. Acesulfame-K, metformin and TCPP were detected in nearly all of the summer samples at these sites, with the exception of no detection of acesulfame-K at RDRRCM. All samples collected in the autumn were negative for these three compounds.

Table 8. Detected compounds at the Rondout, Ashokan and West Branch outflows – summer and autumn, 2019.

Algal Toxins

There were no detections of algal toxins at the Rondout, Ashokan or West Branch Reservoir outflows during this study.

Radionuclides

There were no detections of uranium, radium 226, radium 228 or gross alpha or gross beta at Rondout, Ashokan or West Branch outflows during this study.

Keypoint Summary

USEPA HRC exceedances at keypoints

• None

Perfluorinated Compounds (PFAS)

- No PFAS compounds were detected at the Kensico Reservoir aqueduct inflows or outflow during quarterly sampling.
- No PFAS compounds were detected at the upstate reservoir keypoints for the two quarters sampled.
- Three of the PFAS compounds (PFOS, PFOA and PFHxA) were detected at the New Croton outflow; concentrations were below the USEPA HRC of 0.07 $\mu g L^{-1}$, and below the NYS drinking water MCL of $0.010 \mu gL^{-1}$ for PFOS and PFOA.

PPCPs

- Four of the 97 PPCPs tested were detected at Kensico inflows: caffeine, TCPP and theobromine (1 detect each) and metformin (2 detects).
- Four PPCPs were detected at the Kensico outflow: metformin, lidocaine and quinoline were detected once and TCPP was detected twice.
- Metformin was detected in the summer at both the Kensico inflows and the outflow.
- TCPP was detected at one Kensico inflow in the summer, and at the outflow in the summer and the autumn.
- Lidocaine and quinoline were detected once each at the outflow of Kensico, and both were detected in the spring.
- New Croton was positive for 10 of the 97 PCPPs tested.
- Four PPCPs were detected all four quarters: sucralose, acesulfame-K, iohexol and caffeine, in descending order of concentration.

Other Compounds

- Strontium, manganese and hexavalent chromium were detected all four quarters at the Kensico inflows and outflow, and the three upstate reservoir keypoints. Concentrations remained relatively consistent throughout the year.
- Strontium and manganese concentrations were well below the USEPA HRC levels of 1,500 and 300 μgL^{-1} , respectively; there is no established HRC for hexavalent chromium.
- New Croton was positive for strontium, manganese and hexavalent chromium all four quarters, except hexavalent chromium was not detected in the autumn.
- Vanadium and chlorate were not detected at the Kensico inflows or outflow, nor at the Rondout, Ashokan or New Croton keypoints.
- Vanadium was positive for one of the two samples collected at the West Branch reservoir keypoint.
- No algal toxins were detected at any of the keypoints during this study.

Kensico Stream Results

As with the keypoints, the stream results are presented by site (Figure 4). Since more compounds were detected in the streams, the subsections are laid out with Perfluorinated Compounds first, followed by PPCPs, Other Compounds, Radionuclides (for all streams), Additional Stream Detections, and lastly a Kensico Stream Summary. Streams were not sampled for algal toxins during this study. As a note, Kensico streams comprise <0.5% of the water volume entering Kensico Reservoir during base flow conditions.

Figure 4. Kensico Reservoir Stream sampling sites and surrounding areas, 2019.

Malcolm Brook and stream N5 are located along the western shore of Kensico Reservoir, while N12, Whippoorwill and Bear Gutter creeks flow into the northern area of the reservoir. Streams E9, E10 and E11 are all tributaries to Rye Lake, situated in the eastern portion of the reservoir, with the latter two receiving run-off from the Westchester County airport.

Malcolm Brook (MB-1)

Perfluorinated Compounds

Malcolm Brook samples resulted in the detection of seven of the 14 perfluorinated compounds tested (Figure 5). Five of the detected compounds were detected all four seasons. Neither PFHpA nor PFNA were detected in the winter or autumn samples, and the PFAS compound with the maximum concentration was PFOA.

Figure 5. PFAS detections at MB-1 in 2019.

PPCPs

Malcolm Brook tested positive for eight of the 97 PPCPs studied (Figure 6). All but one, TCPP, were detected below $0.05\mu gL^{-1}$. Caffeine and acesulfame-K were detected most often, occurring in four and three seasons, respectively.

Figure 6. PPCPs detections at MB-1 in 2019.

Other Compounds

Malcolm Brook was positive for strontium each quarter of sampling with a maximum of 170 μ gL⁻¹ (Table 9). This level is well below the HRC of 1500 μ gL⁻¹.

Table 9. MB-1 Seasonal breakdown of positive detections of compounds other than PFAS and PPCPs.

Malcolm Brook chlorate concentrations exceeded the HRC of 210 $\mu g L^{-1}$ in the autumn and winter seasons. Chlorinated water sources within this residential basin may include hot tubs and swimming pools.

The autumn sampling at Malcolm Brook resulted in a manganese concentration which exceeded the HRC of 300 μ gL⁻¹. The other three seasons had manganese concentrations below this exceedance level.

At Malcolm Brook, vanadium was detected in all four seasons of sampling at low concentrations, well below the HRC of 21 $\mu g L^{-1}$.

Malcom Brook levels of hexavalent chromium were below $0.25 \mu gL^{-1}$. There is presently no HRC for hexavalent chromium (USEPA, 2017).

N5 Stream (N5-1)

Perfluorinated Compounds

Site N5-1 was positive for six of the 14 perfluorinated compounds (Figure 7) which match six of the seven detected at Malcolm Brook. Four of the six were detected in all seasons. PFHpA and PFNA were only detected in the summer quarter, and the PFAS compound with the maximum concentration was PFOA.

Figure 7. PFAS detections at N5-1 in 2019.

PPCPs

Nine of the 97 tested PPCPs were detected in the N5 stream (Figure 8) and no detections were made in the first quarter.

Figure 8. PPCPs detections at N5-1 in 2019. First quarter not presented due to non-detection.

Other Compounds

Strontium and manganese were detected during each sampling event, while chlorate was only detected in the summer and autumn (Table 10). The HRC for manganese was exceeded once $(320 \mu g L^{-1})$ as noted with the October sampling results. Vanadium and hexavalent chromium concentrations were below 2 μ gL⁻¹ and their HRCs.

N12 Stream

Perfluorinated Compounds

Samples at N12 were positive for six of the 14 PFAS compounds tested (Figure 9). Two of these were detected during all four quarters, PFHxA was detected three times, PFHxS and PFHpA were detected twice, and PFBS only once. The season with the most compounds detected was summer. Five of the six detected compounds at N12 were the same as those detected at N5 and Malcolm Brook, with PFOA recovered at the highest concentration.

Figure 9. PFAS detections at N12 in 2019.

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PPCPs

Four of the 97 PPCPs examined were detected at N12 (Figure 10) and no PPCPs were detected in the fourth quarter. Artificial sweeteners acesulfame-K and sucralose were most commonly detected and in higher concentrations than 2,4-D and metformin.

Figure 10. PPCP detections at N12 in 2019. Last quarter not presented due to non-detection.

Other Compounds

Strontium, hexavalent chromium, manganese, and chlorate were detected in all four samples collected at N12 (Table 11). Vanadium was positive three of the four quarters. Strontium had the highest concentrations in the winter, spring and summer; however then chlorate was the highest in the autumn. Vanadium was well below its HRC of 21 μgL^{-1} and strontium below its HRC of $1500 \mu gL^{-1}$.

N12	Winter Jan 29	Spring Apr 17	Summer Jul 24	Autumn Oct 15
Strontium $(\mu g/L^{-1})$	140	150	160	38
Vanadium $(\mu g/L^{-1})$	$<$ MRL	0.21	0.42	1.8
Hexavalent chromium $(\mu g/L^{-1})$	0.056	0.19	0.23	0.16
Manganese $(\mu g/L^{-1})$	28	25	21	42
Chlorate $(\mu g/L^{-1})$	26	15	41	160

Table 11. N12 – Seasonal breakdown of positive detections of compounds other than PFAS and PPCPs.

Whippoorwill Creek (WHIP)

Perfluorinated Compounds

Six of the 14 PFAS compounds were detected at site WHIP (Figure 11), and they were the same six compounds detected at N12. This is not surprising as these streams are proximal to each other in the northern part of the reservoir. Three of the compounds were detected during each sampling event. PFOS was detected three times, PFHpA was detected twice, and PFHxS was detected once in the autumn. Similar to previous sites, PFOA had the highest concentration at WHIP compared to the other PFAS chemicals.

Figure 11. PFAS detections at WHIP in 2019.

PPCPs

Of the 97 PPCPs analyzed, 10 were detected at site WHIP (Figure 12). Of those detected, the artificial sweeteners acesulfame-K and sucralose were detected in the highest concentrations each season. TCPP was similar in concentration to sucralose, but only during the summer event. The detection of these compounds may be attributable to many of the neighborhoods in the WHIP basin having septic systems rather than sewers.

Figure 12. PPCP detections at WHIP in 2019.

Other Compounds

Strontium, hexavalent chromium and manganese were detected all four quarters at WHIP (Table 12). Manganese and strontium did not exceed their HRC at this site. Chlorate was positive in three of the seasons, but not during the winter sampling event. Both vanadium (no HRC exceedance) and hexavalent chromium were below $1 \mu g L^{-1}$.

Bear Gutter Creek (BG9)

Perfluorinated Compounds

Six of the 14 PFAS compounds were detected at Bear Gutter Creek (Figure 13), and they were the same six compounds detected at N12 and WHIP and mostly similar to the previous streams discussed. Only two of the six were detected during each quarter – PFOA and PFOS. The other PFAS compounds were detected two or three times with PFHxS only detected in autumn. PFOA was detected in the highest concentrations.

Figure 13. PFAS detections at BG9 in 2019.

PPCPs

Eleven of the 96 PPCPs were detected at BG-9 (Figure 14). The highest concentration was TCPP in autumn $(0.32 \mu gL^{-1})$, followed by TCPP in the summer and sucralose in the winter and spring.

Figure 14. PPCPs detected at BG9 in 2019.

Other Compounds

Manganese had the highest concentrations at BG-9 during three of the sampling seasons, reaching maximum value in the autumn (>HRC) (Table 13). Strontium was also highest in autumn. Chlorate was detected only once in the summer. Vanadium and hexavalent chromium concentrations were less than $0.6 \mu gL^{-1}$.

Table 13. BG9 – Seasonal breakdown of positive detections of compounds other than PFAS and PPCPs.

E9 Stream

Perfluorinated Compounds

Similar to previously mentioned streams, E9 resulted in the detection of the six most commonly found PFAS compounds in the Kensico basin (Figure 15). Three of these six were detected in all four samples, PFOS was detected twice (summer and autumn), while PFHxS and PBFS were each detected once, in the spring and summer, respectively. PFOA maintained the highest concentrations throughout the year at E9.

Figure 15. PFAS detections at E9 in 2019.

PPCPs

Ten of the 97 PPCPs examined during this study were positive at E9 (Figure 16). The PPCP with the highest concentration was TCPP $(0.43 \mu g L^{-1})$; however it was only detected in the summer. Acesulfame-K was the second highest concentration (approx. $0.05 \mu gL^{-1}$) and was detected in three of the four quarters.

Figure 16. PPCP detections at E9 in 2019.

Other Compounds

Strontium and manganese were detected all four seasons at E9, while chlorate was not detected (Table 14). The maximum concentration was manganese in the autumn at 600 μgL^{-1} exceeding its HRC of 300 μ gL⁻¹. Vanadium (not exceeding its HRC) and hexavalent chromium were also detected, once and three times, respectively, and were less than $0.5 \mu gL^{-1}$.

E11 Stream

Perfluorinated Compounds

Data from the six previously discussed streams were presented on a scale of $0.016 \mu gL^{-1}$; however, due to the higher concentrations detected at E11 the scale was increased to 0.07 μgL^{-1} (Figure 17)**.** A reference line marking the maximum value of the other six streams is provided. Seven of the 14 PFAS compounds studied were detected at E11. All seven compounds were detected in all four quarters, and four of those were detected at concentrations higher than the maximum value of the other six streams (PFHxS, PFOA, PFHxA and PFOS, in descending order of concentration). PFHpA and PFNA each exceeded the previous stream maximum for one of the quarters, while PFBS was detected within the concentration range of the other streams. Several potential sources of these compounds exist in this basin, including manufacturing, landfills and the Westchester Country Airport.

Figure 17. PFAS detections at E11 in 2019.

PPCPs

E11 was positive for eleven of the 97 PPCPs tested in this study (Figure 18) and no PCPPs were detected in the first quarter. Not unlike stream E9, the highest concentration was TCPP and it was also detected in autumn, with additional detections in the spring and summer at less than half the concentration.

Figure 18. PPCPs detections at E11 in 2019. First quarter not displayed due to non-detection.

Other Compounds

Strontium and manganese were again detected all four quarters with no detection of chlorate (Table 15). Manganese was considerably higher in the spring, summer, and autumn, exceeding the HRC during these three sample runs, while strontium concentrations were relatively stable throughout the year and below its HRC. Vanadium and hexavalent chromium were also frequently detected (three out of four quarters) and were less than $1 \mu gL^{-1}$.

E11	Winter Jan 29 Results	Spring Apr 17 Results	Summer Jul 24 Results	Fall Oct 15 Results
Strontium $(\mu g/L^{-1})$	110	130	63	160
Vanadium $(\mu g/L^{-1})$	$<$ MRL	0.21	0.88	0.23
Hexavalent chromium $(\mu g/L^{-1})$	0.033	0.14	0.13	\triangle MRL
Manganese $(\mu g/L^{-1})$	62	630	670	550

Table 15. E11 – Seasonal breakdown of positive detections of compounds other than PFAS and PPCPs.

E10 Stream

Data from the first six streams were presented on a scale of $0.016\mu gL^{-1}$; E11 was presented on a scale of 0.07 μgL^{-1} ; however, due to the higher concentrations detected at E10 the scale was increased to 1.4 μ gL⁻¹ (Figure 19). A reference line marking the maximum value at E11 is provided for comparison. Nine of the 14 PFAS compounds were detected at E10, which is the highest number of detections among the Kensico streams. Four of these were detected in all seasons, at concentrations higher than E11 (PFOS, PFHxS, PFOA and PFHxA in descending order of concentration). PFOS and PFOA exceeded the HRC of 0.07 $\mu g L^{-1}$. These are the same four compounds that had the highest concentrations at E11. The other five compounds were at or below the maximum level for E11, with the exception of one sampling event in the autumn when PFNA exceeded the maximum. Similar to E11, E10 potential sources of these compounds include manufacturing, landfills and the Westchester County Airport.

Figure 19. PFAS detections at E10 in 2019.

PPCPs

Quarterly sampling for 97 PPCPs at E10 resulted in the detection of seven compounds (Figure 20). Most commonly detected and in the highest concentrations were acesulfame-K and sucralose, found in four and three quarters respectively. The highest concentration was sucralose in the summer sample $(0.28 \mu gL^{-1})$. The next highest concentrations were acesulfame-K and the only detection of TCPP, also both detected in the summer.

Figure 20. PPCPs detections at E10 in 2019.

Other Compounds

Strontium and manganese were detected all four seasons at E10, with strontium concentrations staying similar throughout the year (below its HRC) and manganese levels decreasing considerably from winter to autumn (Table 16) exceeding its HRC in the January sample. No chlorate was detected at E10. Hexavalent chromium was detected all quarters; however vanadium was detected in the spring and summer. These two compounds were detected at concentrations less than 0.7 μgL^{-1} .

Radionuclides –All Streams

Radionuclide Suite ("EPA Method 200.8" for Uranium; EPA 900.0 for gross alpha and gross beta; GA Method for radium 226 and 228)

Radioactive forms of elements are radionuclides and are naturally occurring in every substance and material on Earth (State of California, 2017b). Gross alpha (particle), gross beta (beta/photon emitters), radium 226 and 228 and uranium are radionuclides (USEPA, 2001) and were assigned under this collective analytical suite derived by Eurofins-Eaton Analytical, LLC. The detection unit is picocuries per liter $(pCiL^{-1})$. A picocurie is the amount of radiation emitted per minute in a liter of water (Ohio Environmental Protection Agency, 2015).

There were no detections of uranium, radium 226 or radium 228 in any Kensico streams during this study.

Gross alpha and gross beta were detected within Kensico stream samples. Gross alpha was detected at E10 and E11 (Table 17), while gross beta was more prevalent and detected at all eight streams with positive samples occurring more often in the summer and autumn, and less often in the winter (Table 18).

Site	USEPA	Jan 29	Apr 17	Jul 24	Oct 15
	MCL				
$MB-1$	15	ND	ND	ND	ND
$N5-1$	15	ND	ND	ND	ND
N ₁₂	15	ND	ND	ND	ND
BG9	15	ND	ND	ND	ND
WHIP	15	ND	ND	ND	ND
E ₉	15	ND	ND	ND	ND
E10	15	3.3	5.6	ND	ND
E11	15	ND	ND	ND	3.6

Table 17. Concentration of gross alpha $+$ adjusted error ($pCiL^{-1}$) at Kensico Streams in 2019.

Table 18. Concentration of gross beta (pCiL⁻¹) at Kensico Streams in 2019.

Site	USEPA	Jan 29	Apr 17	Jul 24	Oct 15
	MCL				
$MB-1$	50	ND	ND	3.8	3.2
$N5-1$	50	3.4	ND	4.3	3.3
N12	50	ND	3.5	4.0	ND
BG9	50	ND	ND	3.8	9.2
WHIP	50	ND	ND	ND	3.5
E ₉	50	ND	3.8	5.1	7.2
E10	50	4.3	4.2	3.8	4.2
E11	50	ND	4.9	3.5	4.6

USEPA has determined an MCL of 15 $pCiL^{-1}$ for gross alpha, and as a screening threshold of 50 pCiL⁻¹for gross beta (State of California, 2017b). Both gross alpha and gross beta results obtained during this study were well below the USEPA MCLs for these analytes.

Gross alpha - Particle activity is a measure of the total radioactivity due to alpha particle emission produced by radioactive decay. The main alpha emitters in ground water are associated with the radioactive decay series of the naturally occurring elements of uranium and thorium (State of California, 2017b)

Gross beta - Particle activity represents the radioactive decay of approximately 200 beta/photon emitters for example, Iodine¹²⁵, and represents a greater array of radioactive emitters than gross alpha (State of California, 2003).

Both gross alpha and gross beta readings represent the radioactive decay of naturally occurring elements within the bedrock of the Kensico Reservoir basin. Detections of both of these radioactive measurements were more common within the Rye Lake Basin (E9, E10 and E11) denoting a greater likelihood of radioactive emitting elements within the bedrock in this part of Kensico as opposed to samples taken west of the Rye Lake Bridge.

Additional Stream Detections

Two compounds were detected infrequently and only at one site each. As such they are included here rather than in the previous section. These compounds are 1,4-dioxane and tebuconazole.

1,4-Dioxane was only detected at one site (E11) during this study, on two sampling occasions: spring (0.18 μ gL⁻¹) and autumn (0.3 μ gL⁻¹). Both detections were below the HRC of $0.35 - 35 \mu g L^{-1}$ (USEPA, 2017) and below the NYS MCL of 1 $\mu g L^{-1}$.

Tebuconazole was detected once at WHIP during the summer season of sampling. It is one of a number of fungicides used on golf courses which is a potential source in this area. The concentration of 1 μ gL⁻¹ was not in exceedance of the Health Advisory of 190 μ gL⁻¹.

Kensico Streams Summary

USEPA HRC/ MCL drinking water exceedances at streams

• Manganese exceeded the HRC level of 300 μ gL⁻¹ at: Malcolm Brook (autumn, 400 μ gL⁻¹), N5 (autumn, 320 μ gL⁻¹), BG9 (autumn, 480 μ gL⁻¹), E9 (autumn, 600 μ gL⁻¹), E10 (winter, 440 μ gL⁻¹), and E11 (spring, 630 μ gL⁻¹; summer 670 μ gL⁻¹; autumn 550 μ gL⁻¹)

Perfluorinated Compounds (PFAS)

- All streams were positive for some PFAS compounds.
- Six of the eight streams had concentrations lower than $0.015 \mu gL^{-1}$. Five of the eight streams were positive for six of the 14 PFAS compounds tested.
- Two streams were positive for seven PFAS compounds (MB-1 and E11).
- E10 had nine detections of PFAS which occurred in all samples, and had the highest concentrations (up to 100 times higher than the other streams).
- PFOA was routinely detected in the highest concentrations in streams, with the exception of E10 (highest was PFOS).
- Two PFAS compounds, PFUnA and PFDA, were found only at E10.
- PFNA was found in each sample at E10 and E11. General sources of these PFAS compounds are surfactants used at airports and airbases and breakdown products of stain and grease proof coatings on food packaging, couches and carpets (Northeastern University, 2019) (United States National Library of Medicine, 2020).
- No analytes within USEPA Method 541 (1-butanol, 2-methoxyethanol, 2-propen-1-ol), were detected within Kensico streams in 2019.
- No analytes within USEPA Method 530 (selected semi-volatile compounds) were detected within Kensico streams in 2019.

PPCPs

- All streams were positive for some PPCPs.
- The number of PPCPs detected were four at N12; seven, eight and nine detected at E10, MB-1 and N5 respectively; 10 detected at WHIP and E9; and 11 found at BG9 and E11.
- The PCPPs detected in the highest concentrations were TCPP, acesulfame-K, sucralose and 2,4-D.
- TCPP was more commonly detected in the summer and autumn sampling in relation to the earlier quarters. This compound is used as a flame retardant in rigid and flexible polyurethane foam.
- The artificial sweeteners acesulfame-K and sucralose were routinely detected in several streams, with the highest concentrations at WHIP, notably the sub-basin with septic systems.
- The winter sampling event had the fewest PPCP detections.
- The summer quarter had the most detections, which corresponds with the season of most precipitation prior to sampling during this study.
- Metformin was the most commonly detected pharmaceutical. It is used to control Type II diabetes.

Other Compounds

- Strontium and manganese were detected at all streams in all quarters; chlorate was detected all quarters at MB-1 and N12.
- Chlorate was detected on one, two and three occasions at BG9, N5-1, and WHIP, respectively.
- Chlorate was not detected at E9, E10, or E11.
- Manganese had the highest concentrations, at E9 and E11 (600-700 μgL^{-1}), while strontium was the highest at E10 and BG9 (300-400 μ gL⁻¹).

 Vanadium and hexavalent chromium were detected at least once at all streams, in low concentrations (<2 μ gL⁻¹).

Precipitation

Runoff from significant precipitation events has the potential to increase the concentration of contaminants found in surface waters. Precipitation was recorded for up to three days before each quarterly sampling event to determine if runoff was a factor (Table 19). The summer sampling event had the most potential for influence by increased transport from runoff with nearly two inches of rain occurring within the three days before sampling. Spring sampling was preceded by approximately a half an inch of rain, but there was none preceding the winter or autumn sampling events.

Table 19. Precipitation in inches preceding the 2019 quarterly sampling events.

Contaminants most likely affected by a significant storm event are those with surface water leaching potential such as water soluble pesticides. The best example of this condition is the detection of the herbicide 2,4-D. The summer quarter showed the most detections, and overall the highest detection of 2,4-D (1.6 μ gL⁻¹); more than 10 times higher than any other reading for this analyte throughout the sampling year. The summer (July) is also a common time period to apply this herbicide as weed season is in full effect. The spring quarter showed lower concentrations, likely due to it being early in the weed growing season with less need of 2,4-D at this time of the year.

Health Implications

Although the human health risks associated with the presence of emerging contaminants 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 contaminants detected in this and other comparable studies (Snyder, et al, 2008). U.S. EPA has summarized the different approaches that have been used to screen for human health risk from contaminants, specifically pharmaceuticals, in drinking water (U.S. EPA, 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). Otherwise stated, the MOE is the ratio of the "no observed adverse effect level" (or other toxicological threshold such as an ADI) to the estimated exposure dose.

Table 20 provides DEP's application of this type of methodology. The table is separated to highlight maximum detections at the New Croton System outflow keypoint versus the CAT/DEL System inflows and outflow keypoints. Specifically, DEP utilized the screening level approach similar to that used by Snyder (Snyder, 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 by the authors from ADIs and other toxicological information. In most instances, either the DWG is based on the lowest therapeutic dose, or a USEPA derived drinking water equivalent level (DWEL). It is important to note that the maximum concentrations listed in Table 20 are from source waters, and not from finished drinking water within the NYC distribution system, making for an even lower risk potential of exposure to these contaminants through drinking an 8-ounce glass of water.

The MOE for caffeine provides some perspective on the low-level quantities of contaminants found in the study. For example, it would take over 94 million 8-ounce cups of water at the maximum concentration of caffeine detected in this study of $0.038 \mu gL^{-1}$ (CROGH) to exceed a drinking water guideline value represented by the amount of caffeine in one 8-ounce cup of water. According to the 2019 NYCDEP Water Quality Annual Report (NYCDEP, 2019) caffeine was not detected during any distribution laboratory analysis during 2019, and therefore represents a negligible risk. With a concentration below the analytical detection level, and using Snyder's formula for drinking consumption (Snyder, et al., 2008) it is impossible to drink enough water to meet any drinking water guideline for caffeine if one were to drink from the tap in NYC.

For the remaining representative contaminants, the number of glasses of water required to exceed an acceptable daily intake, the MOE, is well beyond what one would consume in a day.

Table 20. Number of glasses of water required to exceed derived drinking water guidelines for the compounds detected in this study at source water and upstate keypoint locations.

**- NYS standard for UOCs = 50µg/L and POCs = 5µg/L. MCL – Maximum Contaminant Level. Other detections with an asterisk are New York State standards, but are not a UOC or POC.*

*# # - No. of 8 oz glasses/day = [DWQ (µg/L) * 2 (L/d) * 4.23 8 oz glasses/L (maximium water concentration (µg/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.

Cancer Risk – (µg/L at 10-4 Cancer Risk) The concentration of a chemical in drinking water corresponding to an estimated lifetime cancer risk of 1 in 10,000.

LDTD – Lowest Daily Therapeutic Dose. The LDTD that produces the desired clinical effect.

LOAEL – Lowest Observable Adverse Effect Level – the lowest level of a chemical stressor in a toxicity test that shows harmful effects on a plant or animal.

NI – No information

RfD- Reference Dose. An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

TTC- Thresholds of Toxicological Concern. A guideline value for chemicals for which there is no established guidelines, and for which relevant health or toxicological information does not exist at this time.

1 – American Diabetes Association. 2005. American Diabetes Association Guide to Medical Nutrition Therapy for Diabetes. 1 p. [. www.nafwa.org./sweetener.php](http://www.nafwa.org./sweetener.php)

2- State of California, 2018 Chromium-6 Drinking Water MCL. California Water Boards: State Water Resources Control Board.1 p.

3- State of California, 2000. Proposed Notification Level for Vanadium. California Office of Health Hazard Assessment. 1 p.

4- U.S. EPA 2018b. 2018 Edition of the Drinking Water Standards and Health Advisories Tables. 12 p.

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 Ministerial Council. 159 p.

6 – Gilbert S.G. A Small Dose of Toxicology. CRC Press. Boca Raton, Florida. February, 2004.

7- United States Library of Medicine. 2020b. National Center for Biotechnology Information Compound Summary for Tris (1-chlor-2-propyl) phosphate. 100 p.

Conclusions

Keypoints

PFAS Compounds

New Croton Reservoir was the only keypoint to have detections of PFAS compounds: PFOA, PFOS and PRHxA. The detections of PFOA and PFOS were below the NYSDOH MCL of 0.01 µgL⁻¹. PRHxA has a NYSDOH Unregulated Organic Contaminant (UOC) limit of 50 μ gL⁻¹ and the highest detection of this PFAS compound at New Croton Reservoir was 0.0029 $\mu g L^{-1}$, well below the UOC limit. No other keypoint had PFAS detections.

PPCP Compounds

The PPCPs were the only UCMR4 analyte suite where detections were noted. The New Croton keypoint had the greatest variety of detections. This may be based on the demographics of the Croton watershed. The most commonly detected PPCPs at New Croton were: 2,4-D (herbicide), acesulfame-K and sucralose (artificial sweeteners), caffeine (stimulant) and iohexol (a medication used before X-ray imaging tests). Some other PPCPs detected at keypoints were TCPP (flame retardant/flame inhibitor) and metformin (Type II diabetes medication).

Other Compounds

Kensico and New Croton Reservoir keypoints as well as additional upstate reservoir keypoints had consistent low level detections of the elements strontium and manganese and less consistency of detection of vanadium and hexavalent chromium. These detections were more than likely due to natural erosion of bedrock and ensuing runoff containing these elements. All algal toxin results were below their method reporting limit. Based on the data and current federal and state regulations, detections of UCMR3 and UCMR4 analytes from the keypoints represent no current risk to NYC source water.

Radionuclides

Kensico Reservoir keypoints were negative for radionuclides. There were no detections of uranium, radium 226, radium 228 or gross alpha at the New Croton Reservoir outflow during this study. Gross beta was detected in the first quarter winter sample, at 3.4 pCiL $^{-1}$, and this level of detection is indicative of weathering of local bedrock. Based on the data and current state and federal regulations, detections of radionuclides from keypoints represent no risk to NYC source water.

Kensico Streams

PFAS Compounds

At least one PFAS compound was detected at each Kensico stream site during each survey in the 2019 sampling season. N12 had the fewest detections with two in October, and E10 had the most with the same nine compounds detected during each quarterly sampling run. The

higher number of detections and concentrations at E10 may be influenced by E10 sub-basin demographics.

PPCP Compounds

PPCP detections can be categorized into two basic groups: (1) those with repeated detections – either within a site or spatially over more than one site, and (2) those with a one time or sporadic detection. Examples of the former include 2,4-D (herbicide), acesulfame-K, sucralose (artificial sweeteners), caffeine (stimulant), DEET (active ingredient in an insect repellant) and metformin (Type II diabetes medication). Examples of the latter include sulfometuron methyl (herbicide), thiabendazole (antifungal and antiparasitic agent), and estrone (hormone related to estrogen). Detection of these sporadic or "one-time" detections may be related to the environmental chemistry of the analytes (e.g. runoff of sulfometuron methyl) or the specific use of the product based within a particular sub-basin.

Other Compounds

Metals were commonly detected at all stream sites during the entire 2019 sampling period. Vanadium was detected more often in streams than at the keypoints. Manganese and strontium, were detected at every stream site throughout the sampling year. Manganese is an element ubiquitous within the Kensico basin and its detection is commonplace through DEP monitoring efforts.

Chlorate was detected within Kensico streams that contain a high number of residential properties/subdivisions. Detection may be linked to chlorine's use to disinfect water (e.g. hot tubs and swimming pools). 1,4-Dioxane was only detected at E11. 1,4-Dioxane is used as a solvent.

Tebuconazole was detected once within the WHIP sub-basin in the summer. Tebuconazole is a turf fungicide and may be linked to turf management practices within the subbasin.

Based on the data and current federal and state regulations, detections of UCMR3 and UCMR4 analytes from Kensico streams present no current risk to NYC source water quality.

Radionuclides

Gross beta and gross alpha were the only detected radionuclides in the 2019 sampling period at Kensico streams. Their detection and level of detection are indicative of weathering of local bedrock that emit gross beta and gross alpha. Based on the data and current state and federal regulations, detections of radionuclides from Kensico streams represent no risk to NYC source water quality.

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APPENDIX

Appendix 1. List of PPCP and radionuclide contaminants examined in this study that were not part of UCMR3 or UCMR4. (Micrograms per liter $[\mu g L^{-1}]$ is stated in brackets next to the ng L^{-1} as the data within the report is in micrograms)

I. PPCPs

II. Radionuclides

GA Method (Radium 228)

GA Method

GA Method

USEPA Method 200.8

