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Spatio-temporal bioaccumulation and trophic transfer of ionizable pharmaceuticals in a semi-arid urban river influenced by snowmelt

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ABSTRACT

Bioaccumulation of pharmaceuticals in aquatic organisms is increasingly reported in the peer-reviewed literature. However, seasonal instream dynamics including occurrence and bioaccumulation across trophic positions are rarely studied, particularly in semiarid streams with flows influenced by seasonal snowmelt and municipal effluent discharges. Thus, we selected East Canyon Creek in Park City, Utah, USA to examine spatio-temporal bioaccumulation of select ionizable pharmaceuticals across trophic positions using trophic magnification factors calculated at incremental distances (0.15, 1.4, 13 miles) downstream from a municipal effluent discharge during spring (May), Summer (August), and fall (October). Nine target analytes were detected in all species during all sampling events. Trophic dilution was consistently observed for amitriptyline, caffeine, diphenhydramine, diltiazem, fluoxetine, and sertraline, regardless of seasonal instream flows or distance from effluent discharge. Calculated TMFs ranged from 0.01–0.71 with negative slopes observed for all regressions of chemical residue in tissue and trophic position. We further presents the first empirical investigation of normalizing pharmaceutical concentrations to lipid, phospholipid or protein fractions using pair matched fish samples. Empirical results identify that normalization of ionizable pharmaceutical residues in aquatic tissues to neutral lipids, polar lipids, or the total protein fraction is inappropriate, though bioaccumulation studies examining influences of internal partitioning (e.g., plasma proteins) are needed.

1. Introduction

Over the last 50 years the human population has grown from 2.5 billion to 6.8 billion worldwide, and is predicted to increase to 9.8 billion by 2050 with 66% of people residing in urban centers [1,2]. Global industrialization has focused populations in urban areas including megacities [3,4] and increased fossil fuel consumption has led to climate change, including elevated global temperatures [1]. Water resource management has thus become more complex in response to increased demand for already stressed aquatic resources, and diverse anthropogenic stressors [1,3]. For example, elevated global temperatures and altered weather patterns are decreasing snowpack, which is currently relied on by over 2 billion people annually for water resources and associated instream flows [5]. Further, it is increasingly common for multiple urban centers to utilize common watersheds for water withdrawals and return flows of reclaimed water, leading to an urbanizing water cycle [6] that results in concentrated effluent discharge and constituents therein to receiving systems [7,8]. Such discharges include diverse contaminants of emerging concern (CECs), including active pharmaceutical ingredients (APIs).

With ~3000 APIs currently administered in Europe, the United States, and Asia, studies have increasingly examined bioaccumulation,

Abbreviations: ACE, acetaminophen; AMI, amitriptyline; ARI, aripiprazole; BEN, benzoylecgonine; BUP, buprenorphine; CAF, caffeine; CAR, carbamazepine; DIC, diclofenac; DIL, diltiazem; DIP, diphenhydramine; DUL, duloxetine; FLU, fluoxetine; MPH, methylphenidate; NOR, norfluoxetine; PROM, promethazine; SER, sertraline; AML, amlodipine; DES, desmethylsertraline; SUC, sucralose

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hazards and risks to aquatic organisms [8,9]. Because APIs and their metabolites are designed to be biologically active molecules [10] and have conserved targets across vertebrates, a range of sub-lethal responses and adverse outcomes in aquatic organisms can be linked to therapeutic activity at sufficient internal concentrations [11–13]. Pharmaceuticals were historically considered to be less likely than legacy persistent organic contaminants to bioaccumulate in aquatic systems due to greater water solubility and routine detection at ng/L to μg/L levels in developed countries [4,14]. However, during dry months, particularly in arid and semi-arid regions, base flows of urban rivers and streams can be effluent dominated or even dependent, resulting in increased effective exposure durations of APIs to aquatic life [15]. Effluent influenced urban ecosystems can represent worst-case scenarios for potential accumulation and effects of APIs and other consumer chemicals in surface waters [8,16]. Thus, identifying conditions where APIs pose higher risks to aquatic wildlife and understanding the bioaccumulation potential, exposure pathways, and trophic transfer of APIs in ecosystems was recently identified as major research needs to define ecological risks [13,17,18] and ensure sustainable environmental management and ecosystem services [13,19,20].

Trophic magnification represents a particularly important aspect of bioaccumulation studies and regulatory determinations of chemical safety because dietary exposure can result in increasing concentrations of a contaminant with increasing trophic position, and ultimately present risks of adverse outcomes to aquatic and terrestrial wildlife and humans [21]. The extent of trophic magnification in an ecosystem can be quantified using trophic magnification factors (TMFs), defined as an empirical relationship of contaminant concentration with trophic positions [19–22]. High quality field based TMF studies are proposed as highly relevant to assess and identify substances for regulatory determinations as bioaccumulative because such studies possess all relevant routes of exposure and ecological processes that may influence bioaccumulation [20,21,23]. To date TMF studies have primarily been calculated for nonionizable chemicals [20,27] and TMF studies investigating APIs have mainly occurred in laboratory experiments [28–34], while field studies investigating trophic transfer of ionizable APIs in aquatic ecosystems are scarce [9,35,36]. We reported the first TMF study on APIs from the North Bosque River, a semi-arid effluent dominated stream located in Texas, USA, in which we observed trophic dilution (TMF < 1.0), instead of trophic magnification (TMF > 1.0), for two pharmaceuticals, diphenhydramine and carbamazepine [36]. Subsequent studies in Lake Taihu, China similarly identified trophic dilution for additional pharmaceuticals [9,35]. However, whether such observations extend to other ionizable APIs and systems with different ecological complexity remain elusive.

When deriving a field TMF a common presumption is that exposure and ecosystem conditions are ubiquitous for all organisms, regardless of sampling location. However, this assumption ignores non-uniform patterns in exposure concentrations, which have been shown to significantly affect the calculation of TMFs, at different sampling sites even when such gradients are expected to exist, especially for APIs, due to point source discharges such as wastewater treatment plants [21,23]. Though TMFs have mainly been calculated for hydrophobic chemicals requiring fugacity normalization of lipid content [27], this practice was initially identified by our group as inappropriate for ionizable APIs in fish [37] and more recently confirmed by others [28]. However, normalization of API tissue residues to the protein or phospholipid fraction may be appropriate because a majority of APIs bind to plasma proteins and phospholipids [38].

Herein, we examined the spatial and temporal exposure, bioaccumulation, and trophic transfer of APIs in multiple trophic positions from a semi-arid river, East Canyon Creek, Utah, USA. In this dynamic system, instream flow fluctuates due to seasonal snow melt and continuous effluent discharge. Target pharmaceuticals were quantified in water and biota samples from East Canyon Creek collected during spring, summer, and fall sampling events at an upstream reference site and incremental distances downstream from an effluent discharge. To examine the influence of pharmaceutical partitioning on bioaccumulation in brown trout (*Salmo trutta)* the octanol-water distribution coefficient (D_{ow}), membrane-water distribution coefficient (D_{mw}), albumin-water distribution coefficient (D_{BSAw}), and muscle protein-water distribution coefficient (D_{mpw}) were calculated and regressed against calculated BAFs. Total lipids, neutral (storage) lipids, polar (phospholipids) lipids, and protein content were determined in paired fish samples to examine whether fugacity normalization of ionizable APIs to protein or phospholipids was appropriate. Finally, stable isotopes $\delta^{15}N$ and $\delta^{13}C$ were measured to map functional food chains and identify trophic positions of sampled stream biota, and TMFs were then calculated at each site downstream from a municipal effluent discharge during three seasons to examine whether spatial and temporal differences influenced trophic transfer of APIs.

2. Methods and materials

2.1. Study site

The East Canyon Creek watershed is located east of Salt Lake City, Utah, USA, spread over the western stretch of Summit and Morgan Counties (Fig. 1). The East Canyon Water Reclamation Facility (ECWRF) discharges to East Canyon Creek near Park City, Utah. ECWRF has a design capacity of ~15,000 m^3 day^{-1} (~4.0 million gallons/day) with a mean daily load of ~11,500 m^3 day^{-1} (~3.0 million gallons/day). East Canyon Creek is located in the semi-arid mountainous region of Utah and receives ~60% of annual precipitation during the winter. As a result, stream discharges in East Canyon Creek are elevated due to snowmelt during spring and early summer months.

2.2. Field sampling

Samples from East Canyon Creek were collected during spring (4–7 May), summer (17–21 August), and fall (27–31 October) of 2014. Sampling dates encompassed high flow conditions from snow melt (spring) and lower flow semi-arid conditions later in the year (summer and fall). Collection occurred at an upstream reference site, previously investigated by our research team [39], and at incremental distances downstream (0.15, 1.4, 13 miles) from the ECWRF discharge (Fig. 1). Traditional water quality parameters, pH, specific conductance, DO, and temperature were measured at each site during each season for ~24 h using pre- and post-deployment calibrated multiparameter datasondes. Water samples for total nitrogen, total phosphorus, dissolved nitrogen, and orthophosphate were collected from each site and the effluent discharge. Duplicate water samples for targeted APIs were collected using acetone cleaned 4 L amber glass bottles at each sampling site and from the ECWRF discharge during each sampling event. Utah Department of Natural Resources (UDNR) protocols were followed for backpack electroshock collection of two common fish species, the brown trout (*Salmo trutta*) and mottled sculpin (*Cottus bairdii*). Fish length and weight were measured on site immediately after anesthetization using MS-222. Periphyton was collected by scrapping a 2 x 2 inch cross section of rocks found at each sampling site. We specifically collected and sorted macroinvertebrates including mayflies (*Ephemerella* sp.), crane fly *(Tipula* sp.*)*, snails (*Lymnaeidea* & *Physidae),* and caddis fly (Trichopterans: *Helicopsyche sp*. & *Hydropsyche sp*.) using standard kick net techniques.

2.3. Sample preparation and pharmaceutical analysis

Water samples were filtered and concentrated to solid phase extraction (SPE) cartridges following previously reported methods [40–43]. Similarly, tissue samples of collected organisms were extracted following previously reported methods [36,44–46]. Water and tissue samples of collected organisms were analyzed using isotope-