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

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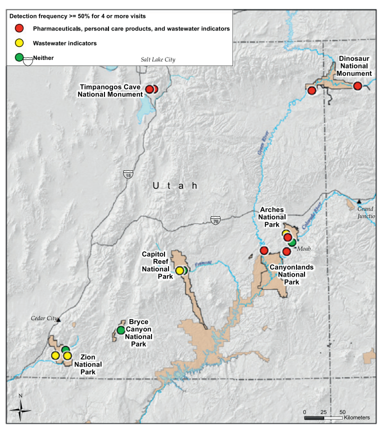
HIGHLIGHTS

- Biologically-active contaminants were detected in waters of Colorado Plateau parks.
- Frequently detected contaminants included DEET, caffeine, BPA, and flame retardants.
- Contaminants were present even in remote and isolated flow conditions.
- Contamination is likely from a variety of sources, including direct visitor contact.
- Concentrations were below thresholds for expected bioactivity in vertebrates.

GRAPHICAL ABSTRACT



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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 to 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 National Park Service

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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.

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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 (USEPA, 2008; Bradley et al., 2017a; Furlong et al., 2014; Sandstrom et al., 2016; Daughton and Ternes, 1999). Trace-level concentrations of CECs can alter aquatic ecosystems at multiple trophic levels, from biofilms to fish (Writer et al., 2010; Proia et al., 2013; Rosi-Marshall et al., 2013a; Battaglin and Kolok, 2014; Niemuth and Klaper, 2015; Niemuth et al., 2015; Kidd et al., 2014; Kidd et al., 2007). CECs with designed-bioactivity (e.g., pharmaceuticals, pesticides, hormones) are particular concerns for the structure and function of aquatic ecosystems (Kidd et al., 2014; Kolpin et al., 2002; Focazio et al., 2008; Dong et al., 2015; Rosi-Marshall et al., 2013b), owing to ubiquitous environmental sources (Bradley et al., 2016a, 2017b; Schäfer et al., 2016; Peters et al., 2013; Malaj et al., 2014; Moschet et al., 2014) and the diversity of evolutionarily-conserved, molecular endpoints (Brown et al., 2014; Gunnarsson et al., 2008; Gunnarsson et al., 2012; McRobb et al., 2014; Carter et al., 2015). CECs characteristically occur as complex environmental cocktails (Bradley et al., 2016a; Vasquez et al., 2014) with multiple modes of action and a commensurate range of potential adverse outcomes in aquatic foodwebs (Kidd et al., 2014; Rosi-Marshall and Royer, 2012; Corcoran et al., 2010; Li, 2014; Monteiro and Boxall, 2010; Hughes et al., 2012; Van Donk et al., 2015; Brönmark and Hansson, 2012; Painter et al., 2009; Schultz et al., 2011; Giacomini et al., 2016; Brodin et al., 2013).

Because environmental CEC contamination is linked to population growth, potential effects are an increasing global concern (Bergman et al., 2013) even in remote and protected lands (Landers et al., 2008). CECs are widely reported as complex mixtures in rivers and streams in densely-populated watersheds (Bradley et al., 2017a; Kolpin et al., 2002; Bradley et al., 2016a; Batt et al., 2016), often in association with wastewater treatment plants (Blair et al., 2013; Bonvin et al., 2011). Growing evidence, however, suggests these CECs are also present in rural areas far from known pollution point-sources (Bradley et al., 2017a; Writer et al., 2010; Bradley et al., 2016a, 2017b; Kay et al., 2017). For example, persistent organic pollutants can be transported via atmospheric deposition to relatively pristine high elevation and high latitude regions (Hageman et al., 2006; Ackerman et al., 2008; Cheng et al., 2013), 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 (Landers et al., 2008).

National parks are increasingly important biodiversity preserves, reference endmembers for environmental-change assessments, and field laboratories for assessing subtle and initial contaminant-exposure effects (Bradley et al., 2015). 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 (Landers et al., 2008; Usenko et al., 2007; Mast et al., 2006) has been recognized for years (Landewe, 2008). 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 (Kettenring and Adams, 2011).

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 (Bradley et al., 2017b, 2016b; Egler et al., 2013; Forrester et al., 2017) and, more recently, in regional park monitoring networks (Hageman et al., 2006; Ackerman et al., 2008; Elliott and VanderMeulen, 2017) 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 (Hinck et al., 2007; Hinck et al., 2006; Hinck et al., 2009). 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 (Hinck et al., 2007; Hinck et al., 2006; Hinck et al., 2009). 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 are reported from our analysis of surface and cave water samples and of 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