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Organic Micropollutants in New York Lakes: A Statewide Citizen Science Occurrence Study

Shiru Wang, Monica Matt, Bethany L. Murphy, MaryGail Perkins, David A. Matthews, Sharon D. Moran, and Teng Zeng*

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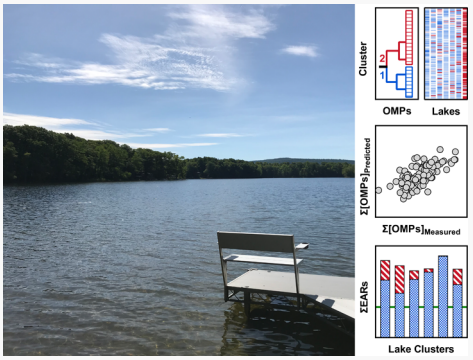
ABSTRACT: The widespread occurrence of organic micropollutants (OMPs) is a challenge for aquatic ecosystem management, and closing the gaps in risk assessment of OMPs requires a data-driven approach. One promising tool for increasing the spatiotemporal coverage of OMP data sets is through the active involvement of citizen volunteers to expand the scale of OMP monitoring. Working collaboratively with volunteers from the Citizens Statewide Lake Assessment Program (CSLAP), we conducted the first statewide study on OMP occurrence in surface waters of New York lakes. Samples collected by CSLAP volunteers were analyzed for OMPs by a suspect screening method based on mixed-mode solid-phase extraction and liquid chromatography-high resolution mass spectrometry. Sixty-five OMPs were confirmed and quantified in samples from 111 lakes across New York. Hierarchical clustering of OMP occurrence data revealed the relevance of 11 most frequently detected OMPs for classifying the contamination status of lakes. Partial least squares regression and multiple linear regression analyses prioritized three water quality parameters linked to agricultural and developed land uses (i.e., total dissolved nitrogen, specific conductance, and a wastewater-derived fluorescent organic matter component) as the best combination of predictors that partly explained the interlake variability in OMP occurrence. Lastly, the exposure-activity ratio approach identified the potential for biological effects associated with detected OMPs that warrant further biomonitoring studies. Overall, this work demonstrated the feasibility of incorporating citizen science approaches into the regional impact assessment of OMPs.



INTRODUCTION

Human-induced environmental changes have significantly altered ecosystem functions and services around the globe.[1−3] One of the well-recognized anthropogenic stressors on aquatic ecosystems is the ubiquitous presence of organic micropollutants (OMPs) that may trigger unforeseen ecological consequences at low exposure concentrations (e.g., ng/L−μg/L levels).[4−6] OMPs consist of a complex mixture of synthetic organic substances,[7−10] many of which are designed-bioactive chemicals,[9,11,12] as well as their transformation products (TPs).[13−16] Given the diverse sources and transport pathways of OMPs, broad-scope monitoring is essential for characterizing their occurrence patterns and ecological relevance but requires concerted efforts to achieve the desired spatiotemporal and analytical coverage.[6,17] To date, the U.S. Geological Survey (USGS) and U.S. Environmental Protection Agency (USEPA) have undertaken the majority of large-scale OMP occurrence studies in the U.S. with a primary focus on streams and groundwater. For example, a USGS-led nationwide reconnaissance first reported the widespread occurrence of pharmaceuticals, hormones, and other organic contaminants in streams surveyed across 30 states,[8] providing one of the earliest evidence for surface water contamination by OMPs in North America. Recently, the USGS and USEPA completed an expanded joint study that detailed the prevalence of over 700 organic contaminants in U.S. streams and associated bioactivities of concern, further highlighting the need for improved biomonitoring of chemical exposures.[9,18] Collectively, these and other investigations underscore the importance for continued research into the occurrence, fate, and effects of OMPs in aquatic ecosystems[10] and the necessity of augmenting professional-led efforts with coordinated public participation as an integral part of future OMP monitoring and mitigation efforts.[19]

Over the past two decades, citizen science-based water quality monitoring has gained increasing popularity worldwide (e.g., over 1500 active programs in the U.S.),[20,21] with emphasis on contaminants of public and environmental health concerns, such as agrochemicals,[22−24] lead,[25,26] fecal indicator

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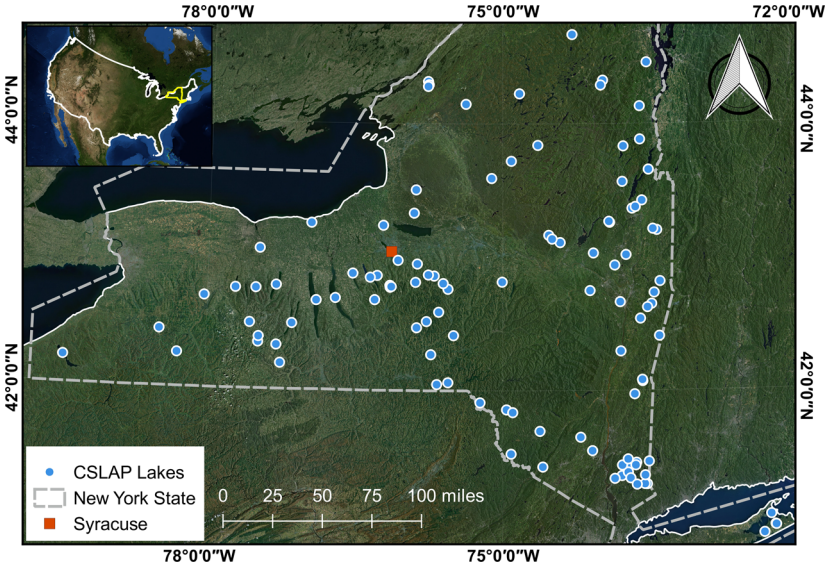

Figure 1. Map of CSLAP lakes participating in this study. Further details about the morphometry, watershed characteristics, and water quality status of lakes are summarized in Tables S1 and S2. Satellite Image Source: Esri, Maxar, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community.

bacteria,[27,28] and microplastics.[29−33] Harnessing citizen science would offer a cost-effective means to collect OMP data at scales or resolutions unattainable by individual investigators or research teams while providing an outreach mechanism to inform and involve the general public. However, the inclusion of citizen science in OMP research has been rare.[34,35] Historically, citizen science has been particularly attractive for professional scientists and government agencies in lake-rich states where citizen volunteers can provide support for local lake and watershed management practices and public outreach missions.[36,37] One notable example is the Citizens Statewide Lake Assessment Program (CSLAP) in New York State, which is among the longest-running water quality monitoring programs in the U.S.[38] Since its inception in 1985, CSLAP has engaged citizen volunteers from over 270 lake communities in water sample collection and on-site water quality measurements.[39,40] CSLAP also forms the basis for one of the most extensive surveillance platforms for harmful algal blooms in the U.S.[41] Given its established volunteer network and logistics support from participating lake associations, CSLAP represents a unique platform for integrating OMP surveillance with a statewide citizen science-based lake water quality monitoring program while promoting public awareness of OMPs.

In New York State, OMPs have been increasingly detected in streams, Great Lakes tributaries, and groundwater,[42−54] but comparatively little is known about the composition and concentrations of OMPs in lakes apart from those located in specific areas of concern.[55−57] In this work, we sought to engage an established network of CSLAP volunteers in a New York statewide OMP occurrence study focusing on lakes with lakefront communities. Our specific objectives of this study were (i) to conduct suspect screening and target quantification of OMPs in water samples collected by citizen volunteers from lakes across New York State, (ii) to prioritize predictors for the interlake variabilities in OMP occurrence using multivariate statistical analysis, and (iii) to perform a screening-level assessment of the potential for biological effects associated with OMPs using the exposure-activity ratio approach.

MATERIALS AND METHODS

Chemical sources and reagent preparation are described in the Supporting Information (SI).

Volunteer Participation and Field Sampling. CSLAP is coadministered by the New York State Department of Environmental Conservation (NYSDEC) and the New York State Federation of Lake Associations (NYSFOLA). Currently, 501 citizen volunteers actively participate in the CSLAP.[58] Volunteer recruitment and training for this study commenced in Spring 2018 following the protocol approved by the Syracuse University (SU) institutional review board. Volunteers were trained in water sample collection, storage, and shipping by experienced staff from NYSFOLA, NYSDEC, or the Upstate Freshwater Institute (UFI). In compliance with trace-level sampling protocols,[59] volunteers were instructed not to wear personal care products or topical medications on the sampling day. Step-by-step written protocols, precleaned sampling bottles, and chain of custody forms were provided to volunteers before sampling. To ensure sample integrity, NYSFOLA and NYSDEC staff conducted routine on-site quality control checks with volunteers. Over the 2018 and 2019 CSLAP sampling seasons (i.e., June to October), a total of 314 one-liter surface water grab samples were collected by 143 volunteers from 111 lakes (Figure 1) at the deepest basin of the lake or multiple designated CSLAP sampling sites on lakes with larger surface areas. Most of the participating lakes feature watersheds that are largely forested, while others have watersheds dominated by agriculture and residential and urban development. These lakes support a variety of uses, including drinking water supply, swimming, and fishing, but differ in water quality trends and trophic state. Lake morphometry and watershed characteristics (e.g., residence time, watershed-to-lake-area ratio, percent watershed land usage) and lake classifications are summarized in the SI (Tables S1 and S2). For each round of sampling, one trip blank (prepared by ultrapure water) was included with lake water samples to assess any contamination from sample handling, transport, and storage. Quality control samples were also collected by NYSDEC staff and submitted with the volunteer-collected

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samples to compare analytical results for the regular CSLAP water quality indicators, which were further reviewed by NYSDEC staff for consistency. Samples for OMP analysis were frozen and shipped overnight with the routine CSLAP samples to UFI and SU.

Sample Analysis. Upon return to the laboratory, lake water samples (duplicate; 500 mL each) were spiked with a mixture of isotope-labeled internal standards (200 ng/L; Table S6), vacuum filtered through 0.7-μm glass fiber filters, and extracted by mixed-mode solid-phase extraction (SPE)[60,61] for analysis by liquid chromatography-high resolution mass spectrometry (LC-HRMS). Suspect screening[57,62,63] was performed to expand the analytical coverage with a focus on OMPs of relevance to U.S. surface waters. To this end, a custom suspect database containing compound-specific information for pharmaceuticals, pesticides, personal care, household and industrial chemicals, and their TPs was compiled from the following sources: the U.S. Food and Drug Administration's approved human and veterinary drug product listings,[64,65] the USEPA's pesticide chemical search database,[66] the U.S. Drug Enforcement Administration's drugs of abuse resource guide,[67] the Personal Care Products Council's cosmetic ingredient listing,[68] and peer-reviewed literature. Compounds with one or more of the following properties were excluded from the suspect list: (1) have an exact mass less than 100 Da or greater than 1000 Da, (2) have a predicted Log*P* value[69,70] of greater than 6.0 or less than −2.0, (3) contain only carbon and hydrogen atoms but no heteroatoms, (4) contain metallic or metalloidic elements, or (5) lack commercially available reference standards from major chemical vendors. The final compound database for suspect screening contained the name, CAS number, molecular formula, and category of 3308 compounds (Table S15). Suspect screening was conducted using *TraceFinder 4.1* (Thermo Scientific) by interrogating the exact masses and isotopic patterns of peaks (i.e., mass spectral features) picked from the full scan mass spectra against those of compounds in the suspect database.[57] Mass spectral database searching was performed with data-dependent tandem mass spectra of picked peaks via *mzCloud*[71] using a node-based workflow in *Compound Discoverer 3.1* (Thermo Scientific) or via *MassBank*[72] using the *RMassBank*[73] package in *R 3.5.3*. Suspect compounds with an *mzCloud* match factor of >30 and/or an *MassBank* score of >0.3 were confirmed or rejected by comparing their chromatographic retention times and tandem mass spectra to those of authentic reference standards. Out of the 156 suspect compounds (Table S12) retained by SPE, 67 were confirmed and quantified using corresponding reference standards. Trip blanks (duplicate; 500 mL each) were processed and analyzed with each batch of samples to identify potential procedural contamination or analytical interferences. Further details on suspect screening workflow development and SPE-LC-HRMS method performance and validation are given in the SI (Section S4). Lake water samples were also analyzed for water quality parameters (i.e., pH, specific conductance, chlorophyll *a*, nitrate-nitrite nitrogen, ammonia nitrogen, total dissolved nitrogen, total nitrogen, and chloride) as well as absorbance and fluorescence properties as detailed in the SI (Section S3).

Data Analysis. For each lake, the mean cumulative concentrations of OMPs ($\sum$[OMPs]) and cumulative detections of OMPs ($\sum OMPs_{(n)}$) were calculated by averaging data from samples taken from multiple sites or on different dates to avoid overrepresentation. Spearman's correlation analysis, linear regression analysis, nonparametric *t* tests, and analysis of variance were performed using *GraphPad Prism 8.4* to explore bivariate correlations and data distributions. Hierarchical cluster analysis was performed on binary OMP occurrence or *z*-score standardized OMP concentration data[48] using the *factoextra*[74] and *pheatmap*[75] packages in *R*. Partial least squares regression (PLSR) was performed using *SIMCA 16.0* (Umetrics) to explore the predictive power of lake-watershed attributes and physicochemical properties of water samples for the overall OMP occurrence in lakes. Briefly, the PLSR model extracted orthogonal principal components from the data set by cross-validation to achieve an optimal balance between the explained variation in the response (i.e., ($\sum$[OMPs] and $\sum OMPs_{(n)}$) and the predictive residual sum of squares.[76] Permutation tests were run to validate the model by randomized reordering the response variable 50 times and retesting the model on every new data set.[77] Each predictor variable was ranked for its relevance in explaining the response variables by the variable importance in the projection (VIP) score, with a VIP score of >1.0 being the most influential.[78] Multiple linear regression (MLR) was performed by stepwise variable selection to identify a subset of PLSR-prioritized variables that could best explain the interlake variability in $\sum$[OMPs] with minimal multicollinearity based on their variable inflation factors (i.e., < 2).[79] Performance statistics of the PLSR and MLR models are summarized in the SI (Table S14). To assess the potential for OMP biological effects, exposure-activity ratios (EARs) were calculated using the *toxEval* package[80] in *R*. For each lake, the cumulative EARs ($\sum$EARs) were determined for the mean exposure scenario assuming additivity of effects as described in previous studies.[18,52,53,81−83] Further details on EAR calculations are provided in the SI (Section S6).

RESULTS AND DISCUSSION

Occurrence Patterns of OMPs. Overall, suspect screening confirmed the presence of 67 OMPs in surface water samples from 111 lakes across New York. Two active ingredients of insect repellents (i.e., *N,N*-diethyl-3-methylbenzamide (DEET) and icaridin), although not detected in trip blanks, were excluded from further data analysis because personal communications with volunteers indicated that usage of bug spray or mosquito repellent products could not be completely avoided under challenging field conditions (e.g., during the black fly season). Of the remaining 65 OMPs, 35 could be operationally classified as pharmaceuticals and their TPs, 20 as pesticides and their TPs, and 10 as personal care, household and industrial chemicals (Table S13). With a few exceptions, OMPs occurred at concentrations within the range of 10−1000 ng/L (Figure S8), including several that have rarely been reported for New York surface waters (e.g., protriptyline, norepinephrine, fluridone, 2-hydroxybenzothiazole). $\sum$[OMPs] ranged from 90 to 5400 ng/L among these lakes with a median concentration of 770 ng/L, while $\sum OMPs_{(n)}$ ranged from 3 to 36 compounds per lake with a median count of 9 (Figures S9 and S10). Similar to prior findings,[9,48] $\sum$[OMPs] correlated with $\sum OMPs_{(n)}$ (Spearman ρ = 0.656−0.739; p < 0.0001; Figure S11). The mean of $\sum$[OMPs] did not vary significantly across different classes of lakes (defined by general protection and pollution management status) according to Tukey's multiple comparison tests (Figure S12).

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Hierarchical cluster analysis based on the binary OMP occurrence data of 314 samples grouped OMPs into two major clusters (Figure 2a). Cluster 1 contains 11 OMPs that were most frequently detected in the samples, indicating consistency in watershed loadings and in-lake persistence of these OMPs. Cluster 2 contains OMPs derived from agricultural, wastewater, or mixed sources with limited detections and highly variable concentration profiles. Most of the cluster 1 OMPs also overlapped with those repeatedly detected in other surface water systems. Benzothiazole, a high production volume manufacturing additive, occurred in 100% of the lakes (93% of the samples) with the highest median concentration (307 ng/L) among all detected OMPs. Benzothiazole and its derivatives (e.g., 2-hydroxybenzothiazole; detected in 13% of the lakes/samples) are used in a variety of consumer and industrial products such as corrosion inhibitors in antifreeze and cooling liquids and vulcanization accelerators in rubber material.[84] Consistent with previous findings,[84−87] the ubiquitous presence of benzothiazole likely reflects sustained inputs from surface runoff generated in the lake watershed (e.g., those of tire abrasion from roads or winterization of lakefront camps and vehicles). Atrazine, metolachlor, and their TPs (i.e., atrazine-2-hydroxy, atrazine-desethyl, metolachlor oxanilic acid, and metolachlor ethanesulfonic acid) also occurred at relatively high frequencies (in 10−100% of the lakes and 17−96% of the samples), providing further evidence to their near-ubiquitous presence in New York streams and rivers.[42,43,48,49] Atrazine and metolachlor are two of the most heavily used agricultural herbicides in the U.S.,[88] but both herbicides are also applied on urban landscapes,[89] suggesting that multiple sources and transport mechanisms might have collectively contributed to the co-occurrence of these herbicides and related TPs. Two wastewater tracer compounds,[90,91] caffeine (a stimulant) and sucralose (an artificial sweetener), occurred in 62 and 43% of the lakes (38 and 50% of the samples, respectively) with a range of caffeine-to-sucralose ratio from 0.014 to 3.92, pointing to the inputs of untreated and/or treated wastewater into some lakes. Paraxanthine, a major TP of caffeine,[92] also occurred in 29% of the lakes with quantifiable caffeine. Other frequently detected OMPs included 2,4-D (herbicide; 48% of the lakes and 37% of the samples), which has high agricultural and nonagricultural uses, as well as protriptyline (antidepressant; 61% of the lakes and 28% of the samples) that is most likely of wastewater origin. Protriptyline is believed to be reported for the first time in lake waters as this compound was rarely targeted in previous occurrence studies[93] and its environmental fate and transport remain poorly defined.[94] With one notable exception, the cumulative concentrations of cluster 1 OMPs showed a strong linear correlation (R^2 = 0.970, p < 0.0001) with ∑[OMPs] with a slope of 1.05 ± 0.02 (Figure 2b), suggesting the usefulness of this compound mixture as an indicator for overall levels of OMPs in the participating lakes. Closer examination of the outlier revealed that its deviation from the linear relationship was driven by the exceptionally high concentration of fluridone (i.e., 3900 ± 540 ng/L). Fluridone is a systemic herbicide applied to control invasive submerged aquatic vegetation such as *Hydrilla verticillata* and *Myriophyllum spicatum* in New York lakes,[95] so the elevated concentration of fluridone in this outlier lake likely resulted from direct impact of such applications. On average, the y-intercept of the linear regression line was 80 ± 23 ng/L, which provided a semiquantitative estimate for the cumulative concentrations of cluster 2 OMPs (i.e., 115 ± 190 ng/L) within the defined chemical space (i.e., OMPs amenable to SPE-LC-HRMS).

Further hierarchical cluster analysis based on the z-score standardized data of cluster 1 OMPs grouped 111 lakes into six clusters (Figure 3). Cluster A contains lakes that were characterized by moderate concentrations of benzothiazole, 2,4-D, atrazine (including its two TPs), and metolachlor (including its two TPs). Cluster B contains over 50% of the lakes that were mainly characterized by high concentrations of

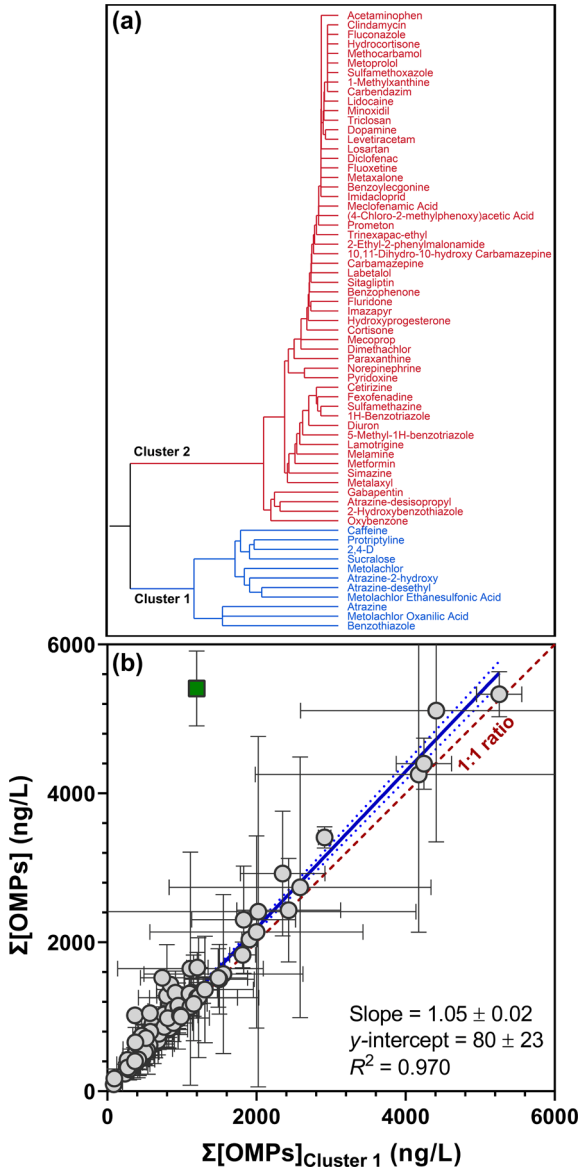

Figure 2. Hierarchical clustering of OMPs by the binary OMP occurrence data (i.e., presence or absence) in lake water samples (n = 314): (a) Dendrogram of OMP clusters. Cluster 1 (blue, bottom) contains 11 OMPs that were most frequently detected in the samples. Cluster 2 (red, top) contains the remaining 54 OMPs. (b) Correlation between the cumulative concentration of OMPs (∑[OMPs]) and the cumulative concentration of cluster 1 OMPs ($\sum[\text{OMPs}]_{\text{Cluster 1}}$) in lakes ($n$ = 111). The green square symbol represents the outlier. The blue solid line represents the linear regression line. The light blue dotted lines represent the 95% confidence intervals of the linear regression line. The red dashed line represents the 1:1 ratio. Error bars represent the standard deviations from duplicate measurements.

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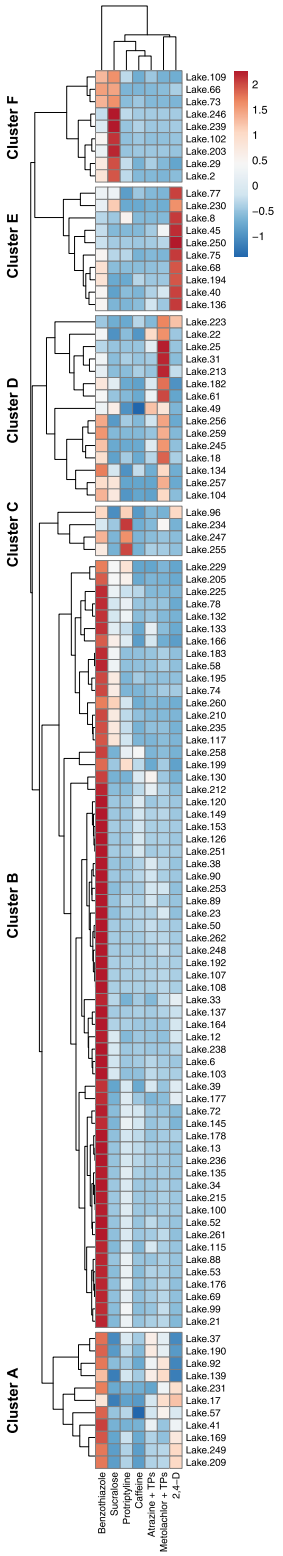

Figure 3. Hierarchical clustering of CSLAP lakes (n = 111) by z-score normalized concentration profiles of cluster 1 OMPs. Heatmap of lakes are labeled with CSLAP IDs (row) and cluster 1 OMPs (column). Lakes are grouped into six clusters (i.e., cluster A, B, C, D, E, and F, respectively). "Atrazine + TPs" represents the summed concentration of atrazine, atrazine-2-hydroxy, and atrazine-desethyl. "Metolachlor + TPs" represents the summed concentration of metolachlor, metolachlor oxanilic acid, and metolachlor ethanesulfonic acid. The color scale (red to blue) indicates the magnitude of normalized OMP concentrations.

benzothiazole but comparatively low concentrations of other cluster 1 OMPs. Compared to clusters A and B, clusters C, D, E, and F contain lakes that were characterized by lower concentrations of benzothiazole but elevated concentrations of protriptyline, metolachlor (and its two TPs), 2,4-D, or sucralose, respectively. Clusters A, D, and E lakes also feature a higher fraction of agricultural land use in their contributing watersheds than cluster B, C, and F lakes (Mann−Whitney U test $p < 0.0001$), which offers a possible explanation for the overall higher concentrations of pesticides in these lakes. Indeed, the cumulative concentrations of 2,4-D, atrazine, and metolachlor showed a positive correlation with the percent agricultural land usage (%Agricultural) across lakes ($\rho = 0.661$; $p < 0.0001$; Figure S13), although the amount of agricultural landscape alone was not necessarily sufficient for predicting the occurrence of specific pesticides. Moving west to east across the state (−79°26′ to −72°17′), the cumulative concentration of these three pesticides decreased ($\rho = -0.399$; $p < 0.0001$), which partly agreed with the farmland density gradient[96] and agricultural pesticide use profile[88] in New York. Clusters C and F lakes feature a higher fraction of urban/residential land use (%Urban/Residential) in their watersheds than other lakes (Mann−Whitney U test $p < 0.0001$). The cumulative concentrations of protriptyline, sucralose, and caffeine also showed a positive correlation with the percent urban/residential land usage ($\rho = 0.578$; $p < 0.0001$; Figure S13), suggesting urban and residential development as a likely source of these wastewater-associated OMPs. Furthermore, the cumulative concentrations of these three OMPs decreased north to south (44°40′ to 40°55′; $\rho = -0.331$; $p = 0.0007$) but increased west to east ($\rho = 0.235$; $p = 0.0182$), which matched the statewide trends in population density[97] and associated regional differences in the abundance of septic and centralized wastewater treatment systems.[98,99] Together, $\sum$[OMPs] correlated positively with the summed percent of agricultural and urban/residential land usage (%Agricultural+Urban/Residential; $\rho = 0.528$; $p < 0.0001$) but negatively with the percent of forested land usage (%Forested; $\rho = -0.459$; $p < 0.0001$), further confirming the association between OMP prevalence and influences of anthropogenic land use in the lake watershed. Of the remaining lake and watershed attributes, $\sum$[OMPs] also exhibited a positive, albeit weak, correlation with the watershed-to-lake-area ratio ($\rho = 0.273$; $p = 0.0039$) and a weak negative correlation with the lake residence time ($\rho = -0.197$; $p = 0.0403$), respectively. Hypothetically, higher watershed-to-lake-area ratios would likely contribute greater OMP loadings to the receiving lakes,[100] while longer residence times may favor abiotic and biotic transformations of OMPs in the lake water column.[101] Still, generalization of mechanistic drivers for OMP occurrence in these lakes requires focused work to quantify the watershed transport capacity and the extent of in-lake processing of OMPs.

Predictors of OMP Occurrence. Many multiregion,[9,53,83,102,103] single-watershed,[48,104−106] and fixed-station studies[17,50] have explored the utility of watershed land-use/land-cover metrics, physicochemical and optical properties of water samples, or their combinations for tracking the spatiotemporal occurrence patterns of OMPs in streams, rivers, and lake tributaries. However, less emphasis has so far been placed on OMPs in lakes. To further identify potential predictors of OMP occurrence, PLSR modeling was performed using $\sum$[OMPs] and $\sum$OMPs$_{(n)}$ as the response variables and a suite of 30 lake-watershed attributes, water quality

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parameters, and optical indices as the predictor variables. Overall, the PLSR model extracted three predictive components with moderate predictive ability and low-background correlations (Table S14). The strength of explained variation and the goodness of prediction for ∑[OMPs] were slightly lower than that of $\sum OMPs_{(n)}$, but both ∑[OMPs] and $\sum OMPs_{(n)}$ clustered near highly influential predictors along the first component axis with limited separation on the second component axis (Figure 4a). On the basis of the VIP scores, the predictors with the most explanatory power (i.e., those with a VIP score of >1.0) for OMP occurrence followed the order of total dissolved nitrogen (TDN) > specific conductance > total nitrogen > nitrate-nitrite nitrogen > freshness index (β:α) > %Agricultural > %Forested > %Urban/Residential > fluorescence index (FI) > the maximum intensity of fluorescent component 5 (C5) > chloride (Figure 4b). Here, C5 was extracted by deconvoluting the excitation−emission matrices of lake water samples with parallel factor analysis[107] from a split-half validated 5-component model (Figures S1−S4). C5 corresponds to the protein-like fluorescent component[78] associated with wastewater-derived organic matter.[108,109] Several of these predictor variables (apart from land use patterns discussed above) have been proposed as surrogates for inferring OMP contamination status in surface waters. For example, several studies have identified positive correlations between the concentrations of OMPs and conductivity (or the concentrations of major inorganic solutes such as chloride),[53,110,111] fluorescence-based indices,[112,113] or nitrogen species (e.g., nitrate)[44,46] in aquatic ecosystems. Other variables less frequently reported to covary with OMPs, such as β:α and FI, also emerged as relevant predictors for OMP occurrence largely due to their covariation with watershed land use patterns. For instance, previous work has shown the increasing export of fresh microbially produced organic matter (measured by β:α and FI) from watersheds along a land use gradient of increasing agricultural coverage.[114] Indeed, both β:α and FI correlated positively with % Agricultural across the watersheds of participating lakes (ρ = 0.471−0.489; $p < 0.0001$).

Considering the multicollinearity among the 11 PLSR-prioritized variables, stepwise MLR modeling was further performed using these predictors to produce the most parsimonious model accounting for the variation in ∑[OMPs]. The final MLR model identified C5, specific conductance, and TDN as the best combination of variables that explained 45.8% of the variation in ∑[OMPs] (Figure 4c). Performance of this MLR model for ∑[OMPs] was less satisfactory compared to that of models developed by previous studies using high-resolution spatiotemporal profiling of OMPs and environmental covariates in individual watersheds.[50,115] Other process-based metrics (e.g., source dynamics, hydrological transport, or in-lake processing) not considered in this study likely drove compound-specific differences in the fate and transport at more localized scales and ultimately contributed to the inhomogeneous occurrence patterns of ∑[OMPs]. Regardless, the PLSR and MLR modeling provided initial insights into predictors of OMP occurrence in lakes across a broad spatial scale by highlighting the connections between the interlake variability in ∑[OMPs] and wastewater influence, agricultural land use, and watershed runoff.

Potential for OMP Biological Effects. Given the limited availability of water quality benchmarks for OMPs detected in

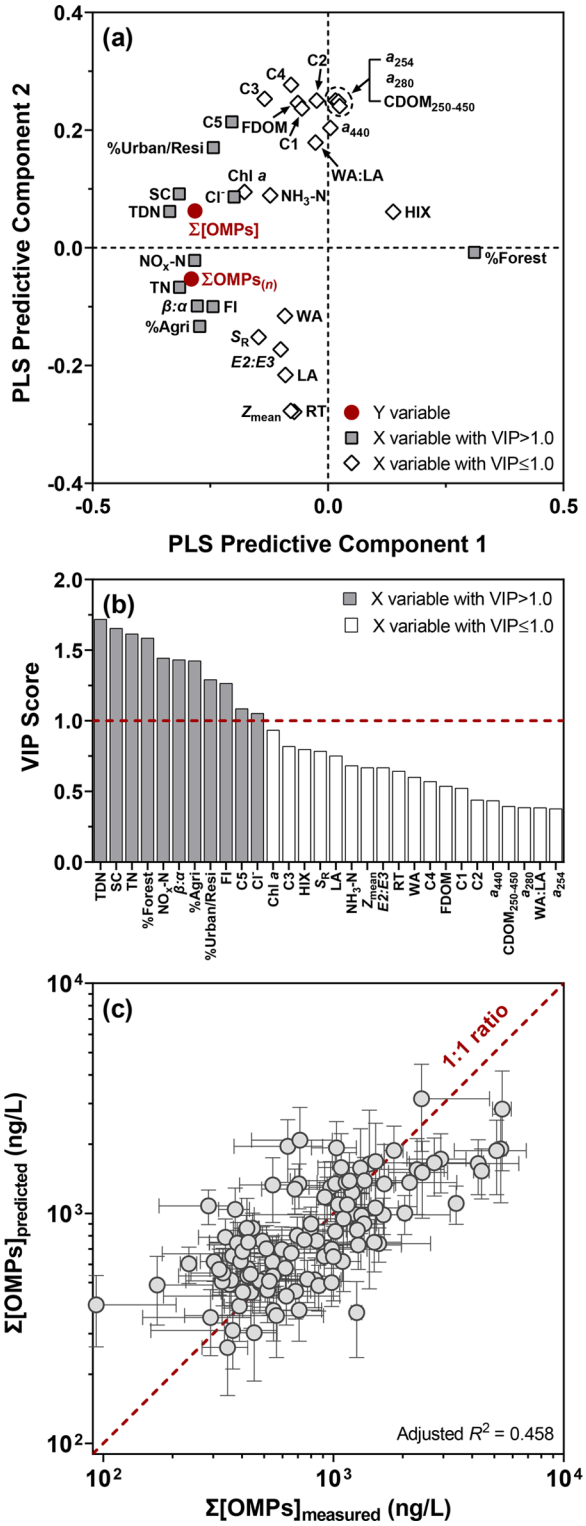

Figure 4. Partial least squares regression (PLSR) and multiple linear regression (MLR) modeling of OMP occurrence data in the lakes (n = 111): (a) Loading scatter plot of PLSR analysis where Y variable (∑[OMPs] or ($\sum OMPs_{(n)}$) is the response variable, X variable is the predictor variable, and VIP is the variable influence on projection. On the plot, ∑[OMPs] represents the mean cumulative concentration of OMPs (ng/L) for each lake, $\sum OMPs_{(n)}$ represents the mean cumulative detection of OMPs for each lake, "%Agri" represents the percent of agricultural land usage in the lake watershed, "%Urban/Resi" represents the percent of urban/residential land usage in the lake watershed, "%Forest" represents the percent of forested land

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Figure 4. continued

usage in the lake watershed, "LA" represents the lake surface area (ha), "Z_{mean}" represents the lake mean depth (m), "RT" represents the lake residence time (year), "WA" represents the lake watershed (ha), "WA:LA" represents the watershed-to-lake-area ratio, "SC" represents specific conductance (μS/cm), "NO_x-N" represents the nitrate-nitrite nitrogen concentration (μgN/L), "NH_3-N" represents the ammonia nitrogen concentration (μgN/L), "TDN" represents the total dissolved nitrogen concentration (μgN/L), "TN" represents the total nitrogen concentration (μgN/L), "Chl *a*" represents the concentration of chlorophyll *a* (μg/L), "Cl^-" represents the chloride concentration (mg/L), "a_{254}" represents the Napierian absorption coefficient at 254 nm (m^{-1}), "a_{280}" represents the Napierian absorption coefficient at 280 nm (m^{-1}), "a_{440}" represents the Napierian absorption coefficient at 440 nm (m^{-1}), "*E2:E3*" represents the ratio of absorption coefficients at 250 and 365 nm, "S_R" represents the ratio of spectral slope coefficient $S_{275-295}$ to $S_{290-350}$, "$CDOM_{250-450}$" represents the integrated absorption of chromophoric dissolved organic matter (DOM) from 250 to 450 nm (m^{-1}), "FI" represents fluorescence index, "HIX" represents humification index, "β:α" represents freshness index, "FDOM" represents the integrated volumetric fluorescence intensity of fluorescent DOM (R.U.; water Raman unit), "C1" represents the maximum intensity of fluorescent component 1 (R.U.), "C2" represents the maximum intensity of fluorescent component 2 (R.U.), C3 represents the maximum intensity of fluorescent component 3 (R.U.), C4 represents the maximum intensity of fluorescent component 4 (R.U.), and C5 represents the maximum intensity of fluorescent component 5 (R.U.). (b) VIP plot of predictor variables where the red dashed line represents the VIP score threshold of 1.0 (*X* variables with a VIP score of >1.0 were most important for the model performance). (c) Cross plot of measured ∑[OMPs] (with the subscript "measured") versus ∑[OMPs] (with the subscript "predicted") predicted by $\log_{10}(\sum[OMPs]) = 0.4312(\pm 0.1150) \times \log_{10}(C5) + 0.3121(\pm 0.0715) \times \log_{10}(\text{specific conductance}) + 0.4696(\pm 0.1287) \times \log_{10}(\text{total dissolved nitrogen}) + 1.115(\pm 0.3396)$ where ∑[OMPs] is in the unit of ng/L, C5 is in the unit of water Raman unit (R.U.), specific conductance is in the unit of μS/cm, and total dissolved nitrogen is in the unit of μgN/L. Error bars indicate the standard deviation of measured ∑[OMPs] or the 95% confidence interval of predicted ∑[OMPs]. The red dashed line represents the 1:1 ratio. Note that data matrices were log-transformed, centered, and scaled to unit variance prior to PLSR and MLR analysis when applicable. Performance statistics of the PLSR and MLR models are summarized in Table S14.

this study,[116] the EAR approach was implemented as a screening tool to assess the potential for OMP biological effects.[81] Fifty-seven of the detected OMPs (87%; including their free and salt forms[81]) had matches in the ToxCast and Tox21 high-throughput screening database at the time of access,[117−119] but only 46 (71%) were included for the final EAR calculations after removal of unreliable exposure-response data with data quality flags (Section S6).

Under mean exposure conditions, 19 OMPs showed one or more EARs above the conservative effects-screening threshold of 0.001 (Figure S14),[52] although a threshold exceedance does not directly translate into ecologically relevant adverse effects on aquatic species.[82,83,120−122] Four cluster 1 OMPs (i.e., metolachlor, caffeine, 2,4-D, and atrazine) had the greatest numbers of EAR threshold exceedances (i.e., 51, 39, 37, and 21 out of 111 lakes, respectively), while two cluster 2 OMPs (i.e., hydroxyprogesterone and hydrocortisone) exhibited the highest EARs (i.e., 0.104 and 0.093, respectively) among OMPs. On average, ∑EARs for 2,4-D, metolachlor, atrazine, and caffeine and other bioactive cluster 1 OMPs (i.e., benzothiazole, protriptyline, metolachlor ethanesulfonic acid, and atrazine-desethyl) accounted for 46% and 16%, respectively, of ∑EARs for all OMPs. Cluster 2 OMPs, while detected with lower frequencies, collectively contributed to 38% of ∑EARs for all detected OMPs, suggesting their importance for prioritization of biological effects. Of the 111 lakes, 88 (79%) had one or more OMPs with individual EARs greater than 0.001, 98 (88%) had ∑EARs greater than 0.001, and 5 had ∑EARs greater than 0.1 under mean exposure conditions (Figure S15), with the top contributing OMPs to elevated ∑EARs being hydroxyprogesterone and 2,4-D. On average, the mean of ∑EARs for the six lake clusters were not statistically different from each other based on Tukey's multiple comparison tests; however, the major fraction of ∑EARs for cluster C, D, and E lakes was attributable to cluster 1 OMPs (i.e., 54−96%), whereas ∑EARs for cluster A, B, and F lakes (i.e., 69−87%) were mainly driven by cluster 2 OMPs (Figure 5).

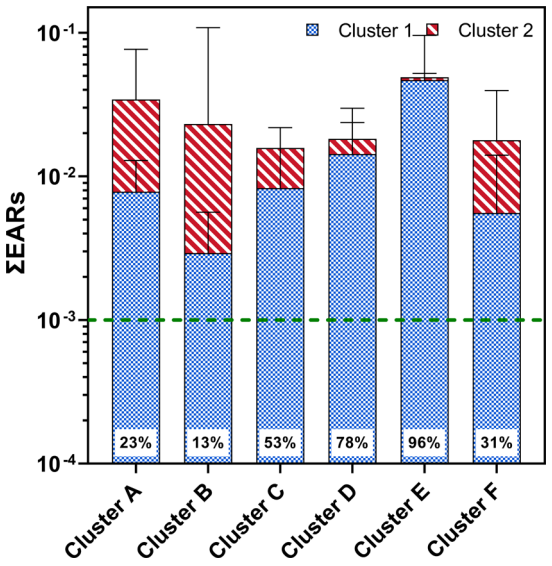

Figure 5. Cumulative exposure-activity ratios (∑EARs) for OMPs in six clusters of lakes (i.e., cluster A, B, C, D, E, or F) under mean exposure conditions. Error bars indicate the standard deviation of ∑EARs for a given cluster of OMPs (i.e., cluster 1 or 2) within a cluster of lakes. The green dashed line represents the effects-screening threshold of 0.001. The bottom percentage within each column indicates the average fractional contribution of ∑EARs for cluster 1 OMPs to ∑EARs for all detected OMPs in a given cluster of lakes.

Consistent with the patterns observed for ∑[OMPs], ∑EARs also showed positive correlations with C5, specific conductance, and TDN (ρ = 0.278−0.465; p < 0.0001−0.0032) as well as the sum of %Agricultural and %Urban/Residential (ρ = 0.447; p < 0.0001; Figure S16), supporting the relevance of these metrics for characterizing the potential impacts of OMPs on lake ecosystems. Like previous bioactivity profiling of river and stream samples,[81,82] most lake water samples had higher incidence of threshold exceedances in nuclear receptor and DNA binding target families (Figure S17) under the current EAR framework, which may serve to inform hypothesis formulation for subsequent evaluation of specific linkages between apical adverse outcomes and OMP exposures.[52] Taken together, the EAR outputs suggested some potential for *in vitro* biological effects associated with

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detected OMPs in the participating lakes; nevertheless, it does not address species-specific sensitivities, the toxic mode of action of detected OMPs, or exposures to untargeted or unknown OMPs not amenable to SPE-LC-HRMS.[81] Thus, translating compound-based EAR predictions to risk assessment bears high uncertainties, and concerted biomonitoring studies will be required to diagnose drivers of ecologically relevant effects. Still, the EAR approach serves as a comparative screening tool to place OMP occurrence data in a broader context.

Environmental Implications. To the best of our knowledge, this work represents the first study that incorporates citizen science approaches into a statewide investigation of OMP occurrence in surface waters. Leveraging existing citizen science sampling efforts via CSLAP, our study completed a broad-scale characterization of OMP occurrence patterns and associated biological effects potential in New York lakes with diverse watershed land use characteristics and water quality status. Our study demonstrated that LC-HRMS screening, multivariate statistical analysis, and EAR calculations together provide multiple lines of evidence for OMP stress in participating lakes. Our study also showed that CSLAP volunteers are a well-trained and motivated workforce who can assist with water sample collection for OMP analysis to guide the regional impact assessment of OMPs. More importantly, our commitment to public outreach ensured that the results and implications of this research are communicated to volunteers and their lake associations as well as other interested stakeholders in an understandable and scientifically accurate manner. For example, prior to the start of this study, each volunteer and lake association received an informational packet describing the project and providing background knowledge about OMPs. Once data collection was completed, they received a detailed written report that included lake-specific OMP concentration data and descriptive text highlighting potential watershed sources of OMPs along with their potential impacts on aquatic ecosystems. Individual lake results were also put into regional context using pie chart maps that depicted statewide OMP occurrence patterns and tables that summarized OMP concentration ranges observed in all participating lakes. Furthermore, multiple in-person presentations and webinars were organized during and after this study to address specific questions from community members regarding individual lake results and mitigation options for OMPs. A project website was also created to share information about this study with the general public.[123] Ultimately, results from this work may serve as a starting point from which systematic investigations can be designed to explore the source attribution, input dynamics, and ecosystem effects of OMPs in lakes. Furthermore, methods developed and lessons learned from this study are expected to inform development of a transferable and scalable framework that can be adopted by other citizen science initiatives to fill existing data gaps in OMP occurrence.

Our study also highlighted several challenges and opportunities for future considerations. One initial objective of this work was to engage citizen volunteers in on-site monitoring of an indicator OMP, atrazine, using commercially available paper test strips. However, the test strips were not sufficiently sensitive to detect low ng/L levels of atrazine in water samples,[24] which hindered a meaningful interpretation of volunteer-collected strip test results (Figure S18). Going forward, improving the sensitivity and robustness of test kits or chemosensors for a wider array of compounds would be essential for expanding the real-time monitoring capability for OMPs. Second, the relatively large sample volume required for SPE-LC-HRMS analysis (e.g., at least 1 L per sampling event), while useful for the purpose of suspect screening, restricted the number of samples that could be collected by volunteers with limited funds and resources. Complementing offline SPE with automated sample preconcentration[124,125] can circumvent the sample volume limitation if target screening of known OMPs is the primary focus, thereby reducing the sample collection and shipping costs while simultaneously increasing the sample throughput and data resolution. Lastly, grab samples analyzed in this study at best provided a snapshot of OMP occurrence in a subset of lakes in New York State. Future work incorporating passive sampling efforts (e.g., from offshore weather buoys)[126,127] would help fulfill the needs of time-integrative sampling but requires more challenging levels of citizen participation and commitment. With appropriate training methodology and timely knowledge sharing, we envision a growing role of citizen science in collaborative OMP research.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c04775.

Morphometry, watershed characteristics, and classifications of CSLAP lakes; summary of water quality analysis and PARAFAC modeling; optimization of suspect screening workflow; summary of LC-HRMS instrument parameters and data analysis; SPE-LC-HRMS method performance (e.g., SPE recoveries, matrix factors, limits of quantification) for suspect compounds; concentration profiles and summary statistics of OMPs; performance statistics of PLSR and MLR models; EAR calculations for individual OMPs and lakes; comparison of atrazine strip test and SPE-LC-HRMS analysis results; compound database for suspect screening (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Teng Zeng − *Department of Civil and Environmental Engineering, Syracuse University, Syracuse, New York 13244, United States;* orcid.org/0000-0002-0374-9549; Phone: +1-315-443-1099; Email: tezeng@syr.edu

Authors

Shiru Wang − *Department of Civil and Environmental Engineering, Syracuse University, Syracuse, New York 13244, United States;* orcid.org/0000-0003-2438-2341

Monica Matt − *Upstate Freshwater Institute, Syracuse, New York 13206, United States*

Bethany L. Murphy − *Department of Civil and Environmental Engineering, Syracuse University, Syracuse, New York 13244, United States*

MaryGail Perkins − *Upstate Freshwater Institute, Syracuse, New York 13206, United States*

David A. Matthews − *Upstate Freshwater Institute, Syracuse, New York 13206, United States*

Sharon D. Moran − *Department of Environmental Studies, SUNY College of Environmental Science and Forestry, Syracuse, New York 13210, United States*

Complete contact information is available at:

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Notes

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