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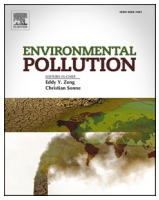

Trace organic contaminants in U.S. national park surface waters: Prevalence and ecological context☆

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ABSTRACT

Surface water samples were collected from 264 sites across 46 U.S national parks during the period of 2009–2019. The number of sites within each park ranged from 1 to 31 and the number of samples collected within each park ranged from 1 to 201. Samples were analyzed for up to 340 trace organic contaminants (TrOCs), including pharmaceuticals, personal care products, pesticides, and various contaminants indicative of anthropogenic influence (e.g., fragrances, surfactants, flame retardants). A total of 155 TrOCs was detected in at least one sample with concentrations ranging from the reporting level of 10 ng/L (multiple contaminants) to 11,900 ng/L (p-cresol). Except for bisphenol A, DEET, theobromine, and gabapentin, TrOCs were detected in <20% of samples. Despite the relatively low detection frequencies, when TrOCs were detected, concentrations were similar to those reported from other regional or national studies. We compared detected concentrations to bioactivity concentrations and water quality benchmarks, when available, to identify occurrences of elevated concentrations and to estimate the potential for biological effects to aquatic biota. Elevated concentrations of 27 TrOCs, mostly pesticides, were detected throughout the study. To gain insight regarding potential sources, we related watershed characteristics (e.g., land cover, presence of point sources) to the number of TrOCs detected at each site. We found that the presence of wastewater treatment plants and the proportion of the watershed classified as agricultural land were the most influential variables for describing the number of pharmaceuticals and the number of pesticides present, respectively. This study represents the largest-scale study characterizing the presence and magnitude of TrOCs in U.S. national park surface waters, to date. These data provide a baseline that can be used to inform future monitoring within the parks and to assess changes in water quality.

1. Introduction

Lands under the jurisdiction of the U.S. National Park Service (NPS) are among the least modified ecosystems in the nation. Despite their protected status, they remain vulnerable to contamination from anthropogenic activities. The NPS's Inventory and Monitoring (I&M) Division was created to initiate and maintain a long-term ecological monitoring program to assess conditions and trends of park natural resources (Fancy et al., 2009). Under this program, approximately 285 monitored park units with significant natural resources were grouped into 32 I&M networks (Fancy et al., 2009; Hansen et al., 2011) representing an area characterized by similar ecosystem and climate (Bailey, 1998), as well as geography and natural resource characteristics (https://www.nps.gov/im/networks.htm; accessed March 1, 2024).

To meet objectives of monitoring programs and assess status of resources, ecological indicators were established based on pressing issues and critical data needs within the parks (Fancy & Bennetts, 2012). Water is a key feature for most parks, and this is reflected in two of the indicator categories, which focus on water quality. Basic water quality data (e.g., temperature, pH) is collected in 211 (74%) of the monitored parks, of which, 30 parks (14%) also monitor organic and inorganic contaminants, and heavy metals (Fancy & Bennetts, 2012). The specific analytes in this latter category vary in scope and sample design based on program objectives and prescriptive needs of each park unit. However, none of the I&M networks currently conduct routine monitoring for trace organic contaminants (TrOCs), which was identified as an information

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gap in network water quality monitoring programs (Landewe, 2008).

There are several key reasons why TrOCs may be a concern. Although TrOCs are typically present at low concentrations (ng/L), they are ubiquitous in the aquatic environment (Richmond et al., 2017; J. Wilkinson et al., 2017), including in protected areas (Mollmann et al., 2022). Even low concentrations can result in adverse effects (Battaglin & Kolok, 2014). Many are known to bioaccumulate and biomagnify in aquatic ecosystems and to transfer to terrestrial ecosystems (Kraus, 2019; Previšić et al., 2021), with potential impacts to human health (Kusturica et al., 2022; Walters et al., 2016). In addition, TrOCs are generally detected in mixtures, which can have a greater toxic effect than that of individual TrOCs (Backhaus, 2014; Relyea, 2009). Exposure to TrOCs usually results in sub-lethal effects (Parrish et al., 2019), including those at the biochemical and molecular level (Daughton & Ternes, 1999). These subtle effects can manifest over time and remain undetected until major, irreversible changes have occurred, which may then be erroneously attributed to natural ecological progression (Daughton and Ternes, 1999).

The current study was established, in cooperation with the U.S. Environmental Protection Agency (USEPA), as a first step in filling the data gaps identified in I&M network monitoring programs by Landewe (2008). There are three objectives for the analysis presented herein. First, the prevalence of TrOCs was characterized predominantly in surface water resources of select parks and results were compared to other protected and unprotected areas to provide context. Second, the potential biological effects of each contaminant detected were characterized by comparing concentrations against available water quality benchmarks and ToxCast (U.S. Environmental Protection Agency USEPA, 2018), a program using high-throughput screening. Lastly, the relations between watershed characteristics and TrOC presence were assessed to identify important sources of TrOCs to park waters. Results from this study provide insight regarding potential TrOC impacts to protected aquatic ecosystems, specifically within U.S. park units.

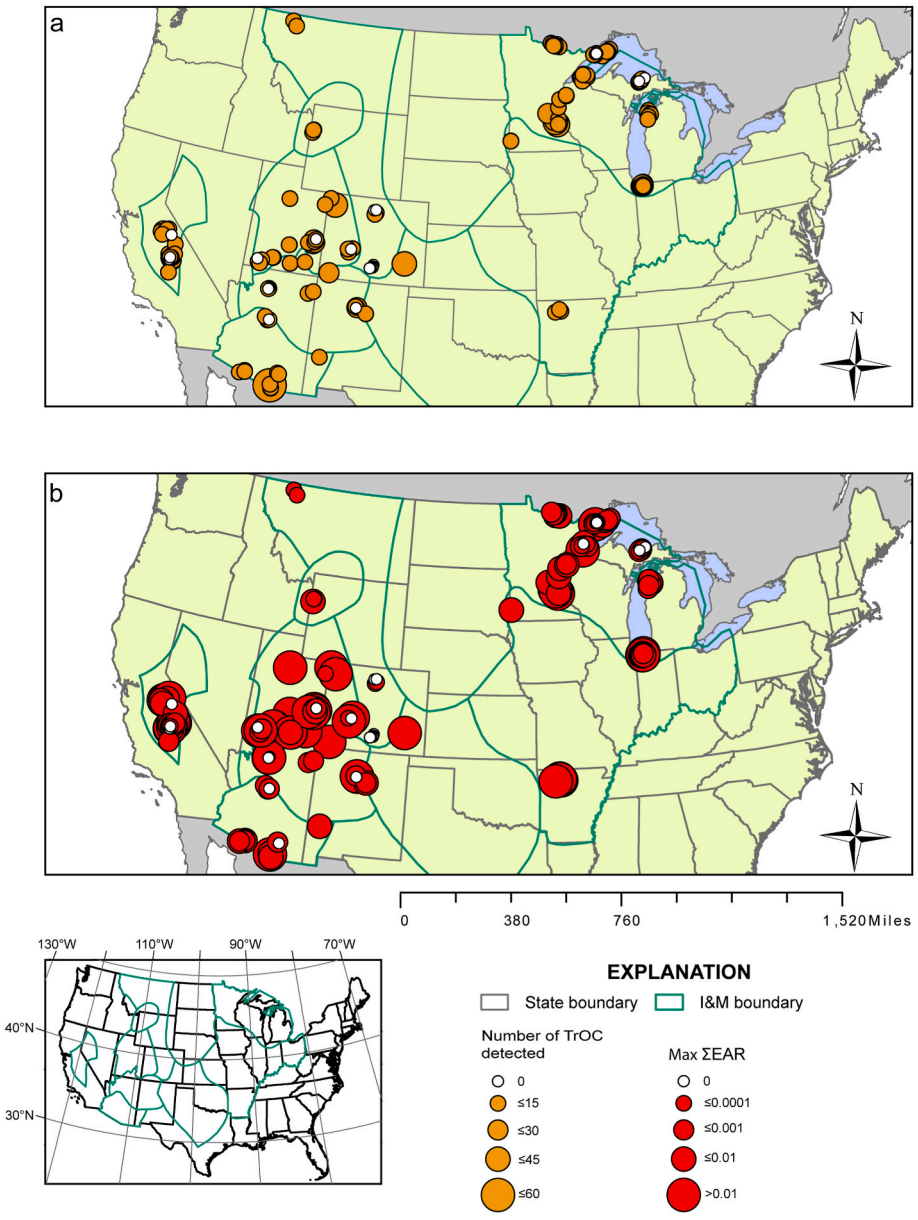

Fig. 1. Maps of (a) number of trace organic contaminants (TrOCs) detected and (b) maximum Exposure-Activity ratios (Max ∑EAR) determined from samples collected at surface water sites within select national park units and Inventory and Monitoring (I&M) networks of the continental United States.

2. Materials and methods

2.1. Study design

From 2009 to 2019, grab surface water samples were collected from 264 sites across 46 U.S. national park units (11% of all units) within 9 I&M networks (Fig. 1; Fig. S1; Table S1). Participation by parks was voluntary and varied throughout the years. The number of sites sampled per park ranged from 1 (several parks) to 31 (Sequoia National Park), with a mean of 6. Sample sites were selected based on 1) the need to establish baseline data, 2) the presence of upstream contaminant sources, 3) data from previous studies, 4) co-location with established monitoring sites, and 5) accessibility. Most sites were sampled ≥3 times, but several were sampled once or twice (Table S1). Several sites were sampled that are hydrologically disconnected from the land surface (e.g., lakes in caves, groundwater seeps) and represent groundwater sources. These data and a summary of the data are provided in supplemental information and Table S2 but are not discussed further. Samples were collected for analysis of up to 340 TrOCs including pharmaceuticals and personal care products (PPCPs), pesticides and transformation products (hereafter referred to as 'pesticides'), and various contaminants indicative of anthropogenic influence (i.e., wastewater indicators or WWIs) (Table S3).

2.2. Field methods

NPS staff collected water samples by lowering pre-cleaned, capped [polypropylene caps with polytetrafluoroethylene (PTFE) septa] amber glass bottles to a depth of at least 45 cm. The cap was removed at depth and the bottle was rinsed twice with sample water. After rinsing, the bottle was filled and capped underwater. Samples intended for WWI analysis were collected in 1L and 250 mL bottles, while 40 mL and 60 mL vials were used to collect samples for PPCP and pesticide analyses. During sample collection, care was taken to avoid disturbing the water column, if possible, and samples were collected upstream of the sampler (s) in lotic environments. Field staff wore clean latex gloves during sample collection and eliminated or reduced the use of personal care products such as insect repellants and lotions, when feasible. Samples were shipped overnight on wet ice to the analyzing laboratory.

2.3. Laboratory methods

Samples were analyzed by the USEPA's Region 8 Laboratory (Golden, Colorado, U.S.) using analytical methods focused on three general TrOC groups (Table S3): WWIs, PPCPs, and pesticides. The number of target analytes varied across years. There was overlap among methods; 13 TrOCs were included in two methods (e.g., bromacil was included in WWI and pesticide methods). WWIs were analyzed in unfiltered samples collected from a limited number of sites during 2010–2014 following a method modified from the USEPA's SW-486 Method 8270D (USEPA, 2014). WWIs were extracted using a methylene chloride liquid-liquid extraction followed by direct injection of extracts into a gas chromatography-mass spectrometer. The method comprised a group of various TrOCs, such as fragrances and phosphate-based flame retardants. Both PPCPs and pesticides were analyzed throughout the study. Analysis of filtered samples was conducted using methods modified from USEPA 1694 (USEPA, 2007a) and 8321B (USEPA, 2007b). Samples were filtered through PTFE filters and filtrate was directly injected into a liquid chromatography-mass spectrometer. Over the counter, prescription, and controlled substances were targeted by the PPCP method, whereas various herbicides, insecticides, and fungicides were targeted by the pesticide method. The presence of specific TrOCs was qualitatively confirmed when the secondary ion of a primary ion was observed at the same chromatographic retention time; the concentration was calculated from the peak area response of the primary ion.

2.4. Quality assurance (QA)/Quality control (QC)

Laboratory QA measures included calibration blank and check samples, blank samples, control spike samples, and surrogate standards. With some exceptions, results of laboratory QA samples fell within acceptable ranges, but when they did not meet acceptable criteria, the laboratory flagged associated results. Bisphenol A (BPA), tris(2-butoxyethyl) phosphate (TBEP), and tris(1,3-dichloro-2-propyl) phosphate (TDPP) were detected in ≥20% of laboratory blank samples. Overall mean percent recovery of surrogate standards was 91.3 ± 22.6%, with a minimum of 2.0% and maximum of 260% (Table S3).

Field-blank (n = 78) and field-replicate (n = 160) samples were collected to assess potential contamination and data variability, respectively, associated with sample collection and processing. Field-blank samples were collected during 42 sample events from 6 I&M networks, with a majority collected from parks within the Northern Colorado Plateau Network (NCPN) (Table S1). A total of 21 TrOCs were detected in 33 of the field-blank samples with concentrations ranging from 10 (methylparaben) to 930 ng/L (TBEP). DEET (N,N-Diethyl-meta-toluamide) was the most frequently detected TrOC in field-blank samples (n = 13), with concentrations ranging from 12 to 450 ng/L (Table S4). With respect to replicate sample pairs, when a TrOC was detected in one of the samples from the pair, it was detected in both for 74% of comparisons. In instances when a TrOC was detected in both samples of a replicate pair, we calculated the relative percent difference (RPD) between the concentrations by dividing the absolute difference in concentrations by the average concentration and multiplying by 100. The RPD ranged from 0 (several TrOCs) to 166 (simazine) and was <20 for 75% of comparisons (Table S5).

2.5. Data preparation

Data from this study are publicly available in the Water Quality Portal (https://www.waterqualitydata.us/) and can be downloaded by performing a query using '11NPSWRD_WQX-National Park Service Water Resources Division' as the 'Organization ID' and 'NPS_3P (STORET)' as the 'Project ID'. More data are available than what was used in this analysis because some TrOCs (e.g., PFAS) were analyzed in few samples (<5), at limited sites, and/or during only one year of the study.

Some TrOCs were included in multiple methods. For example, although atrazine was included in the PPCP and pesticide schedules, it was classified as a 'pesticide' for our analysis and thus results are only included in pesticide summaries (Table S3, 'Primary class'). As mentioned previously, up to 13 TrOCs were included in two different analytical methods. In these instances, only the result from the more sensitive method was retained for analysis.

In some instances, results were censored (i.e., changed to non-detect) based on QA/QC results. First, results flagged by the analyzing laboratory indicating potential contamination, unacceptable spike recovery, or that quality control was not met were censored. Second, environmental concentrations of BPA, TBEP, and TDPP corresponding to the timeframe during which detections in ≥20% of laboratory blank samples were censored. Lastly, environmental concentrations that were <10 times the maximum concentration detected in a field-blank sample were censored. This only applied to environmental samples collected during the same field trip in which the contaminated field-blank sample was collected. Using this method, 9 concentrations of 7 TrOCs were censored based on concentrations detected in field-blank samples; 2 concentrations of DEET and TDPP were censored.

2.6. Data analysis

Data were summarized to characterize the frequency with which TrOCs were detected and the range of concentrations and were compared against bioactivity information and benchmarks to estimate

potential concern for effects to aquatic biota.

2.6.1. Comparison to other studies

Ten studies that included a substantial number of the TrOCs analyzed in the current study, that had a regional focus, and for which data were readily available were selected for comparison. Of the selected studies, 6 focused on TrOCs in Great Lakes tributaries (Baldwin et al., 2016; Elliott et al., 2015, 2018; Elliott & Krall, 2022; Oliver et al., 2023; Pronschinske et al., 2022), 1 focused on wadeable U.S. streams (Bradley et al., 2017b), and 3 focused on streams within Great Smoky Mountains National Park (Bradley et al., 2021), Congaree National Park (Bradley et al., 2017a), and other protected streams under different management strategies (Bradley et al., 2020).

2.6.2. Estimating potential effects to aquatic biota

We compared environmental data to modeled bioactivity data, water-quality benchmarks published in the peer-reviewed literature, and/or USEPA's aquatic life criteria. These screening methods provide information for future monitoring and research by allowing scientists to compare relative potential concern for specific TrOCs or sites. We were able to estimate the potential for biological effects to aquatic biota for most of the detected contaminants. These are likely underestimates because analytical methods target a relatively small fraction of current-use TrOCs and benchmarks are not available for all of the study TrOCs.

Concentration data were screened against bioactivity information available in the USEPA ToxCast database (v. 3.2; USEPA, 2018) using toxEval (v. 1.2.0; DeCicco et al., 2023). The ToxCast database contains bioactivity information derived from medium- and high-throughput assays using cellular, biochemical, or whole-organism exposures for thousands of contaminants as they relate to effects on cells, receptors, etc. (Jeong et al., 2022). Target endpoints mostly represent vertebrate biological processes and provide estimates of the relative potency of environmental data. We followed methods described by others (e.g., Blackwell et al., 2017; Corsi et al., 2019). Briefly, an exposure activity ratio (EAR) was calculated by dividing environmental concentrations by TrOC-endpoint specific benchmarks (i.e., Activity Concentration at Cutoff, or ACC). The ACC is not dependent on chemical-specific activity, but is standardized to a response threshold and thus has been favored over other metrics (Blackwell et al., 2017). The closer the EAR is to one, the higher the likelihood for molecular-level effects to occur. For each TrOC detected within a sample, EAR values were summed across TrOC-endpoint matches ($\sum$EAR). Then the maximum $\sum$EAR was calculated for each site.

To obtain more comprehensive coverage, we compiled chronic benchmarks for 42 pesticides (USEPA, 2023) and pharmaceuticals (Pronschinske et al., 2022). Similar to the EAR approach, a Toxicity Quotient (TQ) was calculated by dividing environmental concentrations by benchmarks. We used thresholds of 0.001 and 0.1 for EAR and TQ, respectively, for screening purposes, in order to identify elevated concentrations that may pose concern for aquatic biota health (Corsi et al., 2019; Oliver et al., 2023). These thresholds were chosen to provide a conservative estimate of potential effects to account for uncertainties associated with the benchmarks and the fact that our data represent grab samples that capture one time point.

2.6.3. Influence of watershed characteristics

Site-specific watersheds were characterized by land cover, size, impervious surface, road density, railroad density, number of point sources and golf courses, and distance to the nearest point source and golf course (Table S8). Spatial data were obtained from publicly available sources including the National Land Cover Database (Dewitz, 2021), U.S. Census TIGER/Line geodatabases (U.S. Census Bureau, 2021), USEPA Permit Compliance System and Integrated Compliance Information System (USEPA, 2021), and Esri (ESRI, 2021). We assessed relations between watershed characteristics and the number of PPCPs and pesticides detected at each site using a conditional inference tree (CIT) method, a non-parametric, unbiased recursive partitioning procedure (Hothorn et al., 2006). CIT is a class of regression trees embedding tree-structure regressions into a well-defined theory of conditional inference procedures. This procedure uses significance tests to select input variables, explanatory variables, and thresholds that lead to discriminated ranges of the response variable. Leave-one-out cross validation (LOOCV) was used to quantify the CIT, in which, one result value from the dataset is taken out for each iteration to test and train the regression. We used the coefficient of determination (R^2) and normalized-root squared error (NRMSE) to assess the fit and accuracy of the analysis. For this analysis, a $R^2 \geq 0.50$ and a NRMSE $<10\%$ were deemed acceptable. Analyses were performed using the party package (v. 1.3–13; Hothorn et al., 2005) in R Studio (v. 4.2.3; R Core Team, 2023) with the minimum criterion for splitting trees set to 0.95 ($\alpha = 0.05$). The CIT plots were created using the partykit package (v. 1.2–20; Hothorn et al., 2011).

3. Results

A total of 1235 water samples were collected from 2009 to 2019 with 277 samples (69 sites) analyzed for WWIs (2010–2014), 1255 samples (261 sites) analyzed for pesticides, and 1158 samples (233 sites) analyzed for PPCPs. A total of 23% of samples were collected from the Great Lakes Network (Table S2), the largest representation of the networks. However, the greatest number of samples (201) collected within a park unit were from four sites within Buffalo National River. The average number of samples collected within each of the 46 sampled park units was 27 ± 33.

3.1. Contaminants in national park surface waters

Overall, TrOCs were detected infrequently. A total of 155 TrOCs were detected at least once with concentrations ranging from the reporting limit of 10 ng/L (multiple contaminants) to 11,900 ng/L (p-cresol) (Table S9). Except for a few TrOCs (e.g., camphor, p-cresol), concentrations ranged two orders of magnitude (Table S9). Detected TrOCs were 35 WWIs, 73 PPCPs, and 47 pesticides. Four TrOCs were detected in ≥20% of all samples: DEET (36%, insect repellant), theobromine (26%, caffeine metabolite/food alkaloid), BPA (22%, plastic additive), and gabapentin (20%, anticonvulsant).

3.1.1. WWIs

WWIs were characterized at 69 sites across 24 parks. All but 3 were detected in <10% of samples: BPA (22%), triclosan (14%, antimicrobial), and TDPP (12%, flame retardant). Several WWIs, including polycyclic aromatic hydrocarbons (PAHs) and octylphenols, were detected in only one sample, indicating relatively low presence in the environment. Detected concentrations ranged from 50 ng/L (several) to 11,900 ng/L (*p*-cresol). More WWIs were detected frequently (9 detected in 20% or more samples) at sites within Tumacácori National Historical Park (TUMA). However, the most WWIs detected within a park was 22 at Dinosaur National Monument (DINO); 10–14 were detected within several others.

3.1.2. PPCPs

PPCPs were characterized at 233 sites across 39 parks. A total of 7 were detected in ≥10% of samples including an antidiabetic (metformin), anticonvulsant (gabapentin), and several PPCPs reflecting lifestyle use and metabolites (e.g., caffeine, paraxanthine). Detected concentrations ranged from 10 ng/L (several) to 1080 ng/L (gabapentin). More PPCPs were detected at sites within TUMA (54), compared to other sampled parks. The next highest numbers detected were 16 at Bent's Old Fort National Historic Site (BEOL) and 15 at Mississippi National River and Recreation Area (MISS). Gabapentin, carbamazepine, and metformin were detected in 100% of all samples collected from BEOL, MISS, and TUMA.

3.1.3. Pesticides

Pesticides were characterized at 248 sites across 45 parks. Four were detected in ≥10% of all samples: DEET, 2,4-D (herbicide), metolachlor (herbicide), and atrazine (herbicide). Concentrations ranged from 10 ng/L (several pesticides) to 1370 ng/L (metolachlor ESA, herbicide degradant). Most of the parks in which pesticides (especially herbicides) were frequently detected (>75%) are in the Upper Midwestern United States. A total of 24 pesticides were detected at sites within Indiana Dunes National Park (INDU), the most detected within any park, while 17 were detected within MISS. DEET was the most widely detected pesticide, present in at least one sample from 35 (78%) of the sampled parks, followed by 2,4-D in 16 (35%) parks.

3.2. Comparison to other studies

A total of 210 TrOCs were in common between our study and others (Table S6); 93 were detected in other studies but not the current one. Generally, contaminants were detected in fewer samples from national parks. However, when detected, concentrations in national parks were often similar to those reported in other studies (Fig. 2a). For some TrOCs, there were differences in concentrations across studies. For example, carbamazepine (Fig. 2b) concentrations were generally higher in the current study compared to Great Lakes tributaries and southeastern U.S. national parks, but similar to concentrations reported in U.S. streams. Concentrations of TBEP (Fig. 2c) tended to be lower in the current study, compared to others. Although detected few times in the current study, imidacloprid concentrations tended to be similar across all studies (Fig. 2d).

3.3. Estimating potential effects to aquatic biota

We were able to assess relative potency for 27 (77% of detected) WWIs, 33 (45%) PPCPs, and 42 (89%) pesticides (Table S11). Of those detected at more than one site, elevated concentrations (i.e., EAR ≥0.001 or TQ ≥ 0.1) were identified for 11 WWIs, 7 PPCPs, and 9 pesticides (Fig. 3, Figs. S3, and S4). Very few TrOCs were detected in Greater Yellowstone (GRYN) and Rocky Mountain (ROMN) networks (Fig. S3). Furthermore, those that were detected resulted in relatively low estimates of potential biological effects, compared to other parks. Parks within the Great Lakes (GLKN), Heartland (HTLN), NCPN, and Sierra Nevada (SIEN) Networks had the most sites with elevated concentrations (Fig. 3). Pesticides were detected more frequently and often at elevated concentrations in midwestern parks (GLKN, HTLN), compared to other parks.

3.3.1. Potential concern of specific TrOCs to aquatic biota health

WWIs identified as having relatively high potential hazard (i.e., detected in several samples at elevated concentrations) include bisphenol A, a couple of PAHs, triclosan (antimicrobial), and a couple of phosphorus-based flame retardants (Fig. S4). EAR values for the three most frequently detected WWIs (bisphenol A, triclosan, and TDPP) were always >0.001, indicating consistently elevated concentrations. More PPCP concentrations were elevated when screening against modeled bioactivity data, compared to published benchmarks. EAR and TQ values for 3 of the 5 most frequently detected PPCPs were relatively low, indicating few occurrences of elevated concentrations (Fig. 4). Conversely, carbamazepine was detected in only 6% of all samples, yet concentrations were always elevated according to both screening methods. Venlafaxine and sulfamethoxazole were only detected in 1% and 8% of samples, respectively, but concentrations always exceeded published water quality benchmarks. Unlike PPCPs, fewer pesticides were detected at concentrations above screening levels (TQ ≥ 0.1) for published benchmarks, compared to modeled bioactivity data (Fig. 4). Pesticides with relatively high EAR or TQ include propiconazole (fungicide), diuron (herbicide), acetochlor (herbicide), and simazine (herbicide). Like PPCPs, pesticides that were detected frequently

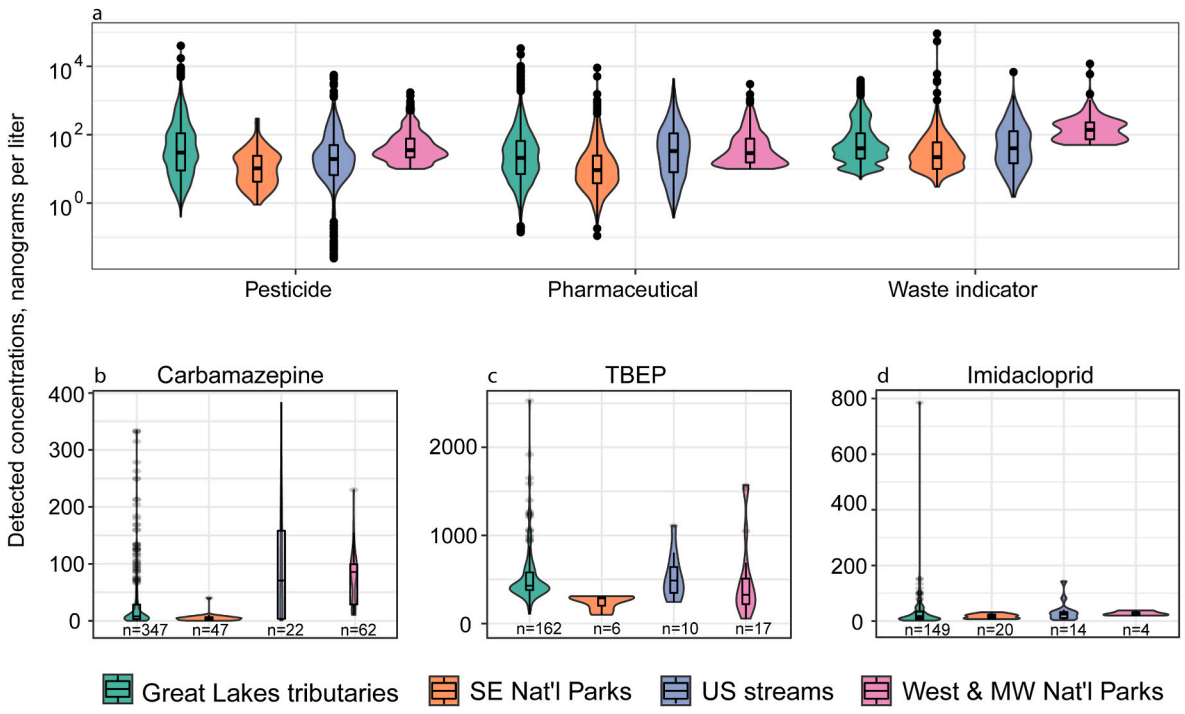

Fig. 2. Violin and boxplot summaries of detected concentrations of wastewater indicators (WWIs), pharmaceuticals and personal care products (PPCPs), and pesticides in surface waters collected as part of the current study and other U.S. studies: overall summary (a), individual summaries for carbamazepine (b), tris-butoxyethyl phosphate (TBEP; c), and imidacloprid (d). The 25th, 50th, and 75th percentiles are represented by the bottom of the box, the black line within the box, and the top of the box, respectively. Whiskers extend to the minimum and maximum values and outliers are represented by individual dots. Number of detections are indicated on the bottom of the graphs in (b, c, and d). SE Nat'l Parks, surface waters within southeastern U.S. national parks; US streams, streams throughout the U.S.; West & MW Nat'l Parks, current study.

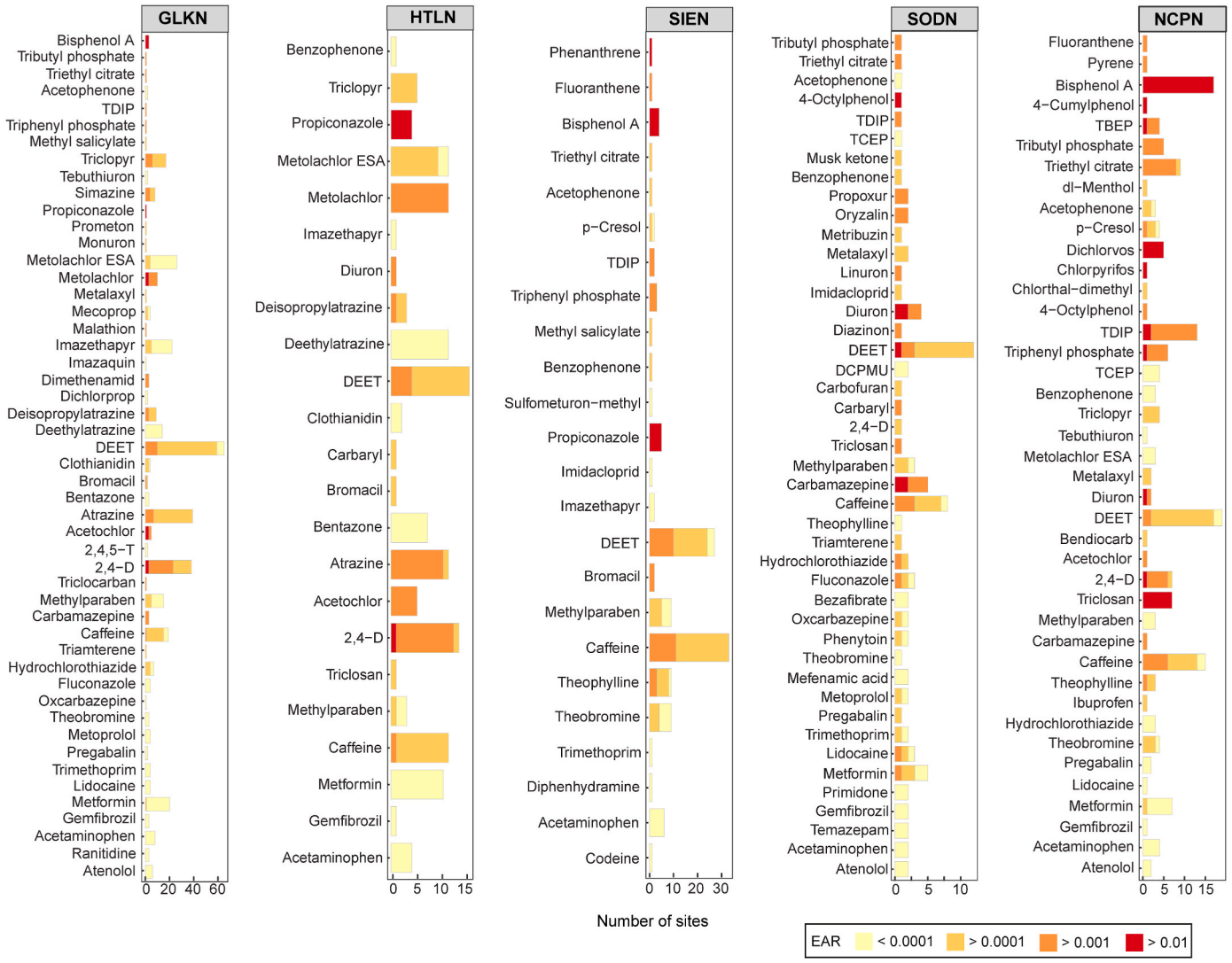

Fig. 3. Stacked bar charts showing the number of sites at which trace organic contaminant (TrOC) concentrations resulted in exposure activity ratios (EAR) of a particular magnitude. Only Inventory & Monitoring (I&M) networks in which at least one TrOC resulted in at least one EAR value are shown. Other I&M networks are shown in Figure S3. I&M network acronyms are defined in Table S2.

(>10%) had relatively low EAR or TQ values. One exception was 2,4-D, which was detected in 14% of samples, often at elevated concentrations (EAR>0.001 at 71% of sites). At individual sites, there were generally few contaminants (<5) that were detected at elevated concentrations. Some exceptions include those from GLKN and HTLN networks where ≥10 pesticides were detected. However, at 56 sites, the sum of the maximum EAR was >0.01, an order of magnitude greater than the threshold used to identify TrOC present at elevated concentrations (Table S11). Although this method assumes simple additivity, it indicates that TrOC mixtures may pose a threat to exposed biota.

3.4. Watershed influence on contaminant presence

Site-specific watershed sizes range from 0.01 to 96,000 km^2 and are generally dominated by forest, shrub scrub, or grassland (Table S8). However, watersheds of several sites have a relatively large proportion of developed or agricultural lands (e.g., MISS, INDU, PIPE). Additionally, at least one point source is present in most watersheds (Table S8). The CIT analysis evaluating the influence of watershed characteristics on the number of pharmaceutical and pesticide detections at each site produced R^2 values of 0.58 and 0.75 and NRMSE values of 0.09 and 0.1, respectively.

Although more than 50% of site-specific watersheds are classified predominately as forest or shrub/scrub, we were able to identify characteristics and thresholds related to the number of TrOCs detected. The number of wastewater treatment plants (WWTPs) within a watershed was the most significant characteristic associated with the number of pharmaceuticals detected (Fig. 5a). Sites with at least one WWTP and with some impervious surfaces (i.e., ≤92.8% of the watershed containing no impervious surfaces) within the watershed had the greatest number and range of pharmaceutical detections. When WWTPs were not present, the proportion of the watershed containing no impervious surfaces was still important, but the presence of wetlands was also important. Pharmaceuticals were generally not detected in watersheds that contained little impervious surface and when the proportion of wetlands was >5.7%.

The proportion of the watershed classified as agriculture was the most significant watershed characteristic related to the number of pesticides detected (Fig. 5b). The greatest numbers and largest range of pesticides detected were observed at sites in watersheds containing >3.6% agricultural lands and ≤16.8% forest lands. When the proportion of agriculture was low (i.e., <3.6%), the number of golf courses was important. More pesticides were detected at sites within watersheds containing golf courses. Although this analysis points to known sources

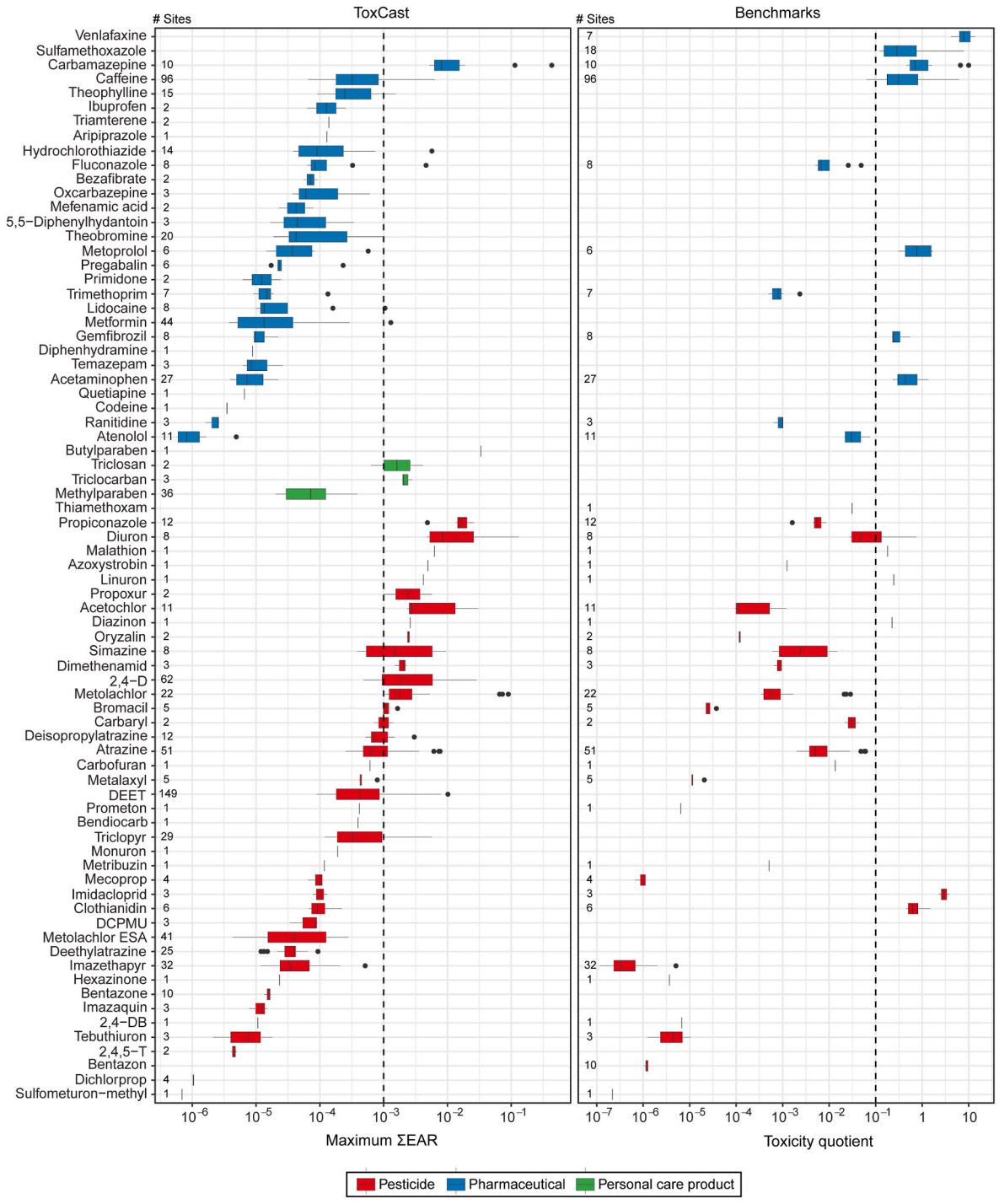

Fig. 4. Boxplot summaries of maximum summed exposure activity ratios (∑EAR) and toxicity quotients for pharmaceuticals, personal care products, and pesticides. Vertical dashed lines indicate a threshold above which there may be higher likelihood of effects to aquatic biota (i.e., elevated concentrations). The 25th, 50th, and 75th percentiles are represented by the left edge of the box, the middle line, and the right edge of the box, respectively. Whiskers extend to the minimum and maximum values and outliers are represented by individual dots.

of TrOCs (e.g., impervious surfaces, WWTP discharge), it provides additional information regarding combinations of watershed variables that may influence the presence of contaminants in the aquatic environment.

4. Discussion

Relatively few TrOCs (about 45% of those analyzed) were detected in the sampled national park surface waters between 2009 and 2019. However, TrOCs that were detected frequently (e.g., metformin, bisphenol A) are also frequently reported in the literature, albeit at higher levels. For example, metformin has been detected in >50% of samples collected from surface waters in non-protected areas across the globe (Ambrosio-Albuquerque et al., 2021; Wilkinson et al., 2022). Bisphenol A is frequently detected in surface waters throughout North America, Europe, and Asia at concentration ranges similar to those observed in our study (Corrales et al., 2015; Staples et al., 2018). While it is encouraging that the presence of contaminants in national park

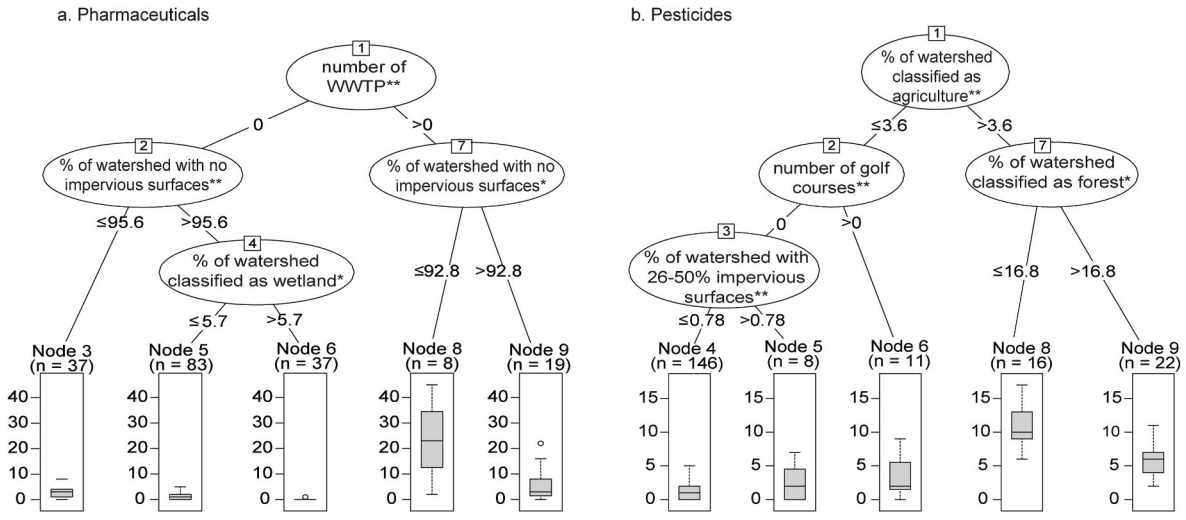

Fig. 5. Decision trees from conditional inference tree analysis to identify relations between select watershed variables and the number of pharmaceuticals (a) or the number of pesticides (b) detected at each site. WWTP, wastewater treatment plant; *p < 0.01; **p < 0.001.

surface waters is relatively low, the fact that similar patterns are observed between protected and non-protected areas indicates the far-reaching effects of anthropogenic activities on the environment. Furthermore, the fact that several contaminants (e.g., atrazine, carbamazepine, gabapentin) were detected in all samples collected from some parks points to continuous inputs in some areas that may be affecting park water resources.

When considering the number of pesticides that were analyzed, relatively few (<30%) were detected. This is consistent with other studies characterizing pesticides in protected surface waters (Bradley et al., 2020, 2021). However, the most frequently detected pesticides align with previously reported results from other studies across the U.S. (e.g., Bradley et al., 2020; Stackpoole et al., 2021; Stone et al., 2014). For example, atrazine, metolachlor, and 2,4-D were the most frequently detected pesticides in U.S. streams within agricultural, urban, or mixed watersheds (Stackpoole et al., 2021). Furthermore, our results show greater detection frequencies for pesticides in midwestern national parks, which follows patterns observed in streams outside of protected park areas and is associated with higher pesticide use (Stackpoole et al., 2021).

Pesticide concentrations detected during our study resulted in relatively minimal estimated potential for biological effects to aquatic biota. Using traditional water-quality benchmarks, similar to analyses in previously cited studies, there were relatively few exceedances of risk or bioactivity screening levels in national park surface waters, especially for herbicides. Conversely, exceedances of aquatic life benchmarks for atrazine and metolachlor, sometimes for multiple taxa, were reported in U.S. streams within agricultural, urban, and mixed-use watersheds during different time periods ranging from 1991 to 2017 (Stackpoole et al., 2021; Stone et al., 2014). Although screening pesticides against water quality benchmarks resulted in relatively few exceedances, exceedances of bioactivity screening values identified several elevated concentrations, including atrazine and metolachlor, which aligns with previously cited papers. These results indicate that the presence and magnitude of pesticides in national park surface waters are generally low, and higher detection frequencies align with parks that are more directly affected by anthropogenic activity (e.g., MISS, INDU). While these data provide a good baseline of pesticides in national park surface waters, future monitoring will be important to capture changes in the environment.

Our analysis indicates that although many of the target contaminants were detected relatively infrequently, the concentrations at which they were detected (e.g., carbamazepine, diuron, acetochlor, sulfamethoxazole) indicate that more monitoring or research may be warranted to fully characterize the hazard to aquatic resources. For many of the infrequently detected contaminants, relatively high concentrations occurred at multiple parks (3–9 parks), based on EAR. Furthermore, for several contaminants, hazard quotients indicated concentrations of concern for potential biological effects in almost all samples. The presence and magnitude of contaminants can vary seasonally and spatially (Bai et al., 2018). Therefore, more detailed sampling of park surface waters that account for seasonality, runoff events, and spatial distribution within a system would be useful to fully characterize the potential hazard to aquatic biota within these protected areas.

Although the results of the CIT analysis did not provide new information about TrOC sources to the environment, the approach did provide new insights into relations between watershed characteristics and surface-water TrOC concentrations. Many studies focus on relations between contaminant presence or magnitude and broad watershed characteristics such as percent of the watershed that is urbanized (Baldwin et al., 2016) or percent of the watershed that is disturbed (Ferrey et al., 2015). Results of these analyses indicate that more contaminants are typically detected and at greater concentrations in more disturbed watersheds and related to increasing urbanization. However, incorporating other watershed characteristics, such as the number and type of point sources, can reveal important information and may be important in watersheds that are relatively undisturbed. For example, Park & Park (2015) identified sub-basins containing major WWTPs as more susceptible to contaminant presence. Our results are similar in that the number of WWTPs located within the watershed was the most important factor related to the number of pharmaceuticals detected in national park unit surface waters. This was especially important at BEOL and MISS where at least 50 wastewater treatment plants exist within the site-specific watersheds and several PPCPs were detected in 100% of samples. Because watersheds within national parks are generally less developed compared to other areas, atmospheric transport may play an important role in TrOC loading to surface waters within these protected areas. Bisphenol A, DEET, caffeine, and nonylphenol were detected in air collected from an urban area (Ferrey et al., 2018). Several pesticides were detected in air samples collected throughout Germany, including national parks and other remote areas, especially in locations where agriculture was nearby (Kruse-Plaß et al., 2021). Although there are relatively few studies that focus on atmospheric transport of TrOCs, evidence indicates that this may be an important transport pathway that is not well understood.

Although geographic gaps remain, the data from this study provide a baseline of the general presence and magnitude of TrOCs within national park surface waters. In some instances, the data were used to inform management activities, increase communication with the public, and/or inform more detailed projects. Some examples include.

- Data collected from the Colorado River near Canyonlands National Park were used to assess if upgrades to a WWTP resulted in reduced concentrations and detection frequency of bioactive chemicals (Battaglin et al., 2023).
- Data were collected from Pipestone Creek at Pipestone National Monument to inform plans to upgrade septic systems that currently discharge into the creek (Krall et al., 2023).
- Within Sequoia and Kings Canyon National Parks, the results were used to develop two additional studies, one focused on prioritizing watersheds for identifying illegal marijuana gardens and the other focused on monitoring TrOCs using passive samplers to monitor visitor use and impacts in specific rivers (Erik Meyer, U.S. National Park Service, personal communication).
- Results from the Buffalo National River revealed episodic events of elevated herbicide concentrations in the river. This information was used to communicate with Department of Transportation staff that were treating rights-of-way in the park, resulting in modification of spraying methods to reduce contamination of park surface waters (Shawn Hodges, U.S. National Park Service, personal communication).

These examples highlight the importance of understanding the current state of the environment so that management agencies can continue to make informed decisions to protect valuable water resources. Furthermore, the data can be used to guide future monitoring programs to fill geographic data gaps related to TrOCs in national park surface waters.

5. Conclusions

Understanding the impact that anthropogenic activities have on protected waters in U.S. national parks is important to ensure that water resources are protected and available for future generations to enjoy. Enhancing our understanding of TrOCs in national parks could be accomplished by filling data gaps and addressing limitations of the current study, including sampling in under- or uncharacterized regions of the country, implementing a more balanced study design (e.g., equal number of samples per site), considering temporal variation, and/or implementing more consistent field QC procedures across parks and networks to allow for more in depth and rigorous analysis and interpretation of the data. Nonetheless, results from this study serve as a first step in filling existing data gaps related to TrOCs in U.S. national park surface waters and provide important information that can be used as a framework to inform future monitoring in protected areas across the globe.

Disclaimer

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

CRediT authorship contribution statement

Sarah M. Elliott: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Kerensa A. King:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Aliesha L. Krall:** Writing – review & editing, Writing – original draft, Validation, Formal analysis. **David D. VanderMeulen:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Conceptualization.

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.

Data availability

Data from this study are publicly available in the Water Quality Portal (https://www.waterqualitydata.us/).

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Appendix A. Supplementary data

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