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Bioactive contaminants of emerging concern in National Park waters of the northern Colorado Plateau, USA

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Abstract

Pharmaceuticals and personal care products (PPCPs), wastewater indicators (WWIs), and pesticides (herein, Contaminants of Emerging Concern [CECs]) have been documented in surface waters throughout the world and have associated risks to aquatic life. While much research has focused on temperate and urbanized watersheds, less is known about CEC presence in semi-arid landscapes, where water availability is limited and populations are low. CEC presence in water and sediment is reported for 21 sites in eight U.S. national parks in the northern Colorado Plateau region. From 2012 – 2016, at least one PPCP and/or WWI was detected at most sites on over half of sampling visits, indicating that CECs are not uncommon even in isolated areas. CEC detections were generally fewer and at lower concentrations than in urbanized or agricultural watersheds. Consistent with studies from other U.S. regions, the most frequently detected CECs in this study include DEET, caffeine, organophosphorus flame retardants, and bisphenol A in water and fecal indicators and polycyclic aromatic hydrocarbons in sediment. Maximum concentrations in this study were generally below available water quality benchmarks, sediment quality guidelines, and risk assessment thresholds associated with vertebrates. Additional work is needed to assess the potential activity of hormones, which had high reporting limits in our study, and potential bioactivity of environmental concentrations for invertebrates, microbial communities, and algae. Potential sources of CEC contamination include upstream wastewater effluent discharges and

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Supplemental data

The Supplemental Data (Tables S1-S7) are available.

Data availability

Complete primary data are downloadable from the USGS National Water Information System: Web Interface [68] and from the EPA STORET Water Quality Exchange [67]. The entire data package is available as a data release at https://doi.org/10.5066/F7NP23PC.

National Park Service invasive-plant-control herbicide applications. CEC occurrence patterns and similarities between continuous and isolated flow locations suggest that direct contamination from individual visitors may also occur. While our data indicate there is little aquatic health risk associated with CECs at our sites, our results demonstrate the ubiquity of CECs on the landscape and a continued need for public outreach concerning resource-use ethics and the potential effects of upstream development.

Keywords

pesticides; pharmaceuticals; personal care products; wastewater indicators; national parks; northern Colorado Plateau

1. INTRODUCTION

Contaminants of emerging concern (CEC) are chemicals and other substances that are largely unregulated in the United States, but which, because of advancements in analytical chemistry, are now reliably and routinely detected in surface waters across the nation [1–5]. Trace-level concentrations of CECs can alter aquatic ecosystems at multiple trophic levels, from biofilms to fish [6–13]. CECs with designed-bioactivity (e.g., pharmaceuticals, pesticides, hormones) are particular concerns for the structure and function of aquatic ecosystems [12, 14–17], owing to ubiquitous environmental sources [18–23] and the diversity of evolutionarily-conserved, molecular endpoints [24–28]. CECs characteristically occur as complex environmental cocktails [18, 29] with multiple modes of action and a commensurate range of potential adverse outcomes in aquatic foodwebs [12, 30–40].

Because environmental CEC contamination is linked to population growth, potential effects are an increasing global concern [41] even in remote and protected lands [42]. CECs are widely reported as complex mixtures in rivers and streams in densely-populated watersheds [2, 14, 18, 43], often in association with wastewater treatment plants [44, 45]. Growing evidence, however, suggests these CECs are also present in rural areas far from known pollution point-sources [2, 6, 18, 19, 46]. For example, persistent organic pollutants can be transported via atmospheric deposition to relatively pristine high elevation and high latitude regions [47–49], and atmospheric transport of bioactive CECs from external sources has been linked to male vitellogenin expression and increased intersex percentages in trout in remote alpine lakes in several western national parks [42].

National parks are increasingly important biodiversity preserves, reference endmembers for environmental-change assessments, and field laboratories for assessing subtle and initial contaminant-exposure effects [50]. While many national parks are considered to be among the most pristine ecosystems in the nation, parks exist within a matrix of surrounding land uses, including urban development, agricultural uses, mineral exploration and extraction, and contamination from wastewater treatment discharges. Thus, the potential for CEC contamination of park ecosystems from diverse sources and mechanisms [42, 51, 52] has been recognized for years [53]. Parks experience heavy visitation that could lead to direct contamination, and CECs may also be introduced through management actions, such as invasive plant herbicide treatments, park maintenance, and landscaping [54].

To better understand the exposure, sources, and potential risk of CECs in the United States national parks, the National Park Service (NPS), U.S. Environmental Protection Agency (EPA), and U.S. Geological Survey (USGS) are evaluating CEC exposures in surface-water habitats in individual parks [e.g., 19, 55, 56, 57] and, more recently, in regional park monitoring networks [e.g., 47, 48, 58] across the nation. The majority of sampling has taken place in temperate settings. In contrast, little is known about CEC risk in arid/semi-arid park units of the southwestern US, where water availability is a primary determinant of flora, fauna, and historic human habitation. Ecosystem impairments, including endocrine disruption, have been documented in large drainage basins in the region [59–61]. The USGS reported elevated tissue concentrations of metals and legacy pesticides as well as elevated male intersex and serum 17β-estradiol (E2) and vitellogenin levels in male black bass *(Micropterus* spp.) in the Colorado River basin in the semi-arid Colorado Plateau region [59–61]. However, exposures to many bioactive CECs, including pharmaceuticals and current-use pesticides, were not assessed. Herein, the occurrence and concentrations of a range of bioactive contaminants were assessed in surface and cave water samples and in sediment samples collected from 21 locations in eight national parks in the NPS Northern Colorado Plateau monitoring network during 2012–2016, in order to assess exposure and potential sources of anthropogenic bioactive contaminants in semi-arid park aquatic habitats.

2. METHODS

2.1. Study area

The Colorado Plateau is characterized by rugged topography, mostly natural landscapes, and river and stream hydrographs dominated by snowmelt in the spring and early summer, high magnitude flash floods from intense summer and fall thunderstorms, and groundwater-driven baseflow. The northern Colorado Plateau overlaps much of the upper Colorado River basin and is the home of over a dozen national parks and no major urban centers. Major river systems in these national parks provide habitat for federally endangered Colorado pikeminnow *(Ptychocheilus lucius),* razorback sucker *(Xyrauchen texanus*), bonytail *(Gila elegans*), and humpback chub *(Gila cypha*), including spawning grounds for humpback chub.

Sampling locations were selected at Arches National Park (NP), Bryce Canyon NP, Canyonlands NP, Capitol Reef NP, Dinosaur National Monument (NM), Hovenweep NM, Timpanogos Cave NM, and Zion NP (Fig. 1). Because of the screening nature of this study, sites were selected to include a broad array of water sources rather than as a representative sample of national park waters on the Colorado Plateau. Twenty-one sampling sites (Supplemental Table S1) were selected for screening for emerging contaminants based on the presence of potential CEC sources (e.g. seepage from park toilets, direct visitor contact, run-off from park orchards, etc.) and management interest. Sample locations included diverse water types and settings from remote springs to cave pools to large, inter-regional rivers. Sites were classified as isolated if they were not connected by perennial flow to potential contamination sources outside of national park boundaries.

2.2. Sampling methods

Samples were collected from 2012 – 2016 at varying intervals for a total of 119 water samples and 71 sediment samples. Sites were sampled between 1–18 times over the course of the study. Springs and cave waters were sampled in base flow conditions, and streams and rivers were sampled during both base flow and snowmelt periods; flash flood events were not sampled. Water grab samples were collected by wading from center of flow where possible (Arches, Bryce Canyon, Capitol Reef, and Zion locations) or near edge of water (Canyonlands, Dinosaur, Hovenweep, and Timpanogos Cave locations) in sterile, 40 mL amber glass, volatile organic analysis vials. Sediment grab samples were collected from the same location as water samples in 125 mL combusted (500° C), amber glass jars. A cut-off, 100 mL sterile high-density polyethylene syringe was rinsed 3–5 times in surface water and then used to collect multiple 2 cm deep surface sediment cores comprising a total sample volume of approximately 50 mL. Samples were immediately placed on ice and shipped to the analyzing laboratories.

2.3. Sample analyses

Water samples were analyzed at the EPA Region 8 laboratory in Golden, CO for 72 pesticides and pesticide degradates (hereafter, pesticides), 184 pharmaceutical and personal care products (PPCPs), and 53 wastewater indicators (WWIs). Pesticides in filtered water were extracted using methylene chloride and then analyzed by liquid chromatography/tandem mass spectrometry with thermospray ionization using SW-846 Method 8321B [62]. PPCPs in filtered water were analyzed by solid phase extraction and high-performance liquid chromatography/tandem mass spectrometry using EPA Method 1694 [63]. Unfiltered WWI samples were extracted using methylene chlorine and analyzed by gas chromatography-mass spectrometry using SW-846 Method 8270D [64]. Bed sediment samples were analyzed at the USGS National Water Quality Laboratory (NWQL) in Denver, CO for concentrations of 57 wastewater indicators [65]. Sediment WWIs were extracted using high-pressure solvents followed by solid-phase extraction and then analyzed by capillary-column gas chromatography-mass spectrometry as described previously [50, 66]. A complete list of CECs and their reporting limits can be found in Supplemental Tables S2 and S3. All data are available in the EPA STORET/WQX database [67] and the USGS National Water Information System [68].

2.4. Quality control

Complete quality assurance and quality control procedures are provided in [69] and results are given in a series of data reports [69–72]. Briefly, potential contamination bias of water samples was evaluated with field and laboratory blank data, and environmental concentrations less than 3x the reported blank concentration were removed from the dataset. Consistency in water results was evaluated using replicate samples and recovery of laboratory matrix spikes. Here we highlight results of most concern to our presentation of the data.

Twelve laboratory grade water blanks (Pesticide/Volatile Organic Chemical grade water) and 2 laboratory grade sediment blanks (coarse sand combusted at 500 °C for 24h); blank media were transferred to sample bottles under field conditions as described previously [73].

Laboratory blank contamination occurred for DEET on one occasion. Fifteen unique CECs were detected in water field blanks, for a total of 21 detections out of 3462 analyses (Supplemental Table S4), of which only 8 CECs were also detected in environmental water samples. Sixteen environmental water samples with detected concentrations less than 3 times that in the corresponding sampling-event field blank detection were removed from the dataset (Supplemental Table S5). No organic CECs were detected in any sediment blanks.

Recovery of laboratory matrix spikes or matrix spike duplicates was >150% for nine CECs detected in water samples (Supplemental Table S6). Maximum concentrations were not affected by high recovery. Recovery of laboratory matrix spikes or matrix spike duplicates was <50% for two PPCPs, Lorazepam glucuronide and Primidone, neither of which were detected in environmental samples. Our results may under-report these two PPCPs.

Nine pesticide and PPCP and 4 WWI water replicate samples were collected. 1818 comparisons were reported below reporting limits in both the environmental water and replicate samples. For the remaining replicate analyses with at least one detection in the replicate or environmental water sample, the median replicate percent difference (RPD) was 14.6% (IQR 5.1% - 24.6%, range 0.4% - 182.8%; Supplemental Table S7). Three WWI sediment replicate samples were submitted. Of 170 comparisons, 167 were reported below reporting limits in both the environmental sediment and replicate samples. For the remaining three replicates, RPDs were all <20%.

2.5. Data summary and analysis

Pesticide and PPCP analyses were completed in 2012–2016 for all 21 sampling locations. Because of laboratory capacity limitations, WWI analyses were completed in 2012–2014 for the subset of 16 sites that were sampled in those years but were not completed in 2015 or 2016. Results are presented using the maximum number of sites available for each type of analytical suite (n = 21 for pesticides and PPCPs; n = 16 for WWIs). To increase the ability to look for chronic contaminants over time and decrease confusion about missing data versus non-detects, for this analysis we included only CECs that were analyzed in at least 3 of the 5 years, which reduced the number of PPCPs to 137. Pesticides and WWIs remained the same. Because sites had varying numbers of samples collected over different time spans, we focus our data summary on the frequency of detections and the maximum detected concentrations.

2.5.1. Exposure-Activity Ratio analysis—Standard biological effects endpoints are not available for many reported CECs included in this study. However, high-throughput screening databases, such as the EPA ToxCast database, contain *in vitro* effects data for thousands of chemicals, including many CECs. The database includes dose-response data for over 9,000 chemicals screened through batteries of cell-based and cell-free *in vitro* assays covering a broad range of biological pathways, including possible indicators of endocrine disruption or neurological effects. To evaluate the highest observed potential for adverse effects on ecological receptors, exposure-activity ratios (EARs) were calculated using maximum concentrations of commonly detected CECs in water samples. The EAR is the quotient of the maximum observed surface water concentration and the minimum effects level concentration, in this case, the activity concentration at cutoff (ACC) for assays within

the ToxCast database. The ACC is the concentration at which a chemical interacts with a molecular target to produce a measurable response above a defined benchmark of assay activity [74]. EAR values ≥1 indicate environmental concentrations at or above the concentration required to modulate molecular targets *in vitro.* As such, elevated EAR values indicate the potential for biological effects from observed CECs and can help prioritize chemicals based on known *in vitro* activity. Since EAR values are derived from in vitro pathway-based bioactivity, EAR analysis should provide a conservative estimate of the potential adverse effects from observed environmental chemicals to vertebrates [74, 75]. Some assay results were excluded from this analysis because they target nonspecific endpoints or baseline assay performance, and not specific effects. For the final EAR calculations, 528 of 1192 assays endpoints were considered [74].

3. RESULTS AND DISCUSSION

3.1. CEC Presence

Of the 262 CECs in the water analytical suite, 23 were detected at least twice (Fig. 2; Table 1), 26 were detected only once, and 213 were never detected. CECs found at more than 30% of sites include personal care products (DEET and caffeine), organophosphorus flame retardants (tri(dichloroisopropyl) phosphate and tri(2-butoxyethyl) phosphate), and bisphenol A. Median concentrations were all less than the reporting limits. Maximum concentrations were generally in the tens of ng/L (Table 1; median 67.0 ng/L; IQR 16.8–253.0 ng/L) and ranged from 10.8 ng/L (butachlor ESA) to 5360 ng/L (p-cresol). Few CECs have aquatic life benchmarks or criteria. Pesticides detected in our study, including 2,4-D, DEET, metolachlor ESA, and triclopyr, did not exceed US EPA aquatic life benchmarks ([76]).

CEC detections in surface water were fewer than previously reported for more urbanized and agricultural watersheds. Nationally distributed stream studies in the U.S. reported higher detection frequencies and median concentrations near 100 ng/L for sulfamethoxazole, metformin, caffeine, and bisphenol A [2, 14], compared to corresponding median concentrations less than the reporting limit in the current study. A recent study in four Midwestern national parks had overlap in some of the most commonly detected CECs, such as bisphenol A, caffeine (total), DEET, gabapentin, metformin, and metolachlor ESA, but at higher frequencies of detections than in our sites [58]. Similarly, mixed contaminants, including pharmaceuticals, have been reported at higher frequencies in a national park in the southeastern U.S. [19]. Metformin, caffeine, and sulfamethoxazole were some of the commonly detected CECs [19] that overlap with our study. In previous studies encompassing gradients in developed landscapes, higher numbers of CECs and higher concentrations were associated with more urbanized streams, and CECs were detected even in remote or less developed areas [2, 14, 58].

Of the 57 CECs in the sediment wastewater indicator suite, 15 were detected at least twice (Table 2), two were detected only once, and 40 were never detected. Nine of the detected sediment CECs were polycyclic aromatic hydrocarbons (PAHs). Maximum concentrations in the sediment samples were generally in the tens of μg/kg (Table 2; median 66.0 μg/kg; IQR 41.0–112 μg/kg), with a range of 22 μg/kg (anthracene) to 480 μg/kg (camphor).

There are no local or regional sediment quality guidelines for comparison to our study results, and few guidelines for any of the sediment CECs in our study. PAHs detected in our study, including anthracene, benzo-a-pyrene, fluoranthene, 2-methylnaphthalene, naphthalene, phenanthrene, and pyrene, were all below Probable Effect Levels used in freshwater systems by the Canadian government [77] and reported for *Hyalella azteca* in [78]. Frequently detected sediment CECs were similar to those found in tributaries to the Great Lakes and in the southeastern U.S., including the fecal indicators indole and 3-methyl-1H- indole and the PAHs fluoranthene, pyrene, and benzo-a-pyrene [79]. Both frequencies and maximum concentrations of sediment CECs found in those regions were higher than in our study.

3.2. Potential sources of pseudo-persistent contamination

To investigate pseudo-persistent contamination, defined as consistent CEC detections in 50% or more of samples from a given site, we evaluated site and CEC combinations with 4 or more samples. This reduced sample sizes to 15 sites for pesticides and PPCPs, 8 sites for water WWIs, and 13 sites for sediment WWIs (Table S1). For both water and sediment, 1–8 pseudo-persistent CECs were detected in 50% or more of samples from 7 sites.

Pseudo-persistence of pharmaceuticals has been linked to wastewater treatment discharges in many studies [5, 30, 33, 80]. Although the northern Colorado Plateau is predominately natural or rural, pseudo-persistence of pharmaceuticals occurred on major inter-regional rivers with upstream communities and associated wastewater treatment discharges: the Colorado River at Potash (gabapentin, metformin, lamotrigine, sulfamethoxazole), Green River at Mineral Bottom (gabapentin), and Yampa River at Deerlodge (metformin and gabapentin). The Colorado River at Potash site, just upstream of Canyonlands NP and about 24 km downstream from the Moab, Utah wastewater treatment plant, had the most pseudo-persistent CECs of any site in this study, including an additional 2 personal care products (caffeine [dissolved] and DEET), 2 pesticides (2,4-D and metolachlor ESA), and 6 sediment WWIs (1-methylnaphthalene, 2,6-dimethlnaphthalene, 2-methylnaphthalene, 3-methyl-1H-indole, indole, and p-cresol). The Green River at Mineral Bottom, approximately 109 km downstream of Green River, Utah, also had additional pseudo-persistent water (DEET) and sediment (indole) CECs. The Yampa River sampling site is about 160 km downstream from Craig, Colorado. Although consistent with a diluted wastewater discharge signal, additional sampling is needed to trace CEC contamination back to sources.

Patterns of pseudo-persistence at other sites in our study cannot be linked to wastewater treatment discharges. Personal care products pseudo-persisted at two cave locations at Timpanogos Cave NM: Hansen Cave (caffeine [dissolved]) and Middle Cave (DEET and galaxolide). Located high in a forested watershed, these two sites are subject to constant, direct visitation (estimated in excess of 100,000 visitors per year). All cave visitors pass directly over the Middle Cave pool, and the Hansen Cave pool is consistently (albeit less frequently) accessed as part of caving activities at the park. The cave is accessed via several doors that minimize air movement within the cave system. Consistent visitation paired with slow atmospheric and cave water turnover may contribute to pseudo-persistent CEC contamination at these sites. In contrast, samples from The Narrows at Zion NP had no

pseudo-persistent CECs, despite thousands of visitors wading in the river each day during the recreation season.

Pseudo-persistent pesticides occurred only at the Colorado River at Potash, as mentioned above, and at Lower Courthouse in Arches NP (triclopyr). Triclopyr contamination may be attributable to park management's use of a triclopyr-based herbicide to control tamarisk, an exotic invasive plant common along riparian areas in the Colorado Plateau. Tamarisk removal occurs at or upstream of many other sites included in this study. As with PPCP contamination at Timpanogos Cave, the pseudo-persistence detection of triclopyr at Lower Courthouse may be due to its status as an intermittent stream with slow flow and sometime stagnant conditions.

Other pseudo-persistent CECs included p-cresol at Upper Courthouse in Arches NP (isolated spring) and the Green River near Jensen, Utah downstream of Dinosaur NM (major inter-regional river). The fecal indicator indole was pseudo persistent at both isolated (Sleepy Hollow at Arches NP, The Grotto at Zion NP) and continuous flow sites (Sulphur Creek at Capitol Reef NP; Green River near Jensen, Utah; and North Creek at Zion NP). An additional fecal indicator, 3-methyl-1H-indole, was also found at two of the sites (Sleepy Hollow; Green River near Jensen, Utah). While all three of these CECs are commonly included as indicators of waste, they can come from natural waste sources in addition to anthropogenic sources.

While pseudo-persistence of the same CEC at an individual site was relatively uncommon, detections of at least one CEC at 50% or more of visits was more common. A majority of sites had a WWI detection during most visits (6 of 8 sites for water and 8 of 13 sites for sediment), and almost half had a PPCP detection (7 of 15). In contrast, only 2 of 15 sites had pesticide detections at 50% or more of visits. Contact with dermally applied PPCP such as the insect repellant DEET or excretion through sweat and urination near or in surface water may introduce some of these chemicals into the environment. The temporally consistent presence of at least one CEC at most sites, regardless of whether the site is isolated or connected by continuous flow to upstream areas, suggests sporadic but frequent unique contamination events, perhaps linked to individual park visitors.

3.3. Ecological Effects of CECs

While water quality benchmarks and sediment quality guidelines are available for relatively few CECs, techniques involving high throughput analysis of various vertebrate endpoints allow for the assessment of potential ecological effects for a much broader array of CECs. We compared the maximum concentration of each CEC detected two or more times in our study to the ToxCast database to calculate EARs. Of the 22 unique CECs detected in water, 19 were present in the ToxCast database (Table 1); five of these CECs were not active within the tested assays, leaving 15 active CECs with calculated EARs. Maximum EARs for each CEC were all below 1.0, and twelve of fourteen were below 0.01, indicating a low risk for potential bioactivity in vertebrates. As a worst-case scenario, we then calculated an EAR mixture value assuming the maximum concentrations were all detected in a single sample, which resulted in a total maximum EAR of 0.12.

Bisphenol A and caffeine (total) had the greatest single chemical EARs at 0.12 and 0.031, respectively, and represent two chemicals that could be prioritized for further investigation at our sites. Focusing on bisphenol A as the compound with the highest observed EAR, the most sensitive assay targets include the constitutive androstane receptor (CAR), which is associated with regulation of xenobiotic metabolism, and the estrogen receptor (ER). Bisphenol A is a known estrogenic compound, and adverse reproductive effects on aquatic organisms from exposure to estrogenic compounds is well documented [13, 81–83]. A review by Crain et al. [81] noted bisphenol A chronic exposure benchmarks ranging from 0.63 – 6300 μg/L in aquatic vertebrates, and a value of 0.014 μg/L in an aquatic invertebrate, the Ramshom snail *(Marisa cornuarietis).* The reported chronic toxicity value of 0.63 μg/L is near the maximum observed concentration of bisphenol A from the current study. This aligns well with the EAR value of 0.12, indicating measured concentrations within 10-fold of the concentration expected to activate targets in vitro. Bisphenol A has a greater binding affinity for the gastropod ER compared to the human ER [84], which is used in the majority of ER-related ToxCast assays. The increased affinity may explain the lower concentration of chronic effects reported in freshwater snail. Since ToxCast assays are based on mammalian targets, EAR analysis will not capture this cross-species difference. Ultimately, given this is a worst-case scenario of observed concentrations, there is likely limited potential for biological activity in vertebrates at the majority of monitored sites, but the potential for effects in aquatic invertebrates remains. Sites with elevated bisphenol A should be prioritized for additional monitoring to better characterize bisphenol A occurrence, which will better inform the risk to aquatic organisms.

One limitation of the EAR analysis is that the ToxCast database (used to calculate EARs) is focused primarily on vertebrate-related endpoints; plant and invertebrate specific processes (i.e., photosynthesis, ecdysis) are not currently represented. Different chemical binding affinities between vertebrate and invertebrate targets could also lead to increased susceptibility of invertebrates, as noted above for bisphenol A. Several detected chemicals are herbicides or herbicide metabolites, and the potential risks from exposure to algae or aquatic plants may also be underestimated by EARs. In addition, several hormones in the analytical suite are known to be biologically active at concentrations below the reporting limit in our dataset [12, 13, 85–87]. Ultimately, assessing the ecological impact of these chemicals is challenging given the limited effects data available for most CECs. However, based on EAR analysis, observed concentrations of CECs at the majority of sites are unlikely to pose a threat to public health, fish, and amphibian species at our sampled locations.

4. CONCLUSION

Screening over multiple years suggests that CECs are commonly present in National Park waters in the semi-arid southwest in both continuous and isolated flow situations. Pseudo-persistence at our sampling locations is likely due to the persistence of wastewater effluent at several sites, park management actions at one site, and direct visitor contact at others. In addition to pseudo-persistence of single CECs, over half of the sites sampled had at least one PPCP (water) and/or WWI (water and sediment) detected in more than 50% of samples. This suggests that even at sites that do not have a continuous source of contamination, CECs

are commonly present, regardless of whether they are isolated from or connected to the surrounding watershed via perennial flow. Recreational use by park visitors may contribute to the unique, but relatively frequent, introduction of various CECs over time. While the presence of CECs is undesirable from the perspective of maintaining or restoring park ecosystems to their pre-settlement state, CECs in our sampling locations do not currently occur at concentrations that suggest management action to protect native vertebrate wildlife is needed. Potential effects on invertebrates, microbial communities, and algae are possible but difficult to evaluate with existing quality benchmarks and risk assessment techniques. Continued public education concerning resource-use ethics and the potential effects of upstream development could help maintain CEC contamination at low levels within National Park waters of the northern Colorado Plateau.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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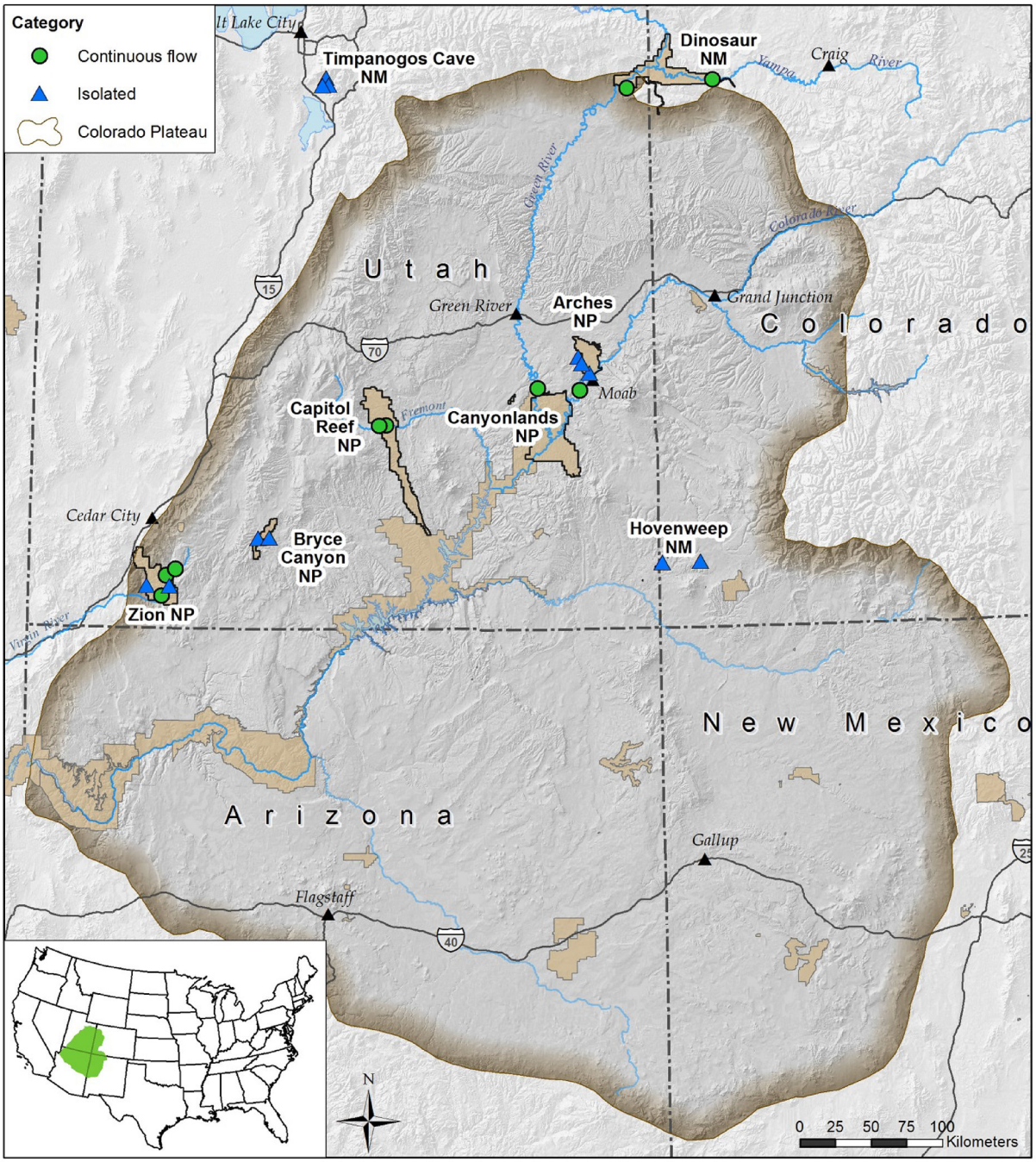

Figure 1.

Sampling locations in and near national parks on the northern Colorado Plateau. Isolated sites lack a connection to upstream areas via perennial flow, while continuous flow sites have an upstream source of perennial surface flow.

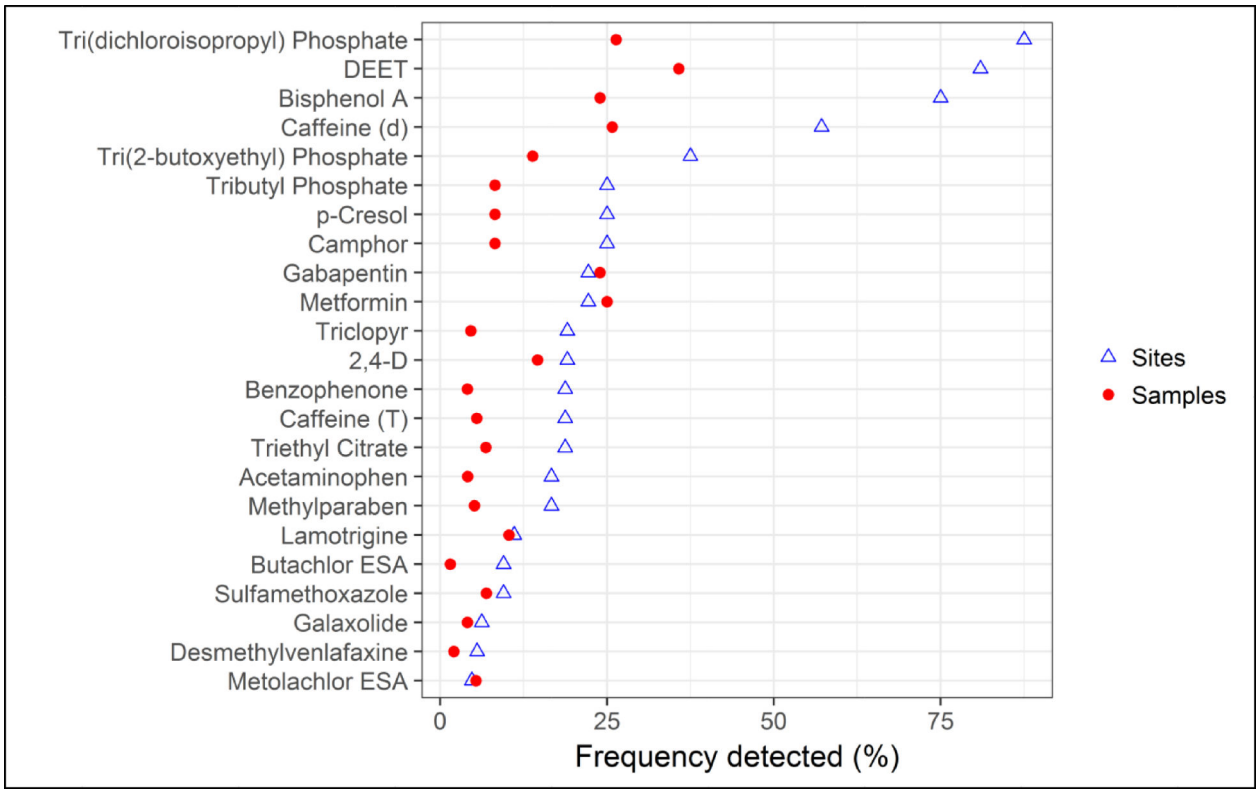

Figure 2.

Frequency of detections for all water samples (red circles) in the study and sites (open triangles) for water CECs with two or more detections in the dataset. Caffeine is present in both dissolved (d) and total (T) analyses.

Table 1.

For all water CECs with two or more detections in all samples; site detections, sample detections, maximum concentrations (ng/L), and Exposure-Activity Ratio (EAR) for the maximum concentration. EAR of zero indicates the chemical has been tested and found to be inactive in the assays. NA indicates no data are available in ToxCast.

CEC	Method	Site detections (Total sites sampled)	Sample detections (Total samples)	Maximum concentration (ng/L)	EAR for maximum concentration
Tri(dichloroisopropyl) Phosphate	WWI	14 (16)	19 (72)	367	0.0052
DEET	PPCP	17 (21)	44 (123)	315	0.0015
Bisphenol A	WWI	12 (16)	17 (71)	607	0.1228
Caffeine (dissolved)	PPCP	12 (21)	33 (128)	464	0.024
Tri(2-butoxyethyl) Phosphate	WWI	6 (16)	10 (72)	1140	0.0066
Tributyl Phosphate	WWI	4 (16)	6 (73)	138	0.0014
p-Cresol	WWI	4 (16)	6 (73)	5360	0.0032
Camphor	WWI	4 (16)	6 (73)	1520	0
Gabapentin	PPCP	4 (18)	23 (96)	509	0
Metformin	PPCP	4 (18)	24 (96)	210	0.006
Triclopyr	Pesticide	4 (21)	6 (130)	55	<0.0001
2,4-D	Pesticide	4 (21)	19 (130)	216	0.0097
Benzophenone	WWI	3 (16)	3 (73)	66.3	<0.0001
Caffeine (Total)	WWI	3 (16)	4 (73)	596	0.0313
Triethyl Citrate	WWI	3 (16)	5 (73)	276	0.0009
Acetaminophen	PPCP	3 (18)	4 (97)	58.9	0
Methylparaben	PPCP	3 (18)	5 (97)	50.8	<0.0001
Lamotrigine	PPCP	2 (18)	10 (97)	34.3	0
Butachlor ESA	Pesticide	2 (21)	2 (130)	10.8	NA
Sulfamethoxazole	PPCP	2 (21)	9 (130)	41.9	0
Galaxolide	WWI	1 (16)	3 (73)	184	NA
Desmethylvenlafaxine	PPCP	1 (18)	2 (97)	13.4	NA
Metolachlor ESA	Pesticide	1 (21)	7 (130)	45.6	<0.0001

Table 2.

Detections across sites and samples for all sediment CECs with two or more detections and maximum concentrations (μg/kg).

National Water Information System parameter code	Parameter name	Site detections (out of 18 sites sampled)	Sample detections (out of 71 samples)	Maximum concentration (μg/kg)
63210	Indole, solids	16	27	320
63171	3-Methyl-1H-indole, solids	16	23	66
63222	p-Cresol, solids	8	12	390
63192	Camphor, solids	8	9	480
63194	Carbazole, solids	6	9	16
63167	2,6-Dimethylnaphthalene, solids	5	8	23
63224	Phenanthrene, solids	3	7	70
63165	1-Methylnaphthalene, solids	2	6	41
63168	2-Methylnaphthalene, solids	2	5	62
63183	Benzo-a-pyrene, solids	3	5	107
63208	Fluoranthene, solids	2	5	148
63227	Pyrene, solids	2	5	112
63180	Anthracene, solids	2	4	22
63220	Naphthalene, solids	2	3	61
63202	Diethyl phthalate, solids	2	2	80