Optimized suspect screening approach for a comprehensive assessment of the impact of best management practices in reducing micropollutants transport in the Potomac River watershed

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A B S T R A C T
The vast number of chemicals potentially reaching aquatic environment pose a challenge in maintaining the quality of water resources. However, best management practices to improve water quality are typically focused on reducing nutrient transport without assessing how these practices may impact the occurrence of micropollutants. The potential for co-management of nutrients and organic micropollutants exists, but few studies have comprehensively evaluated the suite of contaminants associated with different water quality management practices (riparian zone restoration, stormwater management, etc.). Furthermore, most studies dealing with the determination of micropollutants in environmental samples include only a limited number of target analytes, leaving many contaminants undetected. To address this limitation, there has been a gradual shift in environmental monitoring from using target analysis to either suspect screening analysis (SSA) or non-targeted analysis (NTA), which relies on accurate mass measurements, mass spectral fragmentation patterns, and retention time information obtained using liquid chromatography coupled to high-resolution mass spectrometry. The work presented in this paper focuses on a wide-scope detection of micropollutants in surface water samples from the Potomac River watershed (United States). An in-house database composed of 1039 compounds based on experimental analysis of primary standards was established, and SSA workflow was optimized and applied to determine the presence of micropollutants in surface water. A total of 103 micropollutants were detected in the samples, some of which are contaminants that were not previously monitored and belong to various classes such as pharmaceuticals, personal care products, per-and polyfluoroalkyl substances and other persistent industrial chemicals. The impact of best management practices being implemented for nitrogen and phosphorus reductions were also assessed for their potential to reduce micropollutant transport. This work illustrates the advantages of suspect screening methods to determine a large number of micropollutants in environmental samples and reveals the potential to co-manage a diverse array of micropollutants based on shared transport and transformation mechanisms in watersheds.

1. Introduction

Freshwater ecosystems are of vital importance to human existence but can be subjected to a range of anthropogenic pressures resulting to water resources degradation. There are several routes in which a wide array of micropollutants reach the aquatic environment. This include point sources such as outfalls from waste water treatment plants (WWTPs) (Singhal and Perez-Garcia, 2016; Margot et al., 2015) and industrial discharges (Lapworth et al., 2012; Murakami et al., 2009), along with non-point sources such as agricultural runoff (Evans et al., 2019), urban stormwater runoff (Murakami et al., 2009) and others. To reduce loading of these pollutants into surface water, several strategies have been
implemented such as upgrade of WWTPs and implementation of nonpoint source best management practices (BMPs). While these strategies are mostly focused on nutrient reduction, several studies have also demonstrated the capability of these practices to reduce micropollutant transport. For example, advanced oxidation processes in WWTPs such as ozonation can efficiently remove pharmaceuticals and personal care products (PPCPs) (Margot et al., 2015; Angeles et al., 2020). Agricultural BMPs like buffer strips, riparian zones and constructed wetlands can also reduce transport of pesticides and their metabolites in watersheds significantly (Talib and Randhir, 2016).

The Potomac River watershed is the second largest sub-watershed of the Chesapeake Bay in terms of water quantity (Belval and Sprague, 1999), and the fourth largest river on the Eastern coast of the United States. In year 2000, the Chesapeake Bay was listed as an “impaired” water body under the Clean Water Act due to the degradation of water quality and decline in ecological health of the bay and its tributaries (Langland et al., 2004). In this regard, ambient water quality criteria was developed to reduce nutrient and sediment-based pollution entering the bay (USEPA 2003). Implementation of strategies to decrease point-source nutrient loading resulted to a recovery from eutrophication, and a shift of the tidal embayment from phytoplankton - submerged to submerged aquatic vegetation was observed (de Mutsert et al., 2017; Jones, 2020).

The continuous increase in the use of chemicals in consumer products, which eventually end up being discharged into surface waters, delivers challenges to regulatory agencies in their efforts to implement and update water quality criteria. Decisions on which chemicals need to be regulated is highly dependent on their occurrence in the environment (USEPA), hence dealing with toxic emerging contaminants which have not been previously included in monitoring programs is difficult. If environmental monitoring programs will continuously rely on target analysis approach, many contaminants will remain unnoticed. To address this challenge, a shift from pure target analysis to either “suspect screening” analysis (SSA) or “non-targeted” analysis (NTA) (Schymanski et al., 2015) is becoming more and more common in environmental studies. Both SSA and NTA approaches take advantage of the accurate mass measurements afforded by high resolution mass spectrometry (HRMS). In SSA and NTA, the exact mass and isotope patterns of the molecule, together with the molecule’s characteristic fragmentation patterns, are compared to a database or spectral resources of chemical suspects to identify potential matches (Andra et al., 2017). SSA is performed when prior information indicates that a given structure may be present in the sample. Screening for “suspect compounds” are searched within a mass of interest typically included in a suspect list. On the other hand, NTA aims at identifying compounds without searching for certain masses/substances up front, thus, a full non-target identification starting from the exact mass, isotope, adduct, and fragmentation information is performed (Schymanski et al., 2015). Recently, SSA approach was successfully used in the identification of 23 new potentially hazardous substances from the effluents collected in three major WWTPs in Sweden (Gago-Ferrero et al., 2018), in the detection of 27 active pharmaceutical ingredients from WWTPs effluents in Switzerland (Singer et al., 2016); in the identification of 13 pesticide transformation products in groundwater samples (Kierler et al., 2019) and in the prioritization of more than 5200 anthropogenic chemicals authorized in European market (Sjursen et al., 2016). Our group also applied retrospective SSA on previously analyzed samples and discovered high frequency of occurrence of antifungal compounds and amoxicillin metabolites in surface waters (Angelles et al., 2020).

Currently, a more holistic watershed approaches (Chan et al., 2018; Wang et al., 2016) have been developed for large-scale pollutant management in surface waters. Combining smart watershed approaches with advances in analytical testing capabilities (e.g. NTA/SSA approach) can provide sound evaluation of the effectiveness of these measures, co-management of multiple pollutants, regulation of chemicals and sustainable water management (Hollender et al., 2019).

While SSA analysis offers increased chemical coverage and serendipitous discovery, creating a meaningful SSA workflow and reproducible results among scientists is a daunting task (Hites and Jobst, 2018). To bridge this gap, we took advantage of the experience of our laboratory in the analysis of various classes of contaminants in several environmental matrices to: (1) build an in-house Trace-Finder™ database that is traceable to primary standards; (2) optimize SSA workflow by comparing the detection coverage of our previously validated LC methods; (3) apply the optimized workflow to determine the presence of micropollutants in Potomac watershed that were not part of prior targeted analysis; and (4) assess the efficiency of BMPs already in place in reducing transport of micropollutants.

2. Materials and method

2.1. Chemicals

Primary standards of the compounds used in this work were purchased from several suppliers including Acros Organics (Morris Plains, NJ), Cambridge Isotopes (Tewksbury, MA), C/D/N Isotopes Inc. (Quebec, Canada), Chem Service Inc. (West Chester, PA), ICN Biomedicals, Inc. (Irvine, CA), Phenova (Golden, CO), Restek Corporation (Bellefonte, PA), Spectrum Chemical Mfg. Corp (New Brunswick, NJ), Sigma Aldrich (St Louis, MO), Restek Corporation (Bellefonte, PA), TCI (Tokyo, Japan), Willington Laboratories Inc. (Ontario, Canada) and pesticides mixes were provided by US-FDA (Wong et al., 2018) (College Park, MD), Barnstead NANOpure™ Diamond (Waltham, MA) purification system was used to obtain 18.2mΩ water used throughout all experiments. LC-MS grade methanol and acetonitrile (Omnisolv™) was obtained from EMD Millipore Corporation (Billerica, MA). Formic acid (88%) was purchased from Fisher Chemical (Pittsburgh, PA), and ammonium hydroxide (ACS grade) was obtained from J.T. Baker (Phillipsburg, NJ).

2.2. Liquid chromatography coupled with high-resolution mass spectrometry (LC-HRMS)

Two previously validated liquid chromatography tandem mass spectrometry (LC-MS) (using triple quadrupole mass spectrometer) target analysis methods were transferred to the Thermo Scientific Q-Exactive Focus™ with Thermo Scientific UltiMate 3000 UHPLC™ systems. The first method (Singh et al., 2019) was validated for the analysis of multiclass of antimicrobials and pharmaceuticals using a CORTECS™ C18+ (2.7 μm particle size, 2.1 mm internal diameter, 150 mm length) HPLC column from Waters (Milford, Massachussetts) and low pH mobile phases - water with 0.1% formic acid (mobile phase A) and acetonitrile with 0.1% formic acid (mobile phase B). The second method (He and Aga, 2019) was validated for the simultaneous analysis of hormones and pesticides. This method utilized a Waters XSelect CSH™ C18 column (3.5 μm particle size, 2.1 mm internal diameter, 150 mm length) and high pH mobile phases: water – methanol (96:4, v/v) with 5 mM ammonium hydroxide (mobile phase A) and acetonitrile – methanol – water (80:10:10, v/v/v) with 5 mM ammonium hydroxide (mobile phase B). Both methods were run in gradient starting from 5% to 95% mobile phase B at a flowrate of 200 μL/min with a total run time of 45 min.
A solution of mix standard (18 different mixtures totaling to 1227 compounds) prepared at 100 μg L⁻¹ concentration were analyzed using both the low and high pH methods. A full scan with data-dependent MS² (full MS—ddMS²) experiment was used to obtain the HRMS data. Properties for full MS are as follows: scan range: 80—1100 m/z, resolution of 70,000, AGC (automatic gain control) target of 1e⁵ and injection time set to auto. For ddMS², parameters are as follows: resolution of 17, 500, isolation window of 4.0 m/z, collision energies at 10, 30 and 60 eV, AGC target of 1e⁵ and injection time also set to auto. The precursor ion mass of all the compounds were inputted in the inclusion list. Separate injections were done for positive ionization (ESI+) and negative ionization (ESI-) mode analyses.

2.3. Development and validation of the in-house database

Retention time and m/z values of the fragment ions for each analyzed compound were extracted using the Xcalibur™ 4.0 software (Thermo Fisher Scientific Inc., Waltham, MA) and all information was inputted into an in-house database. The format of the database was adopted from the work of Wong et al. (2018) that contained 603 pesticides and their metabolites. An additional of ~500 compounds (other pesticides, hormones, pharmaceutics and personal care products (PPCPs), per-and polyfluoroalkyl substances (PFASs) and other industrial chemicals) were added into the database. Suspect screening was performed using Trace Finder™ version 4.1 (Thermo Fisher Scientific Inc., Waltham, MA) and the sensitivity of the workflow was assessed by comparing tolerance for precursor mass error (5 vs. 10 ppm (parts per million), retention time window of 30s vs. 60s, presence of at least two fragment ions confirmed within 10, 20 or 30 ppm mass error and an isotopic pattern match of at least 80% fit. It was found that the optimized identification and confirmation settings for the suspect screening workflow is set at precursor ion within 5 ppm error, presence of ≥ two fragment ions within 20 ppm error, retention time match within 1 min, and an isotopic pattern of ≥ 90% fit. Using these optimized parameters, we were able to obtain a true positive of 94% using low pH method and 97% using the high pH method with zero false positive. Detailed information of the developed in-house database is summarized in Table S1.

2.4. Sample collection, preparation and LC-HRMS analysis

Water samples were collected from October 2017 to June 2018 along Potomac watershed in Maryland, USA from paired streams in very similar geographic watersheds (for a comparable rainfall patterns) and from Blue Plains WWTP. The paired agricultural streams (with and without BMPs) are located in Ben’s Branch of the Lake Linganore watershed in Frederick County, Maryland. The restored stream is a small headwater tributary surrounded by the Hunting Lotte farm, a 450-acre crop and livestock farm with about 150 head of Black Angus cattle on about 80 acres of pasture. Prior to BMP installation, the stream’s riparian zone was part of a cattle pasture that provided the livestock with unrestricted access to the stream. The BMPs included more than 8800 feet of fencing, three spring developments to replace in-stream cattle watering, improvements to areas heavily used by livestock, including two stream crossings as well as plantings of over 9 acres of cool-season grasses (Shanks and Soehl, 2008). The unrestored stream is a nearby small, unnamed headwater tributary with similar land use and geomorphology. The paired urban streams - with and without BMPs (Paint Branch vs. Brier Ditch) are located in the Anacostia watershed of Maryland Montgomery and Prince Georgy’s County. Both watersheds are dominated by urban land use but only Paint Branch was restored with urban BMPs. In 1995, the Montgomery County Council designated the upper Paint Branch watershed as a Special Protected Area, under a county law that provides additional protections to designated sensitive areas. The Maryland National Parks and Planning Commission purchased undeveloped land along the stream to maintain shaded habitat and leaf litter inputs and implemented regulations that limited impervious area to 10% of all new development in the watershed. The Brier Ditch watershed has not implemented BMP’s and is of the most densely populated regions of the area with the fewest stormwater management controls. Only 13% of the stream has adequate riparian forest buffer compared to Paint Branch’s 53%. On the other hand, the Blue Plains WWTP is the largest treatment plant in the Potomac River watershed and the largest treatment facility of its kind in the USA, with a rated capacity of 384 million gallons per day (MGD). It serves over two million customers with a collection area of Washington DC and surrounding suburbs of Maryland and Virginia. The treatment process utilizes preliminary and primary treatment, secondary treatment, nitrification/denitriﬁcation, efﬂuent filtration, chlorination - dechlorination and post aeration (Blue_Plains 2020). In the last several years, the plant has dramatically upgraded and improved its liquid processing systems. Surface water collection and sample preparation were described in details elsewhere (He and Aga, 2019). Samples and field blanks were collected from speciﬁed sampling locations (Fig. 1) at ﬁve different sampling times (Oct 2017; Dec 2017; Feb 2018; Apr 2018; Jun 2018). A 500 - mL water sample was collected in glass amber bottles pre-rinsed with 10% nitric acid, and pH was adjusted to 2.5 ± 0.5 to reduce bacterial degradation. Samples were then ﬁltered using a 0.45 mm glass ﬁber ﬁlter and spiked with 100 μL of 250 mg L⁻¹ surrogate mixture solution containing E1-3S-d₄, E2-3S-
d4, E2-3G-d3, E1-d4, E2-d3, EE2-d4, imidazolidine-d4, prometon-d14, metolachlor-d6, atrazine-d5, acetochlor-d11, 4-n-nonylphenol-d4, diazinon-d10, and dinofuran-d3. Analytes of interest were extracted and pre-concentrated using solid phase extraction (SPE) with Oasis® HLB cartridge pre-conditioned with 10 mL of methanol, followed by 10 mL of Nanopure™ water. Samples were loaded onto the cartridge at a flow rate of 3–5 mL min⁻¹. Cartridges were then completely dried under vacuum conditions at about 15 psi. Elution was done using 10 mL ethyl acetate (eluate 1) and another 10 mL methanol with 2% ammonium hydroxide (eluate 2), collected separately. Eluates 1 and 2 were slowly evaporated to 500 μL under a stream of nitrogen at 30 °C, and 300-μL aliquots of eluate 1 and eluate 2 were combined in graduated tubes, evaporated until 200 μL, and then brought up to a final volume of 600 μL with water—acetonitrile (95:5, v/v) solution. The solution was centrifuged and the supernatant was collected for LC–MS analysis.

2.5. Target and suspect screening analysis

Samples were analyzed for 37 endocrine disrupting chemicals (EDCs) using a triple quadrupole LC-MS (target analysis) discussed in details in our previous work (He and Aga, 2019). LC-MS parameters, LOD and recovery for target analysis is summarized in Table S2. Accurate quantification was performed using isotope dilution technique to account for any matrix effects and correct for losses during sample preparation and transport (He and Aga, 2019).

For SSA, the same set of samples were analyzed using LC-HRMS wherein ESI+- data acquisition utilized the low pH method and ESI− data acquisition utilized the high pH method. Suspect screening was performed using the developed in-house database for TraceFinder™ software wherein the optimized criteria for positive detection (precursor ion within 5 ppm error, presence of ≥ two fragment ions within 20 ppm error, retention time match ± 1 min, and an isotopic pattern of 90% fit) were used as discussed in section 2.3. Blank subtraction was incorporated in the software settings for integration. For compounds that were also detected in the blanks, only those that have an area in the samples of at least five times higher than the average area of the blanks were considered. Finally, manual checking of peak shape (i.e. Gaussian and not very broad ≤1 min) for each confirmed compound was also performed. For micropollutants detected in the samples using SSA, retrospective semi-quantitative analysis was done by analyzing a mix of standards at 100 μg L⁻¹ concentration and using the areas from this standard mix to estimate the concentrations of the micropollutants based on a one-point external calibration.

2.6. Calculation of micropollutant transport reduction

The concentration obtained from target analysis and SSA (Table S3) for agricultural/urban paired streams were used to estimate reduction of micropollutant transport due to BMP installation. Flow-weighted mean concentrations (FWMC, ng L⁻¹) was computed by multiplying concentrations and corresponding flow, using the following equation:

\[ \text{FWMC} = \frac{\sum_{i=1}^{n}(c_i \times q_i)}{\sum_{i=1}^{n}q_i} \]

where \( c_i \) = concentration in ith month, \( q_i \) = mean flow of ith month. This equation allows the concentration in each sample to be considered in light of the flow volume associated with it. Stream flow data were collected from the USGS webpage (USGS, 2020) if the sampling location was at the USGS gauging station. If not, data from the nearest USGS gauging station with similar land use and surface geology were used. For the WWTP, only the concentration of micropollutant i in the WWTP effluent and downstream for a given sampling time were considered.

3. Results and discussion

3.1. Optimization of chemical coverage for the suspect screening workflow

In non-target approaches, the impact of chromatographic separation is often overlooked or underestimated because of the high selectivity afforded by HRMS. However, previous study (Croley et al., 2012) emphasized the need for a good chromatography in NTA and SSA. This is due to ion suppression caused by co-elution and peak coalescence observed in the Orbitrap™ that caused mass shifts of up to 16 ppm from the theoretical masses. More importantly, the effect of mobile phase pH on the ionization efficiency should be considered in SSA, where many studies have employed switching only the polarity of the ionization mode without changing the pH of the mobile phase (Albergamo et al., 2019; Knolhoff et al., 2019). In particular, methods that use large volume injection or on-line SPE do not amend themselves to re-inject the sample extracts for a second analysis using a different polarity in electrospray ionization. While on-line SPE offers good reproducibility and higher throughput analysis due to automation, this approach may not be the best for suspect screening analysis if increasing chemical coverage is an important goal of the study.

In the optimization of the suspect screening workflow, we compared two validated LC methods that have the highest number of compounds optimized for target analysis. While both methods utilized a C18 HPLC column, the mobile phases were different due to the differences in the ionization efficiencies of the classes of compounds analyzed in each method. To determine which method results in a wider chemical coverage and more efficient chromatographic separation, a 100 μg L⁻¹ standard mix was analyzed in each method; separate injections for ESI+- and ESI− were performed and the detection coverages between the methods were compared. While in total, we were able to detect more compounds using a low pH method (97%) compared to using high pH method (94%), we also analyzed the detection coverage considering the different classes of micropollutants that can be accurately identified using both methods (Fig. 2). For pesticides and metabolites which were analyzed in ESI+, 96% of the 942 compounds were detected using the low pH method and 95% were detected using the high pH mobile phase. Antibiotics, PPCPs and flame retardants were also analyzed using ESI−, and were all detected at the low pH but only 75% were detected using the high pH method. For the class of compounds that ionizes well in ESI− such as PFASs, higher % detection was observed at high pH method (Fig. 2). Based on these results, we analyzed the extracted water samples using the low pH method for ESI+ and high pH method for the ESI-. This approach allowed us to detect several classes of contaminants that could be present in the water samples.

3.2. Micropollutants class and detection frequencies

The non-tidal portion of Potomac River flows through different land use zones that range from agricultural in Fredrick (Maryland), suburban in Germantown (Maryland), and urban in Washington DC, thus monitoring the quality of water in Potomac River is highly important. Previous studies on micropollutants in Potomac River have focused on the determination of estrogenic contaminants such as estrogen and estradiol and their relationship to the high prevalence of male fish intersex observed in the river (Young et al., 2014; Kolpin et al., 2013). Other studies have detected polychlorinated biphenyls, polybrominated diphenyl ethers, and PFASs
for all contaminants was 0.8. The range of concentration observed for each micropollutant along with their detection frequencies (DF). The actual concentrations of each micropollutant were detected using the SSA approach suggesting that a large number of contaminants could be PFASs and organophosphate flame retardants (OPFRs) which are known to be persistent in the environment (Kraft and Riess, 2015; AMAP, 2017). Prevalence of atrazine, simazine, fipronil and metolachlor is consistent with the results presented in a recent study on the spatiotemporal variation of pesticides and other organic contaminants in six rivers of Chesapeake Bay, where these pesticides were found to co-occur most often across sites (McClure et al., 2020).

Until now, the agricultural sector remains the largest nutrient pollution source to the Potomac River and Chesapeake Bay. Agriculturally-derived micropollutants such as pesticides can be degraded by living organisms (generating metabolites) or can form transformation products (TPs) in the environment which can reach concentration levels higher than the parent substances and be even more toxic (Richardson and Ternes, 2014). In this work, several pesticide metabolites and TPs were detected such as metabolites of atrazine (atrazine desethyl; DF = 100%), atrazine desisopropyl; DF = 63%), atrazine desethyl desisopropyl, DF = 31%), dinoterufuran (dinoterufuran UF; DF = 43%), disulfoton (disulfoton sulfoxide; DF = 40%), fipronil (fipronil sulfide; DF = 37%), simazine (simazine -2-hydroxy; DF = 9%), sulprofos (sulprofos sulfoxide; DF = 43%) and fenthion sulfoxide (DF = 37%), a product of photooxidation of fenthion in the environment (Hirahara et al., 1998). Detection of these contaminants is important because historically, monitoring programs do not necessarily consider metabolites and TPs. It was also observed that these metabolites and TPs were detected in all sampling areas, which indicates the need to include these micropollutants in monitoring efforts when implementing BMPs.

3.3. Micropollutant spatiotemporal occurrence

Comparison of the occurrence of these micropollutants in the different sampling areas (agricultural watershed, urban watershed and WWTP) indicated that the highest number of contaminants were detected in the WWTP effluent and receiving downstream surface water samples, followed by the number of detections in the urban watershed samples and in the agricultural watershed samples (Fig. 4).
Fig. 3. Summary of detections and concentrations for the different classes of micropollutants. A- PPCPs, B-Hormones, C-PFASs, D-other industrial chemicals and E-pesticides and metabolites.
industrial wastewater, it is not surprising that the highest number of micropollutants were detected in the effluent. The profile of the contaminants in effluent and downstream samples are comparable (refer to Table S3 for the detailed information), which shows that contamination of downstream samples is mainly from the WWTP outfall.

As shown in Fig. 4, pesticides and industrial chemicals were detected in all sampling sites across the sampling times indicating the prevalence of these micropolllutants in Potomac River watershed. The highest occurrence of PPCPs was observed in the WWTP effluent and downstream samples, while the highest occurrence of PFASs was observed in the urban watershed samples and hormones were detected mostly in the samples collected from agricultural watershed (Fig. 4). Occurrence of PPCPs in WWTPs is common due to their universal consumption, low human metabolic capability, and improper disposal. On the other hand, PFASs reach aquatic environment through discharges from urban runoff contaminated by non-point sources (Murakami et al., 2009; Zushi and Masunaga, 2009) and WWTPs outfalls (Arvaniti and Stasinakis, 2015).

It is also worth noting that more pesticides and metabolites were detected from February to June (spring and summer) compared to samples collected in October and December (fall and winter seasons) (Fig. 4). This influx of contaminants during spring and summer seasons can be attributed to the time of year that many of these chemicals are applied on the landscape (McClure et al., 2020). During this season, there can be winter snowmelt and rain event in this region, which contribute to pulses in contaminant concentrations and fluxes (Kaushal et al., 2014). In addition, sampling occurred during some record wet years, where precipitation events were important in influencing contaminant concentrations.

Knowledge of the relationships between contaminant occurrence and agricultural land use in a watershed and stream discharge can help inform the development and implementation of management efforts, such as BMPs. Watershed BMPs can be used to intercept and dampen contaminant pulses in human-impacted landscapes where contaminants are efficiently transported to surface waters by engineered drainage systems (Kaushal and Belt, 2012; Kaushal et al., 2014). In addition, these BMPs may have some potential for co-managing complex mixtures and/or ‘chemical cocktails’ of different contaminants with similarities in fate and transport, or shared hydrologic flowpaths (Kaushal et al., 2018, 2020). Previous research has demonstrated the potential for additive, synergistic, or antagonistic effects of chemical mixtures on aquatic organisms (Kortenkamp, 2007; Lopez-Doval et al., 2019); thus, a comprehensive information on the spatiotemporal occurrence of micropollutants is necessary to have an accurate assessment of their ecotoxicological risk.

3.4. Impact of BMPs and WWTPs on micropollutant transport in Potomac River

Best management practices are designed to mitigate the negative environmental consequences that come with conversion of natural land for agricultural or urban development. These practices are meant to reduce erosion, manage storm water runoff, control nutrient loading, and stabilize other aspects of the watershed. Impact of agricultural and urban BMPs were evaluated by comparing total concentration of the micropollutants in the streams with and without BMP (Fig. 5). The assumption here is that the difference between the pairs of the stream were only attributed to the installation of the BMPs thus only the micropollutant detected in paired streams were considered in this plot. Similarly, efficiencies of the WWTPs were also compared based on the concentration of micropollutant in the effluent and downstream samples (Fig. 5).

As shown in the Fig. 5, significant reductions in the total concentration of PPCPs (~70%), PFASs (~65%) and other industrial chemicals (~75%) were observed after the wastewater treatment processes. This shows that upgrade of wastewater facilities is an effective means to co-manage point sources of micropolllutants, N and organic C (Duan et al., 2021). The capabilities of primary treatment processes (i.e. sedimentation) in removing PPCPs are very limited because of the hydrophilic nature of most PPCPs (Luo et al., 2014). Thus, it is likely that this co-management occurs during the biological processes (secondary treatment) and nitrification/denitrification steps. Previous research has demonstrated that WWTP with nitrifying activated sludge results in enhanced biodegradation of recalcitrant pharmaceuticals (Batt et al., 2006). The activated sludge process remove micropollutants through adsorption, partial biotransformation, or complete biodegradation (McClellan and Halden, 2010; Jelic et al., 2011). In the nitrification/denitrification steps, ammonia is oxidized to nitrate by aerobic microbes (nitrification), and then nitrate is metabolized into nitrogen gas (N2) under anoxic conditions (Hu et al., 2012). Similarly, the significant decrease in the concentrations observed for the more persistent industrial chemicals, such as PFASs and OPFRs, after the treatment processes can be attributed to the hydrophobicity of these compounds enabling them to partition into the activated sludge during the secondary treatment processes (Sinclair and Kannan, 2006; Dauchy et al., 2017; Cristale et al., 2012; Kaushal et al., 2014). In addition, sampling occurred during some record wet years, where precipitation events were important in influencing contaminant concentrations.

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These results showed that WWTP upgrades with enhanced biological treatment processes could potentially improve efficiencies of WWTPs, and thus reduce point source inputs of micropollutants and nutrients to the Potomac River (Duan et al., 2021).

The BMPs at the urban site (Paint Branch) were designed to minimize the impact of urban development and water runoff from a high level of impervious surfaces by construction of environmental overlay zone (Muthukrishnan et al., 2005). In contrast, the Brier Ditch watershed has not implemented BMPs and is one of the most densely populated regions in the area with the fewest stormwater management controls. The reduction of ~65% in the total concentration of PPCPs and ~40% in the total concentration of the more persistent industrial chemicals observed (Fig. 5) in urban paired stream can be attributed to the constructed urban BMPs. This reduction in micropollutant concentrations is likely due to lesser urban discharge at the Paint Branch as compared to the densely-populated region of Brier Ditch. Additionally, there are several projects to manage stormwater runoff from developed areas, restore stream habitat, create wetlands, and restore the riparian zone in the Paint Branch (EOPB, 2020).

On the other hand, the BMPs at the agricultural site are focused on restricting livestock access to the tributary, and consisted of new fencing and stream crossings and the development of springs to eliminate in stream cattle watering. As a result, hormones and other micropollutant excreted by the livestock were not directly discharged into the stream. This is evident in the significant reduction of the total concentration of hormones (~100%) at the paired streams with BMP and without. Manure and eroded soil cannot also easily reach the stream with shrubs and trees growing in riparian zone making it possible for a co-reduction of micropollutant, N, and P inputs with BMPs installation (Duan et al., 2021).

4. Conclusions

Suspect screening analysis was performed on previously extracted samples that were analyzed using target analysis and were previously published (Duan et al., 2021) to inform us on what additional contaminants need to be included in the next monitoring cycle in future studies on water quality management. All of the compounds that were included in the in-house database were analyzed experimentally using both high pH and low pH methods for high accuracy and good sensitivity. Once the most frequently detected compounds are discovered from SSA, isotopically labeled analogues of these compounds can be purchased and be spiked into the samples prior to SPE. The use of the optimized SSA workflow allows for the reliable detection of important contaminants to include in target analysis and avoid the purchase of irrelevant and expensive isotopically-labeled surrogates without missing highly relevant contaminants. In conclusion, the optimized suspect screening workflow resulted in a detection of >100 micropollutants in the analysis of a subset of samples spanning agricultural non-point, urban non-point, and point WWTP locations in Potomac watershed.

Evaluation of the spatial occurrence of the micropollutants revealed that EDCs are primarily linked to agricultural areas/activities, PFASs and others industrial chemicals are linked to urban areas and WWTP point source, while PPCPs are mostly linked to WWTP. We also analyzed the impact of the BMPs in place and the WWTP upgrades on reducing concentrations or transport of these micropollutants in the Potomac watershed and our results suggest that there is potential to co-manage a diverse array (or chemical cocktails) of pollutants based on shared transport and transformation mechanisms in watersheds. More research is needed to determine the types of substrates used in stormwater management to attenuate groups of contaminants and also tracking shared sources and flow paths integrating environmental chemistry, geochemistry, and hydrology across engineering and management designs. This will require collaborative efforts identifying and quantifying the full spectrum of contaminants, their transport, and their transformation using interdisciplinary research.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wroa.2021.100088.

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