Science of the Total Environment 643 (2018) 651–673

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Pharmaceuticals, hormones, pesticides, and other bioactive contaminants in water, sediment, and tissue from Rocky Mountain National Park, 2012–2013

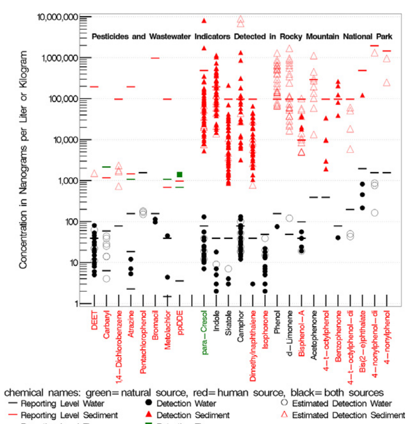
William A. Battaglin [a,*], Paul M. Bradley [b], Luke Iwanowicz [c], Celeste A. Journey [b], Heather L. Walsh [c], Vicki S. Blazer [c]

[a] U.S. Geological Survey, Denver Federal Center, MS 415, Denver, CO 80225-0046, United States of America
[b] U.S. Geological Survey, 720 Gracern Rd, Suite 129, Columbia, SC 29210-7651, United States of America
[c] U.S. Geological Survey, Leetown Science Center, Kearneysville, WV 25430, United States of America

HIGHLIGHTS

- Bioactive contaminants (BCs) in Rocky Mountain NP may threaten native aquatic species.
- BCs were detected in water and sediment from both remote and accessible locations.
- Detected BCs have natural, local human, atmospheric or multiple sources.
- 28 pharmaceuticals were detected in water, most excreted primarily in human urine.
- 12% of male fish had elevated Vtg, 18% of water samples had elevated estrogenicity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 April 2018
Received in revised form 12 June 2018
Accepted 12 June 2018
Available online xxxx

Editor: D. Barcelo

Keywords:
Pharmaceuticals
Hormones
Pesticides
Streams
Lakes
National Parks

ABSTRACT

Pharmaceuticals, hormones, pesticides, and other bioactive contaminants (BCs) are commonly detected in surface water and bed sediment in urban and suburban areas, but these contaminants are understudied in remote locations. In Rocky Mountain National Park (RMNP), Colorado, USA, BCs may threaten the reproductive success and survival of native aquatic species, benthic communities, and pelagic food webs. In 2012–2013, 67 water, 57 sediment, 63 fish, 10 frog, and 12 quality-control samples (8 water and 4 sediment) were collected from 20 sites in RMNP. Samples were analyzed for 369 parameters including 149 pharmaceuticals, 22 hormones, 137 pesticides, and 61 other chemicals or conditions to provide a representative assessment of BC occurrence within RMNP. Results indicate that BCs were detected in water and/or sediment from both remote and more accessible locations in RMNP. The most commonly detected BCs in water were caffeine, camphor, para-cresol, and DEET; and the most commonly detected BCs in sediment were indole, 3-methyl-1H-indole, para-cresol, and 2,6-dimethyl-naphthalene. Some detected contaminants, including carbaryl, caffeine, and oxycodone, are clearly attributable to direct local human input, whereas others may be transported into the park atmospherically (e.g., atrazine) or have local natural sources (e.g., para-cresol). One or more pharmaceuticals were detected in at least 1 sample from 15 of 20 sites. Most of the 29 detected pharmaceuticals are excreted primarily in human

* Corresponding author.
E-mail address: wbattagl@usgs.gov (W.A. Battaglin).

https://doi.org/10.1016/j.scitotenv.2018.06.150
0048-9697/Published by Elsevier B.V.

urine, not feces. Elevated net estrogenicity was observed in 18% of water samples, and elevated vitellogenin in blood was observed in 12% of male trout, both evidence of potential endocrine disruption. Hormone concentrations in sediment tended to be greater than concentrations in water. Most BCs were observed at concentrations below those not expected to pose adverse effects to aquatic life. Results indicate that even in remote locations aquatic wildlife can be exposed to pharmaceuticals, hormones, pesticides, and other bioactive contaminants.

1. Introduction

Pharmaceuticals, hormones, pesticides, and other industrial and household chemicals are bioactive contaminants (BCs), which are commonly detected in surface water and bed sediment in urban, suburban, and agricultural areas because of the proximity and intensity of their use or their association with wastewater treatment plant (WWTP) discharges, landfills, energy and power production, and/or agricultural and urban runoff (Kolpin et al., 2002, 2004; Barber et al., 2006; Focazio et al., 2008; Monteiro and Boxall, 2010; Opsahl and Lambert, 2013; Luo et al., 2014; Masoner et al., 2015; Bradley et al., 2017a; Bai et al., 2018). More recently BC occurrence has been documented in streams, stream sediments, and groundwater that are not affected by WWTP discharges but may be affected by onsite wastewater disposal systems (OWDS) or other local sources (Barnes et al., 2008; Bradley et al., 2016a, 2016b; Fairbairn et al., 2015, 2016; Fisher et al., 2016; Weissinger et al., 2016, 2018).

Bioactive contaminants are released into the environment as complex chemical mixtures (Buxton et al., 2015; Bradley et al., 2017a), and the corresponding environmental risk is cumulative and can include biochemical, organism, and community-level effects caused by toxicity, endocrine disruption, anti-microbial resistance, behaviour alteration, and other non-lethal effects (Corcoran et al., 2010; Hoffmann and Kloas, 2012; Reif et al., 2012; Rosi-Marshall and Royer, 2012; Gonzalez-Pleiter et al., 2013; Kortenkamp, 2014; Carter et al., 2015). Pharmaceuticals and pesticides, for example, are a concern because of their occurrence in mixtures, relatively high solubility and mobility in aqueous settings, designed bioactivity and biorecalcitrance, and bioaccumulation potential in animals and plants (Sabourin et al., 2012; Rosi-Marshall et al., 2013; Zenobio et al., 2014; Oliveira et al., 2015; Schoenfuss et al., 2016; Tanoue et al., 2015; Xie et al., 2016). Pharmaceuticals and pesticides have been shown to affect predator-prey relations (Painter et al., 2009; Relyea and Edwards, 2010) and alter animal behaviour and chemical-information flow (Brodin et al., 2013; Van Donk et al., 2015; Tosi et al., 2017). Hormones associated with water or sediment can cause endocrine disruption or other adverse gender-related health effects at environmentally relevant concentrations (Filby et al., 2007; Sangster et al., 2016; Ankley et al., 2017). Polycyclic aromatic hydrocarbons (PAHs) are formed as by-products of the combustion of organic materials. They are present in auto exhaust, power plant emissions, and wildfire emissions, and are used as chemical intermediates, solvents, and in some personal care products (Abdel-Shafy and Mansour, 2016), and they can be carcinogenic and immunotoxic to wildlife (Reynaud and Deschaux, 2006; Gerner et al., 2017).

There is an abundance of literature on the analytical detection, occurrence, transport, and fate of contaminants of emerging concern (CEC) of which BCs are a subset (Daughton, 2016; Noguera-Oviedo and Aga, 2016). BCs may threaten the reproductive success and survival of native aquatic species, benthic communities, and pelagic food webs; however, studies of BCs occurrence and fate in protected areas are limited (VanderMeulen, 2015; Weissinger, 2015; Weissinger et al., 2016; Bradley et al., 2017b; Forrester et al., 2017), and adverse-effect thresholds for native biota are lacking (Rosi-Marshall and Royer, 2012; Maruya et al., 2013, 2016). Also, endocrine disrupting chemicals may have non-monotonic dose-response relationships with documented effects below historical toxicity thresholds (Vandenberg et al., 2012; Zoeller and Vandenberg, 2015).

The demonstrated occurrence of BC effects (Jorgenson et al., 2018), even in remote areas of National Parks (Ackerman et al., 2008; Landers et al., 2008), illustrates the need for ecosystem-specific information on BC occurrence and distribution in Rocky Mountain National Park (RMNP), an International Biosphere Preserve, which includes 3 distinct ecosystems (montane, subalpine, alpine tundra), 147 lakes, and approximately 1076 (square kilometers) km^2 of area in north-central Colorado, USA. Much of RMNP is at high elevation with 118 named peaks between 3048 and 4346 m. Public infrastructure at RMNP includes 5 visitor centers, 6 campgrounds with about 580 camp sites, about 260 backcountry camp sites, about 200 km (km) of roads, and approximately 571 km of publically accessible trails (National Park Service, 2015). Park use exceeded 3.4 million people in 2014, making RMNP the fifth most visited National Park in that year (National Park Service, 2018). More than 70% of RMNP visits occur during the summer months of June–September. Visitation pressure is greatest near roads and trailheads, and most visitors either do not hike or only hike a short distance when visiting the park (Collingwood et al., 2007; Theobald et al., 2010). At RMNP, toilet facilities are provided at visitor centers, many trailheads, and other heavily visited sites. A 2010 survey of park visitors indicated that toilets were the second most accessed park facility (used by 86% of visitors) after roads (used by 92%) (Blotkamp et al., 2011).

Potential internal BC sources at RMNP include wastewater treatment facilities, flush/vault toilets and septic systems, grey-water sinks, recreational vehicle dump stations, and individual waste releases in backcountry areas. In addition, evidence of airborne BC transport to RMNP from external sources was provided by the Western Airborne Contaminants Assessment Program (WACAP) (Ackerman et al., 2008; Landers et al., 2008), and by others (Goolsby et al., 1997; Mast et al., 2007). Risk management options for BCs depend on whether the primary sources of the BCs are internal and under direct park service management or external and addressable only through indirect mechanisms. The primary sources to and associated chemical compositions of potential BC mixtures are expected to vary significantly from lower altitude, higher-use areas near trailheads (many human and animal sources) to higher altitude, lower-use areas far from trailheads (limited human sources and atmospheric transport from remote sources).

A spatial assessment of BC occurrence was conducted in RMNP to address the expected range of potential BC sources, contaminant profiles, ecosystem sensitivities, and associated management alternatives. Specific study objectives were to: (1) provide a representative assessment of BC occurrence and distribution for surface-water ecosystems within RMNP; (2) interpret BC occurrence and distribution data in the context of U.S. Environmental Protection Agency (EPA) National Water Quality Criteria or benchmarks for aquatic life (U.S. Environmental Protection Agency, 2018a, 2018b), estrogenicity bioassay results, and other factors including distance from trailheads, travel time from trailheads on foot, and site elevation, and (3) provide a scientific foundation for future decisions on management practices or procedures to reduce or remove recognized BC sources (local human and animal) internal to RMNP.

2. Methods

2.1. Study sites

Water and sediment samples were collected from 20 locations in RMNP representing a range of site types including: 9 stream sites, 9