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## Target Screening for Micropollutants in the Hudson River Estuary during the 2015 Recreational Season

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### Abstract

Monitoring studies aimed at assessing water quality and environmental risk from micropollutants are challenging to implement due to the large number of potential analytes and the spatial and temporal variability at which micropollutants occur in surface water systems. We addressed these challenges by collecting samples during the 2015 recreational season from eight sites along the Hudson River Estuary from the confluence with the Mohawk River to the Tappan Zee Bridge. We used solid-phase extraction and high performance liquid chromatography mass spectrometry (HPLC-MS) to quantify the occurrence of 117 micropollutants in each sample. We selected a diverse set of micropollutants including pharmaceuticals, pesticides, and industrial chemicals. We confirmed the occurrence of 83 of the micropollutants in at least one of the collected samples. Eight micropollutants were quantified in every sample collected: atenolol ( $\beta$ -blocker), atenolol acid (metabolite of atenolol), venlafaxine (anti-depressant), caffeine (stimulant), paraxanthine (metabolite of caffeine), sucralose (artificial sweetener), methyl benzotriazole (an industrial chemical), and DEET (an insect repellent). These data represent the first comprehensive survey of micropollutants in the Hudson River Estuary and will be invaluable for developing future research projects aimed at assessing spatial and temporal variability of micropollutant occurrence and the consequent environmental risk.

- First comprehensive monitoring for micropollutants in the Hudson River Estuary.
- The number and types of pesticides measured were spatially and temporally stable.
- The number and types of pharmaceuticals measured were determined by proximity to wastewater treatment plant outfalls.

*Keywords: micropollutants, emerging contaminants, pharmaceuticals, pesticides, mass spectrometry*

## Target Screening for Micropollutants in the Hudson River Estuary during the 2015 Recreational Season

### Introduction

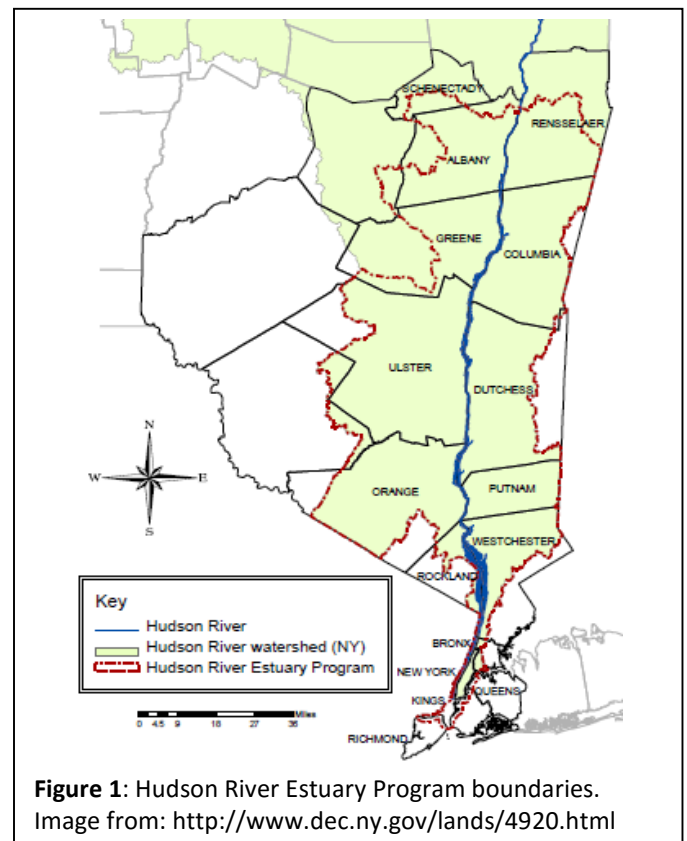
An estimated 84,000 synthetic organic chemicals are used daily in domestic, commercial, or industrial applications (Schnoor, 2014). The life cycle of these chemicals often results in their accumulation in the environment, with many of the more polar and semi-polar chemicals (including most pesticides and pharmaceuticals) known to occur globally in surface water resources (Kolpin et al., 2002; Richardson and Ternes, 2014; Richardson, 2012; Schwarzenbach et al., 2006).

Concern over the occurrence of these so-called micropollutants in water resources is predicated on the notion that exposure to them poses a significant risk to aquatic ecosystem or human health. Although toxicological data are limited relative to the large number of micropollutants known to occur in the environment, the emerging view is that complex mixtures of environmentally relevant concentrations of micropollutants can lead to developmental or genotoxic effects (Altenburger et al., 2012; Pomati et al., 2006). Additionally, for the small subset of chemicals that have been rigorously studied with respect to toxicity, there have been reports of significant developmental, reproductive, endocrine disrupting, and other chronic health effects (Brody and Rudel, 2003; Colburn et al., 1993; Daughton and Ternes, 1999; McKinlay et al., 2008; Murray et al., 2010; Toppari et al., 1996).

The main sources of micropollutants are domestic and industrial wastewater treatment plant discharges, storm sewer outfalls, combined sewer overflows, and diffuse runoff from agricultural or urban landscapes (Brown and van Beinum, 2009; Wittmer et al., 2010). As such, the occurrence and concentration of micropollutants in any watershed is dependent on a variety of local features including land use, weather, hydrology, type of sewer system, and number and type of wastewater treatment plant discharges. Therefore, it is expected that the occurrence and concentration of micropollutants in any surface water system will vary significantly both temporally and spatially within the watershed. The large number of micropollutants and the inherent spatial and temporal variability of their occurrence levels makes it challenging to develop appropriate monitoring programs to assess the potential for exposure and risk to aquatic ecosystems and downstream human populations. Routine monitoring for pesticides and other micropollutants generally starts with the selection of one

to two dozen compounds to study and risk assessments are conducted based on the resulting dataset. This strategy has been shown to significantly underestimate the potential risk associated with micropollutants in surface water resources (Moschet et al., 2014).

The waters of the Hudson River Estuary (delineated in **Figure 1**) are used for recreational purposes (i.e., swimming, boating, fishing) and as a source of drinking water for over 100,000 people. The Hudson River is also a receiver of a number of industrial and sewage treatment plant (STP) discharges, storm sewer outfalls, and combined sewer overflows (New York State Department of Environmental Conservation, 2015). Further, the land use in the Hudson River watershed is mixed, with significant areas of urban, agricultural, and industrial uses (New York State Department of Environmental Conservation, 2015). As such, the Hudson River is expected to be impacted by a wide variety of wastewater-derived, agricultural, and industrial micropollutants. However, there exists a limited amount of data on the occurrence of micropollutants in the Hudson River Estuary. Therefore, it is difficult to assess water quality in the Hudson River Estuary with respect to these emerging contaminants.



**Figure 1:** Hudson River Estuary Program boundaries. Image from: <http://www.dec.ny.gov/lands/4920.html>

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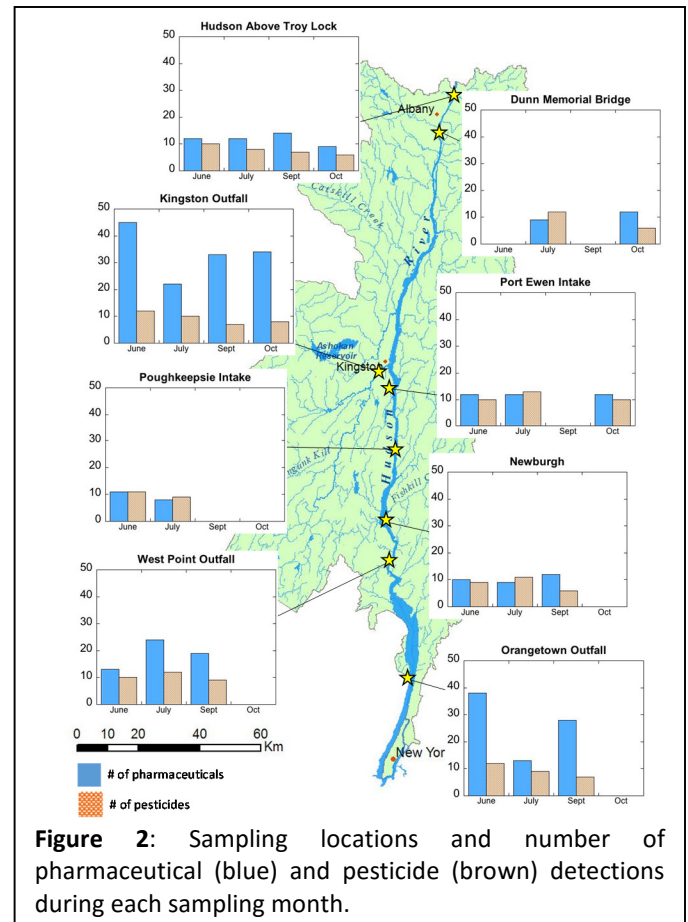
Riverkeeper is a member-supported organization dedicated to monitoring and protecting the waters of the Hudson River Estuary. Riverkeeper uses a patrol boat equipped with a mobile laboratory to collect water samples from 74 sites along the Hudson River Estuary. Samples have been collected monthly throughout the recreational season (May through October) since 2008 and are analyzed for fecal-indicating bacteria of the genus *Enterococcus* along with a suite of other standard water quality indicators including pH, salinity, dissolved oxygen, and turbidity. Records of these data collection efforts are maintained on the Riverkeeper website (Riverkeeper, 2015a).

We partnered with Riverkeeper to collect samples from eight of their 74 sampling locations along the Hudson River Estuary. The sites were sampled in June, July, September and October of 2015. The sites included Hudson above Troy Lock, Dunn Memorial Bridge, Kingston Sewage Treatment Plant Outfall, Port Ewen Drinking Water Intake, Poughkeepsie Drinking Water Intake, Newburgh Launch Ramp, West Point Sewage Treatment Plant Outfall, and Orangetown Sewage Treatment Plant Outfall. A map of the sampling sites are provided in **Figure 2**. Samples were collected in one liter amber glass, trace clean bottles and shipped to our laboratory at Cornell for analysis. Brief details on sampling and analytical methods are provided below.

### Results & Discussion

We collected samples during four months of the recreational season at eight discrete locations along the Hudson River Estuary, for a total of 32 samples. Of those 32 samples, two were lost during sample processing in our laboratory and six were lost during shipping (broken during transit). Therefore, 24 samples were processed and analyzed and the results of those analyses are reported here.

Of the 117 target micropollutants, 83 were detected in at least one of the 24 samples (for a list of target micropollutants and details on their frequency of detection, see **Appendix A**). Data on the spatial and temporal variability of pharmaceutical and pesticide detection are provided in **Figure 2**. There were a total of 36 pesticides on our target list. Of those, 20 were detected in at least one sample and 9 of those were measured in at least half of the samples. In general, every sample measured contained approximately 8 – 10 pesticides, a number that was stable throughout the



**Figure 2:** Sampling locations and number of pharmaceutical (blue) and pesticide (brown) detections during each sampling month.

recreational season and along the length of the Hudson River. This suggests that the main sources of pesticides into the Hudson River are diffuse, likely from agricultural runoff, spray drift, or groundwater infiltration. Understanding the influence of application seasons would require higher sampling frequency with greater temporal resolution, though literature data suggests that the types and concentrations of pesticides will spike during the spring application season (Gilliom, 2007). There were a total of 64 pharmaceuticals on our target list. Of those, 50 were detected in at least one sample. Contrary to pesticides, the number of pharmaceuticals measured was quite sensitive to location. The three sewage treatment plant outfall sites contained the largest numbers of pharmaceuticals. Sites distant from outfalls had much lower and less variable numbers of pharmaceuticals detected. This observation highlights the importance of sewage outfalls as a source of pharmaceutical micropollutants in the Hudson River Estuary.

The high number of micropollutants detected at sewage outfalls could be a cause for concern in communities

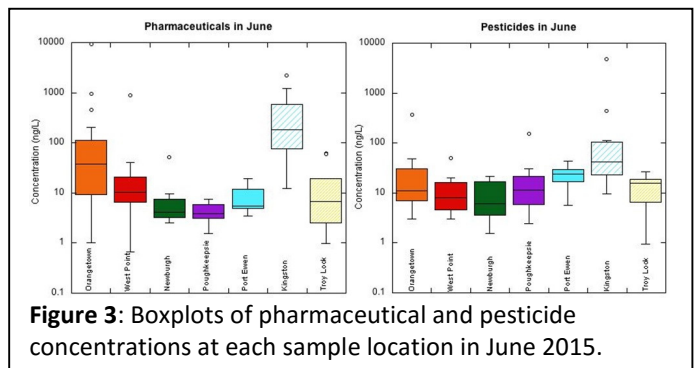
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downstream who rely on the river as their drinking water source. The Kingston sewage treatment plant discharges into Rondout Creek near its confluence with the Hudson River; four miles downstream is the drinking water intake for Port Ewen. While Kingston had the largest number of micropollutants detected in all months, the number of micropollutants detected at the Port Ewen intake was on par with that seen at the rest of the non-outfall sites sampled. This suggests that the micropollutants measured in the Kingston outfall are either being diluted or are degraded once they enter the waters of the Hudson. For example, five  $\beta$ -blocker pharmaceutical compounds (acebutolol, atenolol, metoprolol, nadolol, and propranolol) were detected in the June sample from Kingston outfall. Only atenolol and metoprolol were detected downstream in the Port Ewen sample from June, and both were at much lower concentrations than those in the Kingston outfall. While dilution likely plays a role,  $\beta$ -blockers are also known to adsorb to natural minerals (Kibbey et al., 2007), undergo photolysis in water (Liu and Williams, 2007), and can be microbially transformed (Helbling et al., 2010). Thus, there are many possible fates for micropollutants in water, increasing the complexity of understanding their occurrence, transport, and effects in the Hudson River Estuary. Because our samples were collected at the same time as those used for the *Enterococcus* measurements conducted by Riverkeeper, it was possible to compare the micropollutant findings to the fecal coliform counts at each site. Of the 24 samples, six had *Enterococcus* counts above 60 per 100 mL, the EPA Beach Action Value (Riverkeeper, 2015b). At sites that have counts above this level, public notification is recommended and temporary beach closures may be considered. Three of these samples were from the Kingston outfall site and all three likewise had high pharmaceutical compound counts. However, the September sample at Kingston contained a similar number of pharmaceuticals as in the other months and passed the fecal indicator water quality test. The other three failed samples were all collected at the Hudson above Troy Lock site, which had pharmaceutical and pesticide counts similar to those of other non-outfall sites. Because this is a limited data set, it is difficult to draw conclusions about the relationship between *Enterococcus* counts and the micropollutant counts seen in our study. There have been some efforts made to use micropollutants as indicators of water quality in place of indicator bacteria (Glassmeyer et al.,

2005; Kuroda et al., 2012), but no clear relationship between the number or type of micropollutants detected and the *Enterococcus* counts was readily apparent in this study. Ongoing research aims to analyze these data along with relevant metadata such as rainfall to determine whether any stronger relationships become apparent.

There were eight compounds detected in all 24 of the measured samples, with six others being detected in at least 20 of the samples. The compounds detected in all samples included atenolol ( $\beta$ -blocker), atenolol acid (metabolite of atenolol), venlafaxine (anti-depressant), caffeine, paraxanthine (metabolite of caffeine), sucralose (artificial sweetener), methyl benzotriazole (industrial chemical), and DEET (insect repellent). The additional compounds detected in at least 20 samples included 2,4-D (herbicide), atrazine (herbicide), cotinine (metabolite of nicotine, a stimulant), lidocaine (anesthetic), metolachlor (herbicide), and metoprolol ( $\beta$ -blocker).

Grab samples are excellent for confirming the presence of a particular micropollutant in a given sample (Ort et al., 2010). However, the absence of a micropollutant does not necessarily mean that the compound is not present in the Hudson River Estuary. A negative detection could mean that the micropollutant was simply not present at a detectable level in the sample collected at a particular location and a particular time. Therefore, conclusions should be drawn only on what was detected, not on what was not detected. Similarly, reporting representative concentrations in a particular surface water sample is not always recommended when grab samples are collected (Ort et al., 2010). Nevertheless, we present a summary of the pharmaceutical and pesticide concentrations measured during the June sampling event in **Figure 3**. What we can confirm from the



**Figure 3:** Boxplots of pharmaceutical and pesticide concentrations at each sample location in June 2015.

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concentration data is that the majority of the pharmaceuticals and pesticides are present in the range of 10 – 100 nanograms per liter. Studies of other surface water bodies around the world report pharmaceutical concentrations as high as the 1000 nanograms per liter range (Bartelt-Hunt et al., 2009; Kim et al., 2007; Loos et al., 2009). In our sampling of the Hudson River Estuary, the only sites with comparably high concentrations were those at sewage treatment plant outfalls. A more representative understanding of micropollutant concentrations could be obtained by collecting composite samples that are proportional to the flow of the river (Ort et al., 2010).

In light of these findings, it is imperative to note that the results on the number and types of pharmaceuticals and pesticides identified in the Hudson River Estuary along with the relatively low concentrations are in line with data collected in other surface water systems around the world (Bartelt-Hunt et al., 2009; Hernando et al., 2006; Kim et al., 2007; Loos et al., 2009). Nothing in this dataset suggests that the Hudson River Estuary is more or less impacted by micropollutants than other major waterways in the United States, Canada, or Europe. Nevertheless, the occurrence of micropollutants in the Hudson River Estuary (and around the world) is a major environmental problem and studies have shown that their occurrence can cause a variety of negative effects to aquatic ecosystems and exposed human populations. It is imperative to continue studying micropollutants in the Hudson River to get a better understanding of sources and to ultimately implement best management practices to limit their occurrence.

### Methods

#### *Sampling*

Grab samples were collected by Riverkeeper in 1 L amber, trace clean glass bottles and maintained under cold temperatures on the sampling vessel. The samples were then shipped in a cooler to our laboratory at Cornell at the end of each sampling campaign. Samples were stored at -20°C and in the dark until sample preparation and analysis.

*Sample preparation.* We used a mixed bed solid phase extraction method (SPE) to concentrate the 1 L samples as previously described (Moschet et al., 2013). Briefly, samples were thawed and vacuum filtered through a glass microfiber filter to remove any particulate matter.

The sample pH was adjusted using an ammonium acetate buffer. A cocktail of 21 isotope labeled internal standards were spiked in each sample to control for losses during the solid phase extraction procedure and matrix effects during analysis. All samples and a complete, eight point calibration curve were then passed over a manually constructed multi-layer SPE cartridge containing Oasis HLB, Strata X-AW, Strata X-CW, Isolute ENV+, and envi-CARB. Elution from the cartridges was with ethyl acetate/methanol (50%/50%) with 0.5% ammonia, ethyl acetate/methanol (50%/50%) with 1.7% formic acid and 100% methanol. Combined neutral extracts were evaporated under nitrogen to 0.1 mL and reconstituted with 0.9 mL of nanopure water.

*Analytics and data processing.* The analytical method was previously developed and validated for a broad range of micropollutants (Helbling et al., 2010). Briefly, chromatographic separation was carried out with an XBridge C18 column (Waters) using nanopure and methanol acidified with 0.1% formic acid as mobile phase. High-resolution mass spectra and MS/MS acquisitions were collected from a QExactive (Thermo) mass spectrometer. Separate positive and negative ionization full scans with a resolution (R) of 70,000 were run simultaneously with All Ion Fragmentation scans (R = 35,000). Blanks and QC samples were included in the measurement sequence for quality assurance. A target screening approach was used to quantify the concentrations of 117 micropollutants in each of the samples (see **Appendix A** for a list of micropollutants included in the target screening). Quantification was based on the calibration curves developed during sample preparation. The compounds in this list come from a variety of use classes (pesticides, pharmaceuticals, industrial chemicals) and are generally included due to their known persistence or putative toxicity. Detection limits are generally in the low ng/L range for the micropollutants on this list.

### Outreach Comments

We plan to prepare a one page Fact Sheet describing our methods and results that will be available on our laboratory website and at the Riverkeeper website.

### Student Training

All sample processing and analysis was conducted by Amy Pochodylo, a Ph.D. student.



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### Acknowledgements

We thank Greg O'Mullan (CUNY Queens) and Andy Juhl (Lamont-Doherty Earth Observatory) for their contributions in designing the sampling campaign. Sites were selected to complement their ongoing research on *Enterococcus* counts in the Hudson River Estuary. We also thank Dan Shapely and John Lipscomb from Riverkeeper for their valuable discussions and sampling efforts.

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### Appendix A – List of target analytes and their frequency of detection.

Compound	Use	Frequency of Detection
1,2-Benzisothiazolin-3(2H)-one	Fungicide	11
2,4-D	Herbicide	20
2,6-Dichlorobenzamide	Herbicide degradation product (dichlobenil)	0
2,6-Dimethoxyphenol	Natural component of wood smoke	0
2-Ethyl-2-phenylmalonamide	Pharmaceutical degradation product (primidone)	3
2-Methyl-4-isothiazolin-3-one	Fungicide	12
Abacavir	Pharmaceutical (antiretroviral)	5
Acebutolol	Pharmaceutical (beta-blocker)	2
Acetaminophen	Pharmaceutical (analgesic)	5
Adrenosterone	Pharmaceutical (hormone)	0
Albuterol	Pharmaceutical (asthma)	10
Aldicarb	Insecticide	0
Allopurinol	Pharmaceutical (gout)	4
Amitriptyline	Pharmaceutical (anti-depressant)	1
Amphetamine	Pharmaceutical (stimulant)	3
Atenolol	Pharmaceutical (beta-blocker)	24
Atenolol Acid	Pharmaceutical metabolite (atenolol and metoprolol)	24
Atrazin-2-hydroxy	Herbicide degradation product (atrazine)	15
Atrazine	Herbicide	21
Atrazine-desethyl-desisopropyl	Herbicide degradation product (atrazine)	7
Azoxystrobin	Fungicide	0
Bentazon	Herbicide	12
Benzotriazole methyl-1H	Industrial chemical (corrosion inhibitor)	24
Bromacil	Herbicide	0
Bupropion	Pharmaceutical (anti-depressant)	7
Caffeine	Stimulant	24
Carbamazepine	Pharmaceutical (anti-convulsant)	12
Carbaryl	Insecticide	0
Carbofuran	Insecticide	0
Carisoprodol	Pharmaceutical (muscle relaxant)	1
Celecoxib	Pharmaceutical (NSAID)	4
Chloridazon	Herbicide	1
cis-Diltiazem	Pharmaceutical (Ca channel blocker)	4
Citalopram	Pharmaceutical (anti-depressant)	3
Clofibric Acid	Herbicide	0
Codeine	Pharmaceutical (opiate)	7
Cotinine	Degradation product of nicotine	22
DEET	Insecticide	24



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Dexamethasone	Pharmaceutical (corticosteroid)	0
Dextromethorphan	Pharmaceutical (antitussive)	4
Diclofenac	Pharmaceutical (NSAID)	3
Dimethoate	Insecticide	3
Diphenhydramine	Pharmaceutical (antihistamine)	9
Diuron	Herbicide	6
Efavirenz	Pharmaceutical (antiretroviral)	0
Erythromycin	Pharmaceutical (antibiotic)	0
Estriol	Pharmaceutical (hormone)	0
Estrone	Pharmaceutical (hormone)	0
Ethofumesate	Herbicide	0
Ethyl butylacetylaminopropionate	Insecticide	5
Fexofenadine	Pharmaceutical (antihistamine)	8
Fluconazole	Pharmaceutical (anti-depressant)	8
Gemfibrozil	Pharmaceutical (cholesterol reducer)	2
Hydrocodone	Pharmaceutical (analgesic)	3
Hydrocortisone	Pharmaceutical (skin irritation)	0
Ibuprofen	Pharmaceutical (NSAID)	3
Imidacloprid	Insecticide	8
Iopromide	Pharmaceutical (contrast agent)	2
Ioxynil	Herbicide	0
Isoproturon	Herbicide	0
Ketoprofen	Pharmaceutical (NSAID)	1
Lidocaine	Pharmaceutical (local anesthetic)	23
Linuron	Herbicide	2
Malaoxon	Insecticide degradation product (malathion)	0
MCPA	Herbicide	4
Mecoprop	Herbicide	18
Meprobamate	Pharmaceutical (anxiolytic)	2
Metamitron	Herbicide	0
Metaxalone	Pharmaceutical (muscle relaxant)	4
Methadone	Pharmaceutical (opioid)	1
Methocarbamol	Pharmaceutical (muscle relaxant)	10
Methomyl	Insecticide	1
Metolachlor	Herbicide	20
Metoprolol	Pharmaceutical (beta-blocker)	23
Metribuzin	Herbicide	0
Morphine	Pharmaceutical (opiate)	6
Nadolol	Pharmaceutical (beta-blocker)	7
Naproxen	Pharmaceutical (NSAID)	7
Oxcarbazepine	Pharmaceutical (anti-convulsant)	5

## Target Screening for Micropollutants in the Hudson River Estuary during the 2015 Recreational Season

Oxybenzone	UV absorber	7
Paraxanthine	Stimulant degradation product (caffeine)	24
Penciclovir	Pharmaceutical (antiviral)	3
Pentoxifylline	Pharmaceutical (muscle pain)	0
Perfluorobutanoic acid (PFBA)	Industrial chemical (fluorocarbon polymer)	11
Perfluorooctanoic acid (PFOA)	Industrial chemical (fluorocarbon polymer)	15
Phenytoin	Pharmaceutical (anti-convulsant)	2
Pirimicarb	Insecticide	0
Primidone	Pharmaceutical (anti-convulsant)	3
Progesterone	Pharmaceutical (hormone)	0
Prometon	Herbicide	16
Propachlor	Herbicide	0
Propachlor-ESA	Herbicide degradation product (propachlor)	0
Propachlor-OXA	Herbicide degradation product (propachlor)	0
Propranolol	Pharmaceutical (beta-blocker)	7
Propyzamide	Herbicide	0
Pseudoephedrine	Pharmaceutical (decongestant)	16
Siduron	Herbicide	0
Simazine	Herbicide	12
Sitagliptin	Pharmaceutical (antihyperglycemic)	6
Sucralose	Artificial sweetener	24
Sulfadimethoxine	Pharmaceutical (antibiotic)	0
Sulfamethoxazole	Pharmaceutical (antibiotic)	9
Sulfathiazole	Pharmaceutical (antibiotic)	0
Terbutylazine	Herbicide	0
Testosterone	Pharmaceutical (hormone)	0
Theophylline	Pharmaceutical (methylxanthine)	14
Thiabendazole	Fungicide	2
Triamterene	Pharmaceutical (diuretic)	6
Tributyl phosphate (TBP)	Industrial compound (organophosphorus)	9
Triclosan	Pharmaceutical (antibiotic)	2
Trimethoprim	Pharmaceutical (antibiotic)	19
Trinexapac-ethyl	Herbicide	2
Tris(2-chloro-ethyl)phosphate	Plasticizer	9
Valsartan	Pharmaceutical (blood pressure)	16
Venlafaxine	Pharmaceutical (anti-depressant)	24
Verapamil	Pharmaceutical (Ca channel blocker)	0
Warfarin	Pharmaceutical (anti-coagulant)	0