

Water Quality in the Twenty-First Century: New Tools for the Characterization and Remediation of Emerging Chemical Contaminants

Damian E. Helbling, Corey M.G. Carpenter and Yuhan Ling

Abstract

There are hundreds of thousands of chemicals used around the world to meet the global demands for food, energy, and a higher standard of living. Decades of environmental monitoring studies have demonstrated that many of these chemicals accumulate in the aquatic environment. The incredible number of chemicals that may be present in any given water system poses challenges for water quality monitoring and associated engineered solutions. In the first part of this contribution, new techniques for water quality monitoring afforded by high-resolution mass spectrometry will be introduced. Case studies will be used to highlight the advantages and challenges associated with target screening and nontarget screening techniques. In the second part of this contribution, a new polymer will be introduced that outperforms many conventional adsorbents for the removal of organic chemicals from water at environmentally relevant concentrations. The polymer is derived sustainably from cornstarch, and characterization studies demonstrate that it exhibits rapid adsorption kinetics, excludes interactions with natural organic matter (NOM), and can be regenerated with a mild washing solution at ambient temperatures without a loss in performance. These features all suggest that the polymer may be a promising alternative adsorbent for the removal of trace organic chemicals during water and wastewater treatment.

Keywords: water quality, micropollutant, adsorption, cyclodextrin, pharmaceutical, pesticide

1. Introduction

Data from monitoring studies have routinely confirmed the occurrence of thousands of organic micropollutants in surface water resources around the world [1–3]. The main targets of these monitoring studies have been pharmaceuticals [4], personal care products [5], illicit drugs [6], pesticides [7], industrial chemicals [8], or other anthropogenic chemicals [9] that have known or putative toxic effects on aquatic ecosystems or exposed human populations [10–15]. The potential sources of these chemicals are varied, with much attention focused on sewage treatment plant (STP)

outfalls [5], combined sewer overflows [16], industrial discharges [17], stormwater outfalls [18], and diffuse runoff from agricultural and urban landscapes [2], though many other potential sources have not yet been fully explored.

Improved understanding of the sources of micropollutants that are present in surface water resources is essential for risk assessment and for developing mitigation strategies. Recently, long-term monitoring data characterizing micropollutant occurrence at the watershed scale has been used to identify the relative contributions of various sources within particular watersheds. Mass balance and multivariate analyses revealed three distinct sources of micropollutants in the Minnesota River including upstream diffuse runoff, mixed pathways, and sewage outfalls [19]. High-resolution temporal sampling was used to identify an industrial source that was emitting pollutants to a river in Germany at randomly spaced temporal intervals [17]. Long-term longitudinal sampling along the Rhine River was used to identify several previously unknown sources of micropollutants, particularly from tributaries and industrial sources [3]. In each of these examples, the identification of micropollutant sources was predicated on two major features of the studies. First, each of these studies examined a diverse set of micropollutants; the selected micropollutants contained chemicals that might be expected to originate from a variety of sources including agriculture, wastewater treatment plants, or industrial discharges. Second, each of these studies employed high-frequency sampling within the watersheds, investigating either a large number of samples from a single location or a large number of samples distributed spatially throughout the watershed. Data has shown that evaluating the spatial and temporal variability of micropollutant occurrence can lead to key insights on sources of micropollutants.

In addition to micropollutant monitoring, there is a clear need for solutions to remove micropollutants during drinking water production. Adsorption processes are widely employed to remove organic chemicals from water and wastewater. Activated carbons (ACs) are the most widespread adsorbents used to remove micropollutants; their efficacy derives primarily from their high surface areas, nano-structured pores, and hydrophobicity [20]. However, AC adsorption is relatively slow [21], performs poorly for many polar and semipolar micropollutants [22], and can be fouled by natural organic matter (NOM) [23]. Further, activation and regeneration of AC are energy-intensive and slowly degrade its performance relative to the

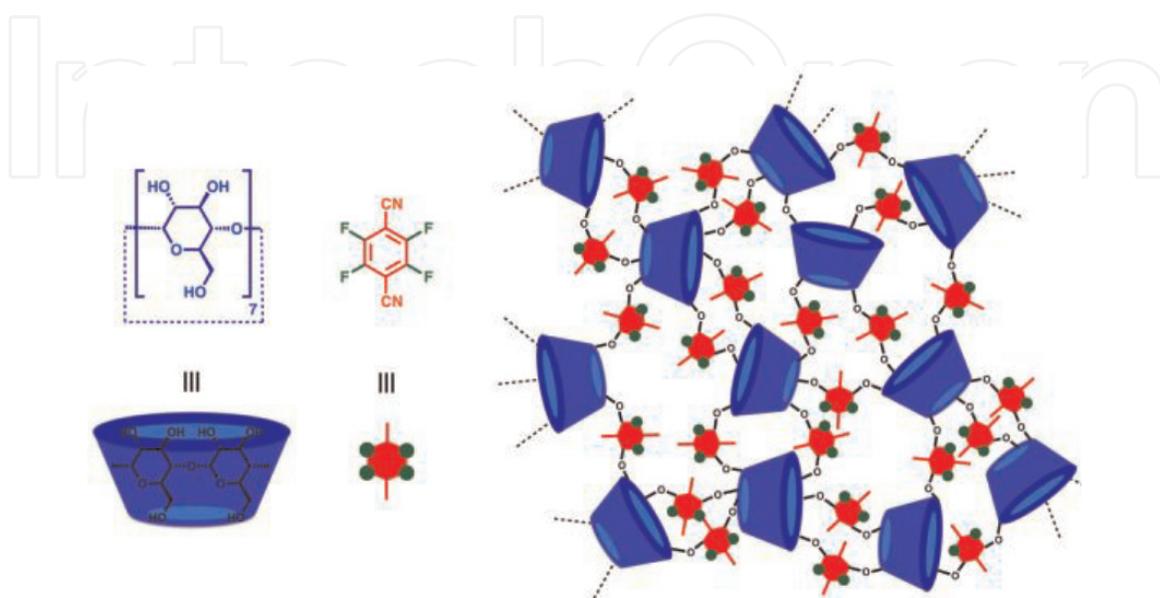


Figure 1.

Schematic of the β -CD polymer. β -CD is a macrocycle of glucose (blue) and is cross-linked with tetrafluoroterephthalonitrile (red) to generate the first mesoporous, high-surface area β -CD polymer.

new AC [24]. New adsorbents that address these deficiencies of ACs will lead to more efficient removal of micropollutants during water and wastewater treatment.

We have recently discovered a promising alternative adsorbent that removes organic molecules from water with unprecedented speed and high capacity and can be regenerated by washing with benign solvents at room temperature [25]. This material is the first mesoporous, high-surface area polymer containing β -cyclodextrin (β -CD), which is a macrocycle comprised of seven glucose molecules (Figure 1). β -CD's cuplike shape provides a distinct hydrophobic interior cavity, which forms host-guest complexes with thousands of organic molecules. This property suggests that CDs would make ideal adsorbents for water purification, though CDs must first be rendered insoluble by incorporating them into a polymer network. Several CD-containing polymers have been previously described, though none have had the required porosity or surface area to perform as well as AC as an adsorbent [26–29]. Our new β -CD polymer combines the molecular recognition

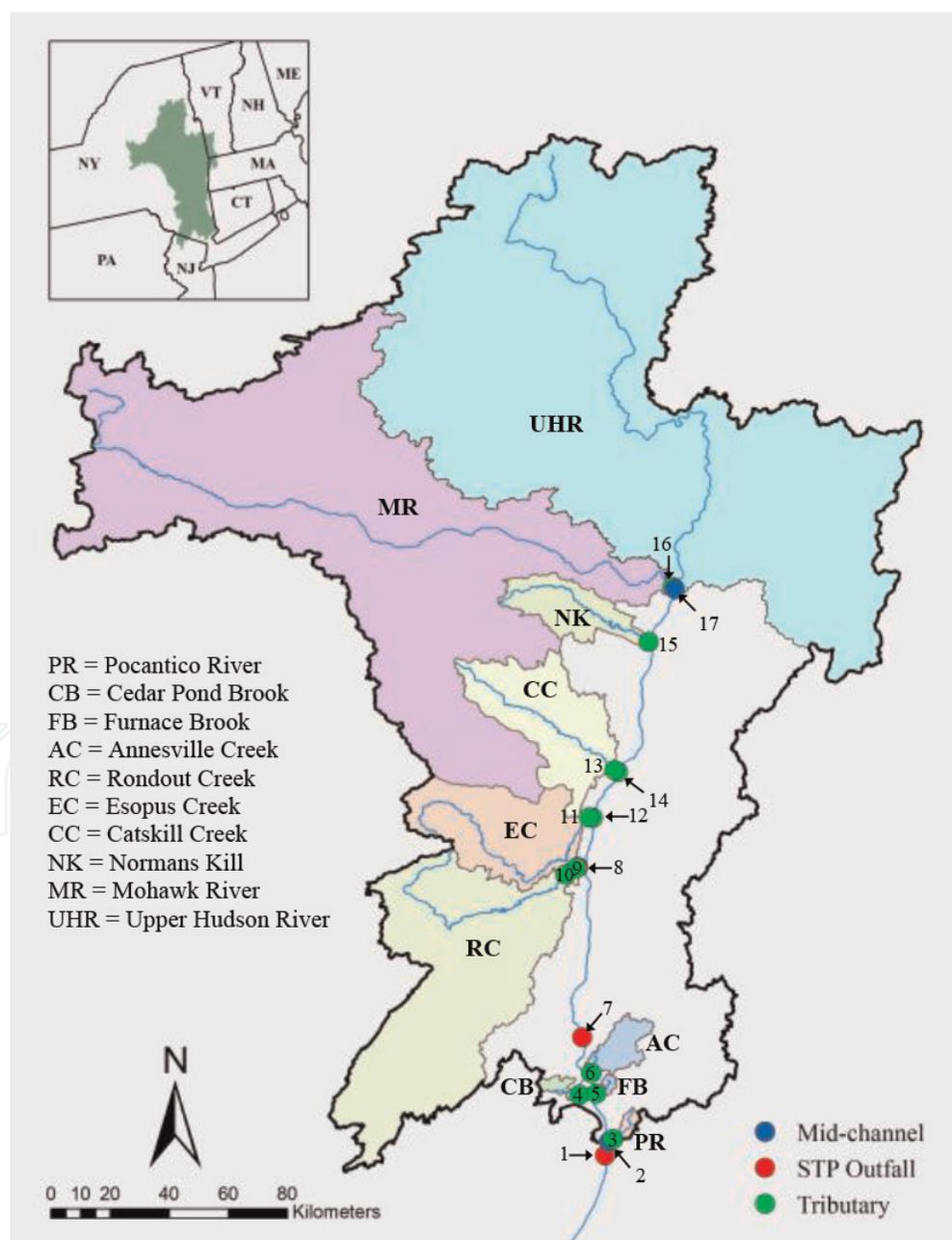


Figure 2.
Map of the Hudson River Estuary and select tributary watersheds. The sampling locations are represented with circles and site ID.

properties of CDs with the porosity and high surface area of ACs to yield an adsorbent with superior adsorption kinetics and an adsorption capacity on the order of AC. However, we have not yet tested our β -CD polymer against diverse groups of micropollutants and under environmentally relevant conditions.

The objectives of this research were twofold. First, we aimed to assess the relative contributions of various sources to micropollutant occurrence in the Hudson River Estuary, a major freshwater system in New York. We collected grab samples at 17 sites along the Hudson River Estuary between the Mohawk River and the Tappan Zee Bridge. Samples were collected in May, July, and September of 2016. A map of the 17 sampling sites is provided in **Figure 2** along with a delineation of the watersheds for each of the tributaries. The sites include three sewage treatment plant outfalls, five sites at the mouth of tributaries of the Hudson River, seven sites inside the tributaries of the Hudson River, and two control sites in the midchannel of the Hudson River at the northern and southern ends of the study boundaries. The samples were analyzed using a target screening analysis to quantify the occurrence of up to 200 micropollutants commonly identified in surface waters around the world. Second, we aimed to evaluate the performance of porous β -CD polymers (P-CDPs) as adsorbents of micropollutants in aquatic matrices. Adsorption kinetics and micropollutant removal were measured in batch and flow-through experiments for a mixture of 90 micropollutants at environmentally relevant concentrations ($1 \mu\text{g L}^{-1}$) and in the presence and absence of natural organic matter (NOM). The performance was benchmarked against a coconut shell activated carbon (CCAC). Data reveal slower and nonselective uptake on CCAC and faster and selective uptake on P-CDP. The presence of NOM had a negative effect on the adsorption of micropollutants to CCAC but had almost no effect on adsorption of micropollutants to P-CDP. These data highlight advantages of P-CDP adsorbents relevant to micropollutant removal during water and wastewater treatment.

2. Methodology

2.1 Micropollutant monitoring

All spatial analyses and mapping were conducted with ArcMap 10.4. All of the data used is freely available online including the digital elevation models used to delineate the Hudson River Estuary catchment area and tributary watersheds, land cover data, and industrial discharge sites including wastewater treatment plants, hospitals, and population data. Grab samples were collected in 1 L amber, trace clean glass bottles. The samples were shipped in a cooler to our laboratory at Cornell University at the end of each sampling campaign. Samples were stored at 4°C and in the dark until sample preparation within 24 h of arrival in our laboratory. We used a mixed-bed solid-phase extraction (SPE) method to concentrate the 1 L samples as previously described [7, 30]. The high-performance liquid chromatography and tandem mass spectrometry (HPLC-MS/MS) method was previously developed and validated for a broad range of micropollutants [30, 31]. A target screening approach was used to quantify the concentrations of 200 micropollutants in each of the samples. Detection limits are generally in the low ng L^{-1} range for the micropollutants on this list. Statistical analyses were conducted using R Statistical Software and an alpha level of 0.01 was used to determine significance. The *hclust* function was used to cluster micropollutants using Ward's method based on the occurrence profiles for all the detected micropollutants at each sample site during each sampling event. Paired Wilcoxon rank-sum tests were used to assess the differences between micropollutant concentration profiles across sample sites.

2.2 Micropollutant adsorption

P-CDP was synthesized as previously described [25], and the CCAC is commercially available (AquaCarb 1230C, Westates Carbon, Siemens, Roseville, MN). To increase the similarity in particle size between the P-CDP and CCAC, the CCAC was pulverized with a mortar and pestle until >95% (mass) passed a 74 μm sieve (200 US mesh). The P-CDP and the pulverized CCAC were dried under a vacuum in a desiccator for 1 week and stored in a refrigerator at 4°C. We selected 90 micropollutants based on their environmental relevance and previous reports of their adsorption onto AC. Stock solutions of each compound were prepared at a concentration of 1 g L⁻¹ using 100% HPLC-grade methanol. The stock solutions were used to prepare an analytical mix containing all 90 micropollutants at a concentration of 10 mg L⁻¹ using nanopure water.

2.3 Batch experiments

Batch experiments were performed in 125 mL glass Erlenmeyer flasks with magnetic stir bars on a multi-position stirrer (VWR) with a stirring rate of 400 revolutions per minute (rpm) at 23°C. Batch experiments were performed at an adsorbent dose of 10 mg L⁻¹. The micropollutants were spiked to generate an initial concentration of each adsorbate of 1 $\mu\text{g L}^{-1}$. Samples were collected in 8 mL volumes at predetermined sampling times (0, 0.05, 0.17, 0.5, 1, 5, 10, 30, 60, 90, 120 min) and filtered through a 0.22 μm PVDF syringe filter (Restek). Control experiments to account for other micropollutant losses were performed under the same conditions with no addition of adsorbent. All samples were analyzed by means of HPLC-MS/MS to determine the aqueous phase concentration of each micropollutant as a function of contact time with the adsorbent.

2.4 Flow-through experiments

Flow-through experiments were performed with a 10 mL Luer Lock glass syringe and Restek 0.22 μm PVDF syringe filters at 23°C with a constant flow rate of 25 mL min⁻¹. Flow-through experiments were performed with either nanopure water or nanopure water amended with humic acid (HA) as a surrogate for NOM and NaCl as a surrogate for inorganic matrix constituents. Syringe filters were loaded with adsorbent by passing 1 mL of the adsorbent suspension through the inorganic syringe filter to form a thin layer of 1 mg of adsorbent on the filter surface. Following the loading of the filters with adsorbent, 8 mL of the analytical mix (1 $\mu\text{g L}^{-1}$) was pushed through the adsorbent-loaded filter with constant pressure over 20 s. Control experiments were performed in the same way with no adsorbent on the filter to account for losses through the filter. The filtrates were analyzed by means of HPLC-MS/MS to determine the aqueous phase concentration of each micropollutant.

3. Results

3.1 Micropollutant monitoring

To complement the micropollutant data analysis and to enable a more comprehensive study of micropollutant sources, we first collected geospatial data for the Hudson River Estuary catchment area. We used ArcGIS and publically available data to develop maps of the Hudson River Estuary catchment area that include

geospatial references for land cover, industrial discharge locations, sewage outfalls, and hospitals. We expected that the occurrence and concentrations of certain types of micropollutants would be associated with the geographic distances to these types of catchment features. For example, a recent geospatial analysis of poly- and perfluoroalkyl substances (PFASs) revealed that PFASs were found at higher concentrations in more urban areas and different types of PFASs were associated with different point sources such as airports, textile mills, and metal smelting [1]. Another recent study used spatial analysis techniques to predict mass flows and concentrations of pharmaceuticals in surface water samples using hospital locations, departments, and the number of beds [32]. These examples demonstrate powerful ways in which geospatial data can be combined with micropollutant occurrence data to improve our fundamental understanding of micropollutant sources. We collected grab samples in May, July, and September 2016 from the 17 locations along the Hudson River Estuary. The sample collected in May 2016 from Rondout Creek-Kingston STP Outfall was lost during sample shipment; therefore, a total of 50 samples were processed and analyzed in our laboratory. Our target list was comprised of 200 total micropollutants which included 134 wastewater-derived compounds (pharmaceuticals, industrial compounds, personal care products, hormones, food additives, and illicit drugs) and 66 pesticides (including herbicides, insecticides, and fungicides). From our target list, 160 of the micropollutants were detected in at least 1 of the 50 samples; 111 were wastewater-derived compounds and 49 were pesticides. **Figure 3** presents the distribution of detected micropollutants by use class. Twelve of the 200 micropollutants were detected in all 50 samples, with an additional 25 being detected in at least 40 samples. The micropollutants detected in all samples included acesulfame (artificial sweetener), atenolol acid (metabolite of atenolol and metoprolol), atrazine (herbicide), benzotriazole-methyl-1H (corrosion inhibitor), carbamazepine (antiepileptic), DEET (insect repellent), gabapentin (antiepileptic), lamotrigine (anticonvulsant), metolachlor (herbicide), sucralose (artificial sweetener), desvenlafaxine (metabolite of the antidepressant venlafaxine), and valsartan (angiotensin II antagonist). The highest occurrence and concentrations of all micropollutants were detected in the STP outfall samples. Sucralose, atenolol acid, and metformin (antidiabetic) were detected at the highest concentrations in the mid-mg L⁻¹ range. It must be noted that data derived from grab samples do not necessarily reflect the expected dynamics of micropollutant occurrence or concentration in surface water systems [33]. However, longer time series of grab samples can be analyzed to provide more robust estimates of the likelihood of occurrence and average concentrations of specific micropollutants at a particular sample site. The majority of micropollutants that were detected were measured in the 1–100 ng L⁻¹ range.

We next aimed to investigate how the micropollutant occurrence profiles (defined as the occurrence of individual micropollutants in a sample) compared among the 17 sample sites. To do this, we used Ward's method to cluster each micropollutant based on its spatiotemporal occurrence pattern. The resulting dendrogram is presented in **Figure 4** and reveals four distinct micropollutant clusters that describe the relationship in spatiotemporal occurrence among the micropollutants. Cluster 1 contains 56 micropollutants that are present in most samples, regardless of sample type (tributaries, control sites, and STP outfalls) or sample date. Cluster 2 contains 28 micropollutants that were detected most frequently in the tributary and control sites but rarely in the STP outfalls. Cluster 3 contains 33 micropollutants that were detected more often in the STP outfalls than the tributary or control sites. Cluster 4 contains 43 micropollutants that were detected mostly in STP outfalls and in 2 separate tributary samples collected on different dates.

a more representative metric of overall contribution to the Hudson River. Nevertheless, concentration data enabled us to preliminarily identify specific tributaries that are likely important sources of micropollutants to the Hudson River.

Rondout Creek and Normans Kill were identified as the major contributors of wastewater-derived micropollutants to the Hudson River Estuary. Rondout Creek was also identified as a major contributor of agricultural micropollutants. Our analysis confirms that the Hudson River Estuary is more impacted by micropollutants as it flows south toward New York City. Additionally, our geospatial analysis revealed several associations between the spatiotemporal occurrence clusters and certain geographic catchment features including the extent of total agricultural land cover, extent of cultivated cropland land cover, number of the major STP outfalls, and hydraulic distances to the major STP outfalls. It is important to note that while this sampling campaign had high spatial resolution and a large number of targeted micropollutants, it has low temporal resolution with only three separate grab sampling events during the 2016 recreational season. Large-scale sampling campaigns such as these can benefit from higher temporal resolution to gain a more representative understanding of micropollutant concentrations and increase the power of the statistical tests.

3.2 Micropollutant adsorption

Data from the batch experiments were first evaluated to estimate pseudo-second-order adsorption rate constants (k_{obs}) for each micropollutant and each adsorbent. The estimated values of k_{obs} for each micropollutant on each adsorbent are summarized in **Figure 5**. Generally, if a k_{obs} could be estimated from the data for a particular micropollutant, its value was significantly greater on P-CDP than CCAC. These data corroborate our earlier observations of nearly instantaneous equilibrium adsorption of several model organic molecules on P-CDP [25]. The rapid micropollutant uptake by P-CDP is attributed to the accessibility of the β -CD binding sites in the polymer due to its porosity and high surface area.

The estimated values of k_{obs} describe the rate at which adsorption equilibrium is attained but do not provide any insight on the affinity of each micropollutant for

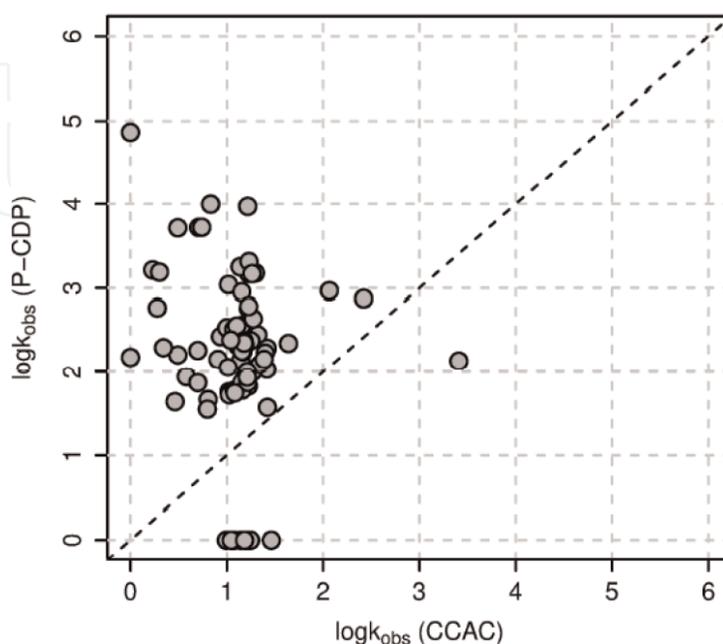


Figure 5. Comparison of pseudo-second-order rate constants (k_{obs}) for the adsorption of each micropollutant by P-CDP and CCAC.

each adsorbent. To enable a more robust interpretation of micropollutant affinity for each adsorbent, we measured the percent removal of each micropollutant after 5 min for CCAC and P-CDP and summarize the data in **Figure 6**. Despite the faster adsorption kinetics exhibited by P-CDP relative to CCAC, the extent of micropollutant uptake at 5 min is more evenly split between the two adsorbents, which we attribute to differences in the affinities of each micropollutant for each adsorbent under the experimental conditions. Whereas most micropollutants have moderate affinity for CCAC, the distribution of micropollutant affinity for P-CDP is more variable, with some micropollutants having very strong affinity (more than 80% removal) and others having relatively weak affinity (removal less than 20%). Overall, these data from the batch experiments demonstrate that micropollutant uptake on P-CDP is generally rapid but selective, with some micropollutants attaining complete uptake in 5 min and others being removed to only minor extents. In contrast, CCAC exhibits relatively slow uptake kinetics, though uptake is rather nonselective with increasing extents of uptake of most micropollutants over time.

We also characterized the performance of P-CDP as an adsorbent by evaluating the instantaneous removal of micropollutants in flow-through experiments designed to simulate filtration-type adsorption processes. The same mixture of 90 micropollutants was pushed through thin layers of each adsorbent immobilized on a nonadsorbent membrane at a constant flow rate. Experiments were conducted with an adsorbent dose of 1 mg. Differences in measured concentrations before and after filtration were used to calculate the removal of each micropollutant in each experiment. The removal percentages of each micropollutant on each adsorbent are summarized in **Figure 7**.

A total of 47 micropollutants were removed to greater extents by P-CDP in flow-through experiments designed to simulate filtration-type adsorption processes. This provides another example of how the rapid adsorption kinetics exhibited by P-CDP can lead to significant removal of micropollutants even in processes providing limited contact time. These data again suggest a selectivity to micropollutant uptake on P-CDP. Finally, despite this selectivity, it is important to emphasize that the micropollutants that are efficiently removed by P-CDP are nearly completely removed in the flow-through experiments; 24 of the micropollutants exhibit greater than 95% removal in these experiments, whereas only 1 micropollutant is removed to that extent by CCAC.

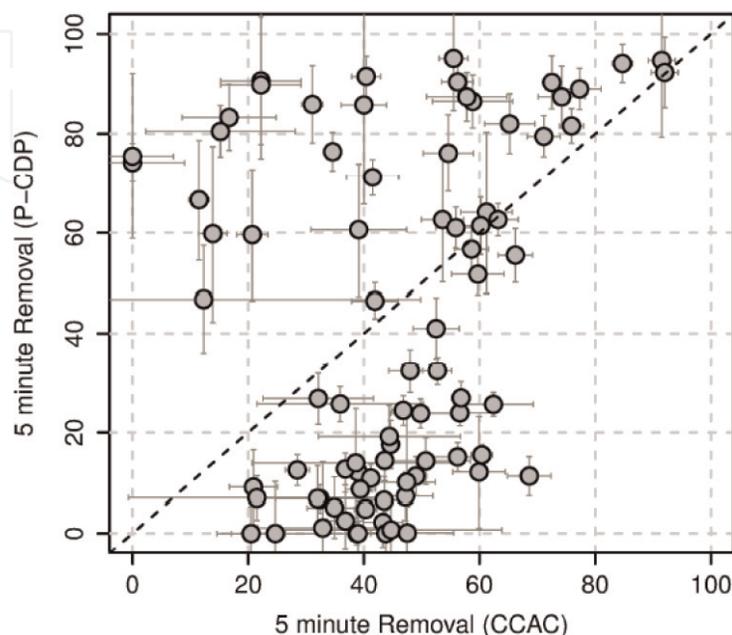


Figure 6. Comparison of the percent removal of each micropollutant after 5 min contact time with either P-CDP or CCAC.

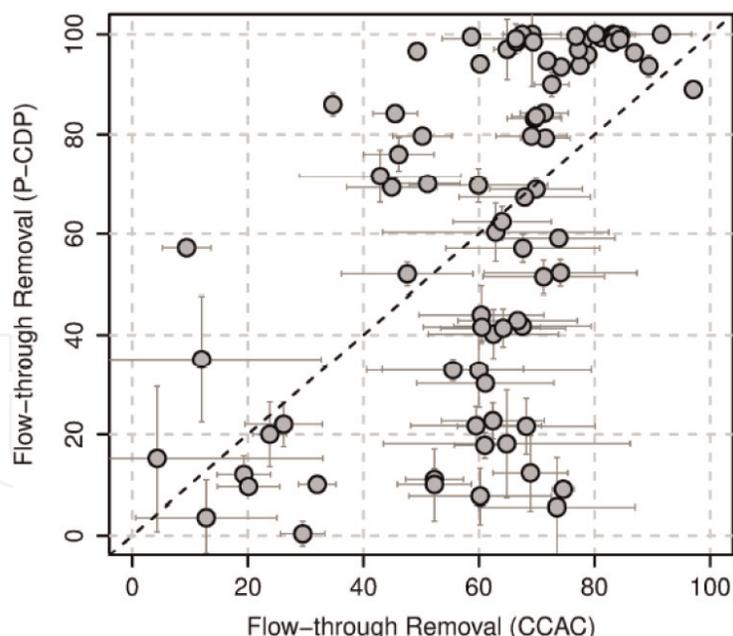


Figure 7.
Comparison of the removal percentages by P-CDP and CCAC measured for each micropollutant from flow-through experiments.

One of the main deficiencies of CCAC as an adsorbent is its tendency to be fouled by NOM and other matrix constituents [23]. Therefore, we evaluated the performance of both adsorbents in the presence of NOM and inorganic ions. We repeated the flow-through experiments in the presence of 20 mg L^{-1} of humic acid (HA, as a surrogate for NOM) and 200 mg L^{-1} of NaCl to simulate the conditions in a typical surface water system. The removal percentages of each micropollutant are summarized in **Figure 8**. As expected, the addition of matrix constituents had a significant negative influence on the adsorption of micropollutants to the CCAC, likely as the result of a direct site competition or pore blockage mechanism [34, 35]. In contrast, no significant negative effect was observed for P-CDP. This was not necessarily unexpected; the binding sites of β -CD are contained inside its

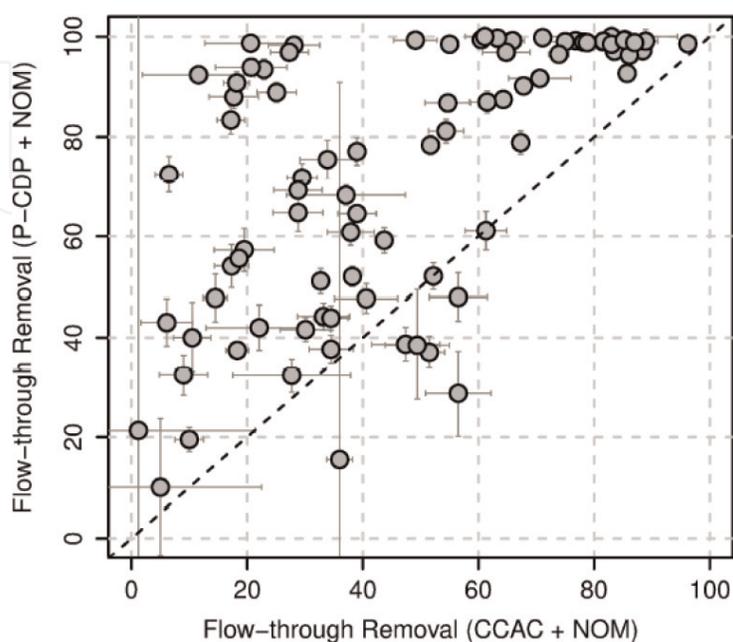


Figure 8.
Comparison of the removal percentages by P-CDP and CCAC measured for each micropollutant from flow-through experiments conducted with added matrix constituents (20 mg L^{-1} NOM and 200 mg L^{-1} NaCl).

0.78-nm-diameter interior cavity [26]. Host-guest complex formation requires that organic molecules fit inside the interior cavity of β -CD and large organic molecules do not bind well with β -CD, presumably due to a size exclusion mechanism. This result is particularly exciting because it suggests that P-CDP might not be fouled by NOM in natural waters, instead reserving its binding sites for smaller organic molecules. Remarkably, 75 micropollutants were removed to greater extents by P-CDP in the presence of matrix constituents. Of those, 44 were removed to greater than 80% on P-CDP, whereas only 13 micropollutants were removed to greater than 80% on CCAC in the presence of NOM and matrix constituents.

4. Conclusions

The first aim of this research was to improve our understanding of the sources of micropollutants in the Hudson River Estuary. We collected samples from 17 locations along the Hudson River Estuary during May, July, and September 2016. The sample locations were selected to target sewage treatment plant (STP) outfalls and tributaries that are expected to be the major sources of micropollutants in the Hudson River. The samples were analyzed to quantify the occurrence of 200 wastewater-derived micropollutants and pesticides. The data was analyzed to identify the relative contributions of various sources of micropollutants and specific outfalls or tributaries that are significant sources of micropollutants in the Hudson River Estuary and revealed four distinct clusters of micropollutants grouped by their occurrence profiles. Rondout Creek and Normans Kill were both identified as the major contributors of wastewater-derived micropollutants to the Hudson River Estuary. Rondout Creek was also identified as a major contributor of agricultural micropollutants. Our geospatial analysis revealed several associations between the spatiotemporal occurrence clusters and certain geographic catchment features including the extent of total agricultural land cover, extent of cultivated cropland land cover, number of the major STP outfalls, and hydraulic distances to the major STP outfalls. These data can be used to develop targeted micropollutant mitigation strategies in the Hudson River Estuary. An expanded survey of micropollutants in the Hudson River Estuary that contains the data presented here has been published in the peer-reviewed literature [36].

The second aim of this research was to study cost-effective and energy-efficient technologies to enhance the removal of micropollutants in water and wastewater treatment systems. Despite their expense, AC adsorption processes have emerged as a leading alternative, though they are limited by relatively slow adsorption kinetics and a tendency to become fouled by NOM and other matrix constituents. Our results suggest that β -cyclodextrin polymer adsorbents address these specific deficiencies and therefore might be developed into a viable alternative or complementary adsorbent in water and wastewater treatment. Further, β -cyclodextrin polymer adsorbents are prepared in a single step from commercially available monomers, including the commodity chemical β -CD. Because it is synthesized through a rational process, many related compositions of β -cyclodextrin polymer adsorbents can be designed to target improved performance or different selectivity. These factors make it possible that β -cyclodextrin polymer adsorbents might be produced at large scales and deployed with competitive life cycle costs to ACs used in water and wastewater treatment. Together, these features all suggest that β -cyclodextrin polymer adsorbents may be a promising alternative adsorbent for the removal of micropollutants during water and wastewater treatment. An expanded study of micropollutant adsorption on cyclodextrin polymers has been published in the peer-reviewed literature [37].

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