Science of the Total Environment 737 (2020) 140222

Contents lists available at ScienceDirect

Science of the Total Environment

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

Spatial and seasonal occurrence of semi-volatile organic compounds (SVOCs) in fish influenced by snowmelt and municipal effluent discharge

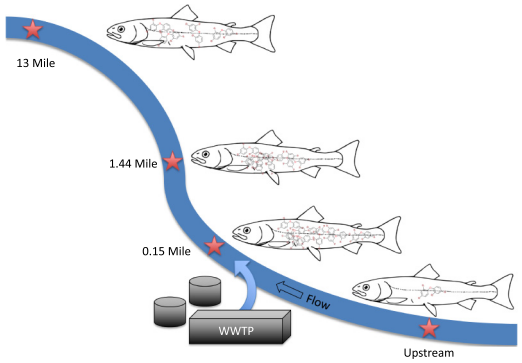
Yelena Sapozhnikova [a,*], Amina Salamova [b], Samuel P. Haddad [c], S. Rebekah Burket [c], Michael Luers [d], Bryan W. Brooks [c,e]

[a] USDA, Agricultural Research Service, Eastern Regional Research Center, Wyndmoor, PA, USA
[b] Paul H. O'Neill School of Public and Environmental Affairs, Indiana University, Bloomington, IN, USA
[c] Department of Environmental Science, Center for Reservoir and Aquatic Systems Research, Baylor University, Waco, TX, USA
[d] Snyderville Basin Water Reclamation District, Park City, UT, USA
[e] Guangdong Key Laboratory for Environmental Pollution and Health, School of the Environment, Jinan University, Guangzhou, China

HIGHLIGHTS

- Seasonal and spatial accumulation of 218 lipophilic contaminants was examined in fish.
- The sampling sites were influenced by snowmelt and municipal effluent discharge.
- No seasonal differences or snowmelt influence were observed.
- PBDEs were detected at highest levels in fish collected close to the effluent discharge.
- Screening level consumption risks were calculated following EPA methods.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 September 2019
Received in revised form 8 June 2020
Accepted 12 June 2020
Available online 15 June 2020

Editor: Damia Barcelo

Keywords:
SVOCs
Pesticides
Environmental contaminants
Fish
Municipal effluent discharge

ABSTRACT

In the present study we examined spatial and seasonal trends in the levels of a wide suite of semi-volatile organic compounds (SVOCs) in brown trout (*Salmo trutta*) and mottled sculpin (*Cottus bairdii*) in East Canyon Creek, Utah, USA, an effluent-dominated stream during summer months. Fish samples were collected from four sampling sites, including one reference site upstream, and three sites at incremental distances downstream of the effluent discharge over multiple seasons. The samples were analyzed for 218 lipophilic contaminants, including pesticides and their metabolites, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and polybrominated diphenyl ethers (PBDEs) and other flame retardants. Some PAHs, pesticides and their metabolites, PCBs, PBDEs and other flame retardants were measured in mottled sculpin (11 analytes) and brown trout (17 analytes). Hexachlorobenzene (HCB), *p,p′*-DDE, BDE-47 and triphenyl phosphate (TPHP) were the most frequently detected contaminants in mottled sculpin and brown trout, while BDE-47 and *p,p′*-DDE were measured at the highest concentrations, reaching up to 73 and 19 ng/g wet weight, respectively. Our results indicated that snowmelt did not alter accumulation of the examined lipophilic contaminants, and no consistent seasonal differences were observed in their accumulation. A spatial pattern was observed for PBDE congeners, where lowest levels were measured in fish tissues from a reference site, and highest concentrations were measured in fish collected downstream of the effluent discharge, indicating that municipal effluent discharge contributes to the elevated PBDE levels in fish residing in this effluent-dominated stream. We further calculated screening level consumption risks following United States Environmental Protection Agency (EPA) methods,

* Corresponding author.
E-mail address: yelena.sapozhnikova@usda.gov (Y. Sapozhnikova).

https://doi.org/10.1016/j.scitotenv.2020.140222
0048-9697/Published by Elsevier B.V.

and identified the importance of considering discharge gradients in effluent-dominated systems during bioaccumulation assessments.

Published by Elsevier B.V.

1. Introduction

Water resources are often influenced by return flows from wastewater treatment plant discharges, and in arid and semi-arid regions instream flows of surface waters can be dominated by or even dependent on effluent discharges (Brooks et al., 2006). Because introduction rates of contaminants in these effluents often exceed environmental degradation rates, effective exposure duration to organic contaminants is elevated in effluent-dominated and dependent streams and rivers (Ankley et al., 2007). Such urbanizing aquatic systems are recognized as important locations for water management (Luthy et al., 2015), particularly in the western United States where climate change is predicted to further stress water resource management efforts. Relatively little information is known about environmental exposure to and bioaccumulation of contaminants in effluent-dominated systems influenced by snowmelt. For example, over 2 billion people rely on snowmelt for potable source water, which also sustains instream flows in numerous regions around the world (Mankin et al., 2015). Herein, understanding influences of climate change on the fate and effects of environmental contaminants has recently been identified as a priority environmental quality research need (Fairbrother et al., 2019).

Many anthropogenic contaminants such as semi-volatile organic compounds (SVOCs) tend to bioaccumulate in fish. SVOCs include contaminants such as organochlorine pesticides, polybrominated diphenyl ethers (PBDEs), organophosphate esters (OPEs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs), among others. Some of the most persistent and toxic SVOCs are recognized as persistent organic pollutants (POPs) and included in the Stockholm Convention, calling for a global ban on the production and use of these compounds. For example, PBDEs used as flame retardants since the 1970s, were phased out in the United States during 2004–2013 due to their bioaccumulation potential and toxicity. As a result, other chlorinated, brominated, and phosphorous compounds are now widely used as flame retardants in many commercial formulations, thus entering the environment in high quantities (Ali et al., 2012; Covaci et al., 2011). Several scientific reports have emerged on the occurrence of flame retardants in municipal wastewater treatment plants (WWTP) effluents and the streams they discharge. For example, a study from China reported total PBDE concentrations (the sum of BDE-28, -47, -99, -100, -153, -154, -183, and -209) at 37 ng/L in the WWTP effluent, while at 33 and 8 ng/L in the river water downstream and upstream of the discharge, respectively (Wang et al., 2013). Because WWTPs are not designed to remove PBDEs or other contaminants, these contaminants are discharged into the surrounding streams and bioaccumulate in aquatic organisms in the effluent dominated streams. A study by Anderson and MacRae (2006) examined PBDE concentrations in tissues of mouth bass (*Micropterus dolmieui*) collected upstream and downstream of WWTP outfall in Maine, USA (Anderson and MacRae, 2006) and found PBDE levels at 800–1810 and 5750–29,000 ng/g lipid in fish collected from upstream and downstream locations, respectively. Besides PBDEs, other flame retardants were found in WWTP effluents, including *tris*(2-chloro-isopropyl)phosphate (TCIPP), *tris*(2-chloroethyl) phosphate (TCEP), and tributyl phosphate (Krzeminski et al., 2017), but information on their occurrence in fish in effluent dominated streams is scarce.

In the present study, we expanded our earlier work in East Canyon Creek, Utah, USA (Haddad et al., 2018), an effluent-dominated river that is influenced by snowmelt, to examine spatial and seasonal accumulation of selected SVOCs in brown trout (*Salmo trutta*) and mottled sculpin (*Cottus bairdii*). East Canyon Creek is managed as a brown

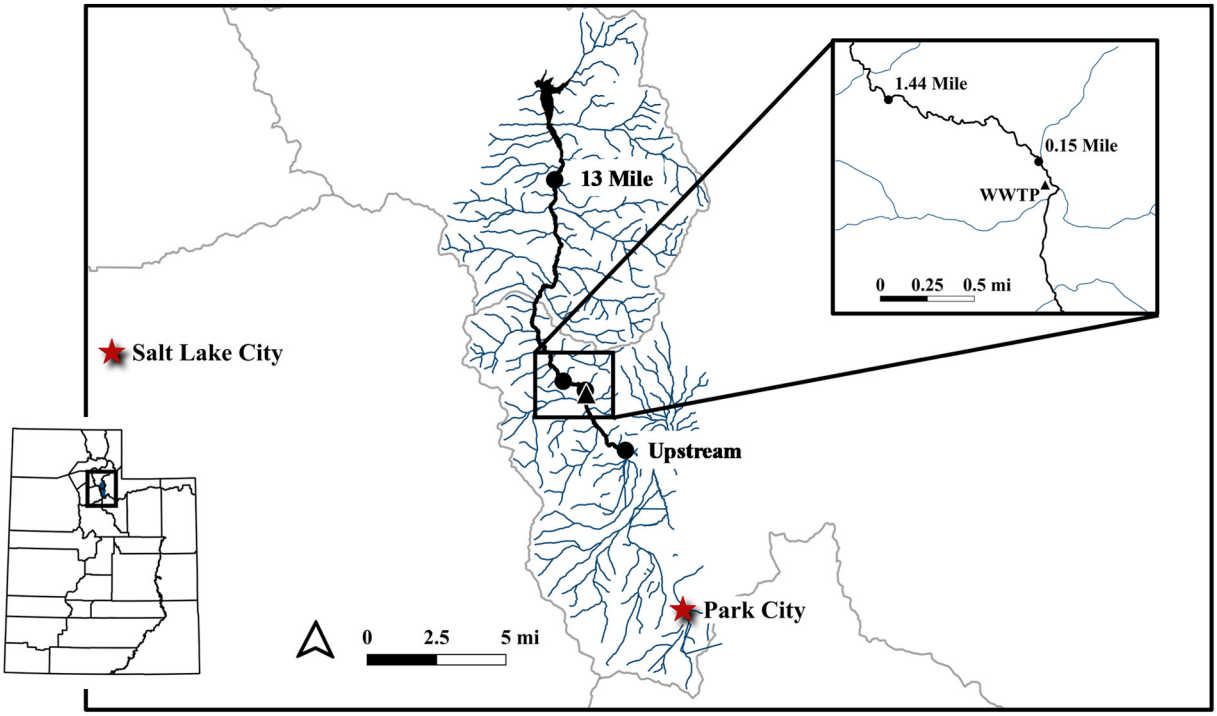


Fig. 1. East Canyon Creek is located in Utah, USA. Black dots represent 4 sampling locations: reference site and 0.15 mile, 1.44 miles, and 13 miles downstream from the effluent discharge.

trout fishery (SWCA Environmental Consultants, 2010). Brown trout is a relatively large predatory fish with a life span of >10 years, and a predator of mottled sculpin, which is a smaller fish with a life span of ~6 years, and thus occupies a lower trophic position (Haddad et al., 2018). The East Canyon Creek watershed presents a unique semi-arid ecosystem for study, and is located east of Salt Lake City, Utah (Fig. 1). It is influenced by effluent discharge from the East Canyon Water Reclamation Facility (www.sbwrd.org/east-canyon-water-reclamation-facility) and seasonal snow melt, but often becomes effluent-dominated during summer months when instream dilution from snowmelt ends (Haddad et al., 2018). As previously reported (Du et al., 2012), a physical barrier upstream of the effluent discharges prevents fish exposed to the effluent from swimming upstream. Most of the annual precipitation (65–75%) is received as snow in the winter months. During recent droughts, instream dilution of the effluent discharge has disappeared, resulting in effluent dependent downstream flows. Following multiple sampling events, fish tissues were analyzed for 218 contaminants, including 152 pesticides and their metabolites, 14 PCBs recommended for monitoring by the World Health Organization, including dioxin-like PCBs, PAHs, including those from the US EPA priority list and the European Union (EU) 15 + 1 priority PAHs, PBDEs, and other brominated and organophosphate flame retardants.

2. Materials and methods

2.1. Sampling

Following previously reported methods, samples of mottled sculpin (*Cottus bairdii*) and brown trout (*Salmo trutta*) were collected by electrofishing in East Canyon Creek, Utah, USA (Haddad et al., 2018). Fish samples were collected at four sites: upstream (reference site), close to effluent discharge of East Canyon Water Reclamation Facility, and downstream at incremental distances of 0.15, 1.44, 13 miles from the facility (0.24, 2.3, and 21 km, respectively) (Fig. 1). East Canyon Water Reclamation Facility with a capacity of 4 million gallons per day (MGD) and a mean daily load of 3 MGD, collects wastewater from the surrounding areas, returning the reclaimed water to East Canyon Creek, which then flows into East Canyon Reservoir. This WWTP is the only regulated point source discharge within the watershed. To examine potential seasonal trends associated with varying instream flows, sample collection occurred during spring (May) reflecting highest flow from snow melt, summer (August) and fall (September, October) of 2014, representing lowest flow conditions (Fig. 2). Fish samples of both species were collected in triplicate from each site at each sampling event (total $n = 84$). However, only brown trout samples were collected in September. Collected mottled sculpin fish ($n = 36$) ranged from 7 to 13 cm (average 10 cm) in length with 5–30 g (average 14 g) weight. Brown trout fish ($n = 48$) were 30–58 cm long (average 40 cm) and 255–1852 g (average 620 g) weight.

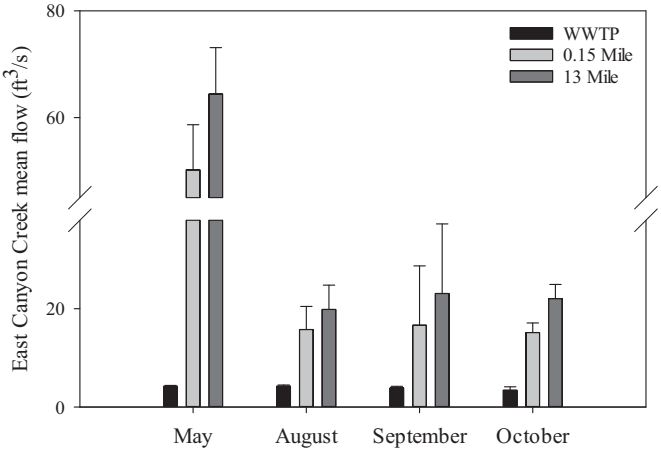


Fig. 2. Average flow ($ft^3/s \pm$ std. deviation) for the WWTP, 0.15 and 13 mile sites. Discharge data for the 0.15 and 13 mile sites was obtained from USGS stream gages, while effluent discharge data was provided by East Canyon Water Reclamation Facility. In May, effluent discharge accounted for ~8% of total stream flow, compared to August (~26%), September (~23%) and October (~22%).

2.2. Chemicals and materials

Standards of pesticides, PAHs, PCBs, PBDEs, and other flame retardants were purchased from Accustandard (New Haven, CT, USA), Sigma Aldrich (St. Louis, MO, USA), Santa Cruz Biotechnology (Santa Cruz, CA, USA), and Restek (Bellefonte, PA, USA). Isotopically labeled internal standards were acquired from C/D/N Isotopes (Pointe-Claire, Quebec, Canada), Cambridge Isotope Laboratories (Andover, MA, USA), Sigma Aldrich, and Accustandard.

Organic solvents were HPLC-grade, and were from Fisher Scientific (Pittsburgh, PA, USA). Anhydrous magnesium sulfate and sodium chloride were purchased from UCT (Bristol, PA, USA). Mini-SPE columns for automated robotic instrument top sample preparation (ITSP) contained 45 mg of anh. $MgSO_4$/primary secondary amine (PSA)/C18/Carbon X sorbents in 20/12/12/1 (w/w/w/w), and were from ITSP Solutions (Hartwell, GA, USA).

2.3. Sample preparation and instrumental analysis

Details on sample preparation were previously reported elsewhere (Burket et al., 2018; Lehotay et al., 2016). Briefly, aliquots of whole-body fish homogenate (2.0 g wet weight (ww)) were placed into 15 mL centrifuge tubes, spiked with the mixture of internal standards (listed in Table S1), vortexed and allowed to stand for 15 min uncapped for the solvent to evaporate. Acetonitrile (2.0 mL) was added, and the tubes were shaken on a vortex shaker for 10 min. A mixture of anh. magnesium sulfate and sodium chloride (2.0 g, 4/1, w/w) was added and the tubes were shaken again for 1 min on the vortex shaker and centrifuged for 3 min at 4150 rpm. Aliquots of the extracts (0.8 mL) were transferred to autosampler vials and subjected to an automated robotic mini solid phase extraction (SPE) cleanup as previously described (Lehotay et al., 2016; Sapozhnikova, 2018). Analysis was conducted by low pressure vacuum outlet gas chromatography-tandem mass spectrometry (GC–MS/MS) operated in the electron ionization (EI) mode (Sapozhnikova and Lehotay, 2015) for 218 analytes and 14 internal standards. The analyte list included 152 pesticides and metabolites, 14 PCB congeners, 23 PAHs, 7 PBDE congeners and 22 other flame retardants listed in Table S1.

2.4. Quality assurance/quality control

Reagent blanks, replicated fish samples, spiked fish samples and NIST SRMs 1946, 1947, and 1974c were analyzed with each batch of samples. Reagent blanks (1.6 mL DI water) were spiked with isotopically labeled internal standards and subjected to the same sample preparation protocol as the samples. Each batch of samples contained fish samples analyzed in replicates to check precision and fish samples fortified with a standard mixture of analytes to check method efficiency. Calibration curves used the ratio of analytes to internal standards and were run in the beginning and the end of each instrumental sequence to ensure the instrument performance.

Method detection limits (MDLs) were calculated based on the student *t*-value $_{(n-1,\ 1-\alpha=0.99)}$ and sample standard deviations for the replicated spiked samples and ranged from 0.2 to 1 ng/g ww (Table S1). Analyte recoveries normalized to internal standards for spiked samples were 65–121%. Reported concentrations were not adjusted for recoveries. Accuracy of measurements for SRMs 1946, 1947, and 1974c ranged from 78 to 123% for PBDEs, 98–140% for PCBs, 67–130% for pesticides, and 56–118% for PAHs (SRM 1974c only).

2.5. Statistical analyses

Statistical analyses were performed using the programming language R (R Core Team, 2013) and the statistical package PAST3 (Hammer et al., 2001), with an alpha of 0.05. Spatial and temporal accumulation of target analytes in brown trout and mottled sculpin were visualized with non-metric multidimensional scaling (NMDS) ordinations constructed in unconstrained space using the Bray-Curtis dissimilarity measure in the R package vegan (Oksanen et al., 2017) and plotted using the package ggplot2 (Wickham, 2016). Observed patterns in multivariate space were tested for significance by performing a one-way randomized/permutation analysis of variance (PERMANOVA; location or season were experimental factors; permutation N = 9999) (Anderson, 2001) with post-hoc pair-wise analysis (Holm-Bonferroni method) using Bray-Curtis dissimilarity in PAST3. Interaction effects were tested using a two-way PERMANOVA (season and location were experimental factors; permutation N = 9999) in PAST3. Target analytes measured <MDL were substituted with half MDL values to represent a detect and non-detect values were substituted with a zero for that sample (Clarke et al., 2006; McCune and Grace, 2002).

Analysis of variance (ANOVA) was conducted to compare chemical concentrations detected in both brown trout and mottled sculpin to determine possible statistical differences (at $p < 0.05$). The concentrations were log-transformed and the non-detects were treated as empty cells.

2.6. Calculations of risk based consumption limits

East Canyon Creek hosts cold water game fishing and is managed as a brown trout fishery (SWCA Environmental Consultants, 2010). Therefore, fish consumption limits were calculated for target analytes detected in brown trout following guidelines described by the US EPA (US EPA, 2000). Several input parameters and assumptions are required for consumption risk calculations and are listed in Table S2. Screening-level consumption risks can be calculated for chemical contaminants with carcinogenic and noncarcinogenic effects. Consumption limits were calculated based on available data for carcinogenic and/or noncarcinogenic health effects in the US EPA Integrated Risk Information System (IRIS) database (https://www.epa.gov/iris). Calculations for daily consumption limits (CR_{lim}) for chemicals associated with carcinogenic health effects followed Eq. (1):

$$CR_{lim} = \frac{ARL * BW}{CSF * C_m} \quad (1)$$

where ARL is the maximum acceptable individual lifetime risk level, BW is consumer body weight (kg), CSF is the oral cancer slope factor $(mg/kg\text{-}d)^{-1}$, and C_m is the maximum measured concentration of the target analyte in fish tissues (mg/kg).

For chemicals associated with noncarcinogenic health effects, CR_{lim} was calculated following Eq. (2):

$$CR_{lim} = \frac{RfD * BW}{C_m} \quad (2)$$

where RfD is the oral reference dose (mg/kg-d) based on a contaminant's noncarcinogenic health effects. BW and C_m are described in Eq. (1).

In both cases, CR_{lim} is representative of the maximum lifetime (assuming 70 years) daily consumption rate that would not be expected to cause adverse health effects and was utilized to calculate weekly fish meal consumption limits following Eq. (3):

$$CR_{mw} = \frac{CR_{lim} * T_{ap}}{MS} \quad (3)$$

where CR_{mw} is the maximum acceptable fish consumption rate (meals/week), CR_{lim} is the maximum acceptable daily fish consumption rate (kg/d), MS is meal size (0.227 kg fish/meal), and T_{ap} is the time averaging period (7 days/week).

3. Results and discussion

3.1. Contaminants in fish tissues

Overall, 11 and 17 contaminants out of 218 targeted analytes were detected in the mottled sculpin and brown trout samples, respectively. Table 1 lists concentration ranges (ng/g ww) and detection frequencies (%), and Tables S3–8 list average concentrations and standard deviations for each sampling site.

Four pesticides and their metabolites, including pentachlorobenzene, pentachloroaniline, *p,p′*-DDE, and hexachlorobenzene (HCB) were detected in both mottled sculpin and brown trout. No trends in concentrations were observed in relation to season or sampling site (Tables S3 and S5) for detected pesticides and metabolites. However, concentrations of *p,p′*-DDE measured in brown trout were significantly higher ($p < 0.001$) compared to mottled sculpin, while the levels of HCBs were significantly greater ($p < 0.001$) in mottled sculpin tissues.

Pentachloroaniline is a metabolite of pesticide pentachloronitrobenzene (Teng et al., 2017) (common name quintozene), widely used in agriculture on variety of crops. Pentachlorobenzene was used in the past as a fungicide and flame retardant, among other applications (Bailey et al., 2009). HCB was used as a fungicide, and *p,p′*-DDE is a metabolite of insecticide DDT. HCB, *p,p′*-DDE, and pentachlorobenzene are POPs included in the Stockholm Convention and their use is banned globally. Similar to our results, both HCB and *p,p′*-DDE were measured in brown trout muscle in another study (Vives et al., 2005b), where HCB and *p,p′*-DDE mean concentrations were 0.3–0.7 ng/g ww and 2–30 ng/g ww, similar to our findings of not detected (ND)-4 and 3–19 ng/g ww for HCB and *p,p′*-DDE, respectively. While *p,p′*-DDE was found at highest concentrations, they were still below the US Food and Drug Administration (US FDA) action level of 5000 ng/g ww for edible fish portion.

Among PAHs, acenaphthylene and phenanthrene were detected in mottled sculpin tissues, while phenanthrene, fluoranthene, pyrene, and cyclopenta(*cd*)pyrene were detected in brown trout (Table 1). Similar to our findings, phenanthrene, fluoranthene, and pyrene were also predominant low molecular weight PAHs measured in brown trout liver collected from a lake in Spain (Vives et al., 2005a), although direct

Table 1
Concentration ranges (minimum-maximum), ng/g wet weight (ww) and detection frequencies (DF) % for detected analytes in mottled sculpin and brown trout tissues.

	Analytes	Mottled sculpin		Brown trout	
		Range, ng/g ww	DF, %	Range, ng/g ww	DF, %
Pesticides	Pentachlorobenzene	ND–3.6	28	ND–19.0	56
	Pentachloroaniline	ND–13.5	54	ND–6.7	44
	p,p′-DDE	ND–2.9	67	2.5–18.8	100
	HCB	2.3–8.5	100	ND–3.8	56
PAHs	Phenanthrene	ND–4.5	64	ND–1.1	23
	Acenaphthylene	ND–1.2	81	ND	
	Fluoranthene	ND		ND–10.2	10
	Pyrene	ND		ND–2.2	25
	Cyclopenta(*cd*)pyrene	ND		ND–3.1	6
PBDEs	BDE-28	ND–1.0	39	ND–3.9	29
	BD-47	ND–22.2	78	ND–72.8	90
	BDE-99	ND–0.7	11	ND–18.1	58
	BDE-100	ND		ND–6.9	56
OPEs	TDCIPP	ND–14	47	ND–3.1	4
	TPHP	0.8–10.1	100	ND–2.8	38
	TBA	ND		ND–4.9	8
	TCIPP	ND		ND–3.1	73
PCBs	PCB 180	ND		ND–2.9	58

ND: not detected.

comparison of concentrations is not possible due to data presented in ng/g dry weight (Vives et al., 2005a) *vs.* wet weight in our study. PAHs were more frequently detected in mottled sculpin (64–81%) compared to brown trout (10–25%) (Table 1).

Out of 14 PCBs tested in this study, only one congener, PCB 180, was detected in brown trout at concentrations of up to 2.9 ng/g ww (Table 1). PCB 180 is a highly chlorinated PCB congener with the log $K_{ow} = 7.2$, suggesting a high bioaccumulation potential in fish. Interestingly, Vives et al. (2005a, 2005b) found that fish age, not lipid content, was the main factor affecting variability of accumulation for contaminants with log $K_{ow} > 5$ (Vives et al., 2005b), including organochlorine pollutants, such as PCBs, in brown trout from a remote high mountain lake in Spain. In their study, PCB 180 was measured at mean concentration of 1.5 and 2.9 ng/g ww for 1 and 13–15 years old brown trout, respectively. In our study, positive correlation was observed between PCB 180 concentrations and fish weight with the highest concentration of PCB 180 (2.9 ng/g ww) measured in a brown trout with highest body weight (1852 g). While fish age was not measured in our study generally higher fish weight is associated with older age.

Among the contaminants measured in this study, PBDE congeners were measured at the highest levels (see Table 1 for ranges, Tables S4 & S7 for average concentrations). The most prevalent congener was BDE-47 measured in 78 and 90% of mottled sculpin and brown trout samples, respectively. BDE-47 concentrations were the highest compared to the levels of other PBDE congeners (22.2–72.8 ng/g ww), followed by BDE-99, −100, and −28. Similar to our findings, BDE-47 was also the most dominant congener found in lake trout from the Great Lakes (Zhou et al., 2019), followed by BDE-99 and -100. However, concentrations of BDE-47 in the Great Lakes trout in 2011–2014 (following the PBDE ban) were ~10 ng/g ww (Zhou et al., 2019). PBDE concentrations found in brown trout tissues were significantly greater ($p = 0.014$) compared to those found in mottled sculpin.

Four organophosphate ester (OPE) flame retardants (triphenyl phosphate (TPHP), *tris*(1-chloro-2-propyl) phosphate (TCIPP), *tris*(1,3-dichloroisopropyl)phosphate (TDCIPP), and 2,4,6-tribromoanisole (TBA)) were detected in fish at concentrations of up to 14 ng/g ww (TDCIPP). Interestingly, TDCIPP and TPHP were found at higher levels in mottled sculpin compared to brown trout, which was contrary to accumulation of PBDEs, suggesting there may be a fish-specific pattern of accumulation, perhaps due to diet, habitat, and migration patterns of fish (Goerke et al., 2004; He et al., 2019). Moreover, TPHP concentrations in mottled sculpin were significantly higher ($p < 0.001$) compared to those in brown trout.

Overall, more contaminants were detected in brown trout (17) compared to mottled sculpin (11). Furthermore, generally the levels measured in brown trout were higher compared to those measured in mottled sculpin. The latter was expected, given that brown trout is at a higher trophic level and has a longer life-span. The exceptions were pentachloroaniline, HCB, phenanthrene, TDCIPP, and TPHP detected at greater levels in mottled sculpin *vs.* brown trout. Choo et al. (2019) examined fish species and habitat-dependent accumulation of PBDEs and other flame retardants for 20 different biota species, and found that species type and habitat play a significant role in the pattern and magnitude of contaminants' accumulation (Choo et al., 2019).

3.2. Seasonal and spatial differences

As noted in Fig. 2, mean discharge from the WWTP did not vary appreciably among the four sampling events. However, mean instream flows during the May sampling event were marked elevated at both the 0.15 (50 ± 8.4 CFS) and 13 miles (64 ± 8.7 CFS) sampling locations compared to August, September, and October, when stream flows were three fold lower at both the 0.15 and 13 miles sites (Fig. 2). Such observation directly relays the importance of snowmelt during the May sampling event in markedly elevating instream flows (Fig. 2). Comparing seasonal concentrations for contaminants found in mottled sculpin, levels of phenanthrene measured in May (0.3–1.5 ng/g ww) were slightly higher compared to other months (0.1–0.9 ng/g ww) (Table S3). The same trend was observed for the flame retardant TDCIPP with concentrations of up to 7.4 ng/g ww in May and 0.2–1.9 ng/g ww in other months (Table S4). Such observations indicate that instream dilution from snowmelt did not reduce exposure to these contaminants and suggest increased discharge or nonpoint source runoff during May. In brown trout, however, highest concentrations of pentachlorobenzene were observed in August (12.6 ng/g ww) and September (19.0 ng/g ww) and were several times higher in comparison to levels measured in May and October (0.2–2.7 ng/g ww). Similarly, the highest concentrations of *p,p′*-DDE were also observed in August (12.3 ng/g ww) and September (18.8 ng/g ww) (Table S5) when instream flows were markedly reduced compared to May. For other contaminants found in fish, no differences were observed among their seasonal levels. These observations starkly contrast our previous observations for more polar ionizable contaminants (Haddad et al., 2018), in which instream flows altered exposure levels and subsequent observation in fish tissues.

We also examined potential for spatial differences in accumulation, and observed PBDE congeners at lowest concentrations from the reference upstream sampling site, and at the highest levels at 0.15–1.44 miles sites downstream from the effluent discharge, following by lower levels or no detection at the 13 miles downstream site (Figs. 3–4). This pattern is likely attributed to PBDE congeners entering East Canyon Creek from wastewater discharge. Most WWTPs are not designed to remove anthropogenic contaminants, including PBDEs. For example, Tabe et al. (2016) reported that during the wastewater treatment process, PBDEs can be removed at 86–96% (based on BDE-209) in WWTP in Ontario, Canada (Tabe et al., 2016), and a similar removal rate of ~80% was reported in China (Wang et al., 2013), but other reports indicated only 20–53% removal efficiency (Deng et al., 2015). Nevertheless, even after ~80% PBDE removal, treated effluent can contain PBDE concentrations of as much as 37 ng/L (Wang et al., 2013), which can explain greater PBDE levels found in fish collected near the municipal discharge in the present study.

Non-metric multidimensional scaling (NMDS) ordinations for mottled sculpin and brown trout displayed spatial and temporal dissimilarity in accumulation patterns for each organism in multivariate space by site and season (Figs. 5–6). Location (shape) and season (color) were applied to organisms in multivariate space as categorical variables to investigate dissimilarity in spatial and temporal accumulation of target analytes in individuals. Spatial accumulation in mottled sculpin tissues was significantly different ($F = 5.684$, $p = 0.0001$) among all sites, while temporal accumulation was again not significantly different ($F = 1.554$, $p = 0.1604$) among all seasons (Fig. 5). Accumulation in brown trout tissues at the 13 mile site was significantly different from the 0.15 and 1.4 miles site ($F = 4.621$, $p = 0.0002$). Temporal accumulation was not significantly different ($F = 0.7172$, $p = 0.7039$) among seasons (Fig. 6). No interaction effects between seasons or locations were observed for mottled sculpin ($F = 1.05$, $p = 0.4129$) or brown trout ($F = 1.4712$, $p = 0.1121$). Here again, lack of seasonal difference in accumulation of these lipophilic organic contaminants contrasts with our previous seasonal observations with accumulation of ionizable pharmaceuticals in fish from East Canyon Creek (Haddad et al., 2018). Such observations identify the importance of dietary exposure for these lipophilic contaminants, compared to ionizable pharmaceuticals for which bioaccumulation appears to be governed by inhalational exposure from water (Haddad et al., 2018).

3.3. Weekly meal consumption limits

Screening-level weekly consumption limits were calculated for target analytes detected in brown trout tissues following EPA guidelines (US EPA, 2000). Risk values for noncarcinogenic and carcinogenic effects are listed in Table 2 and were collected from the EPA IRIS database (https://www.epa.gov/iris). Of the 17 contaminants detected in brown

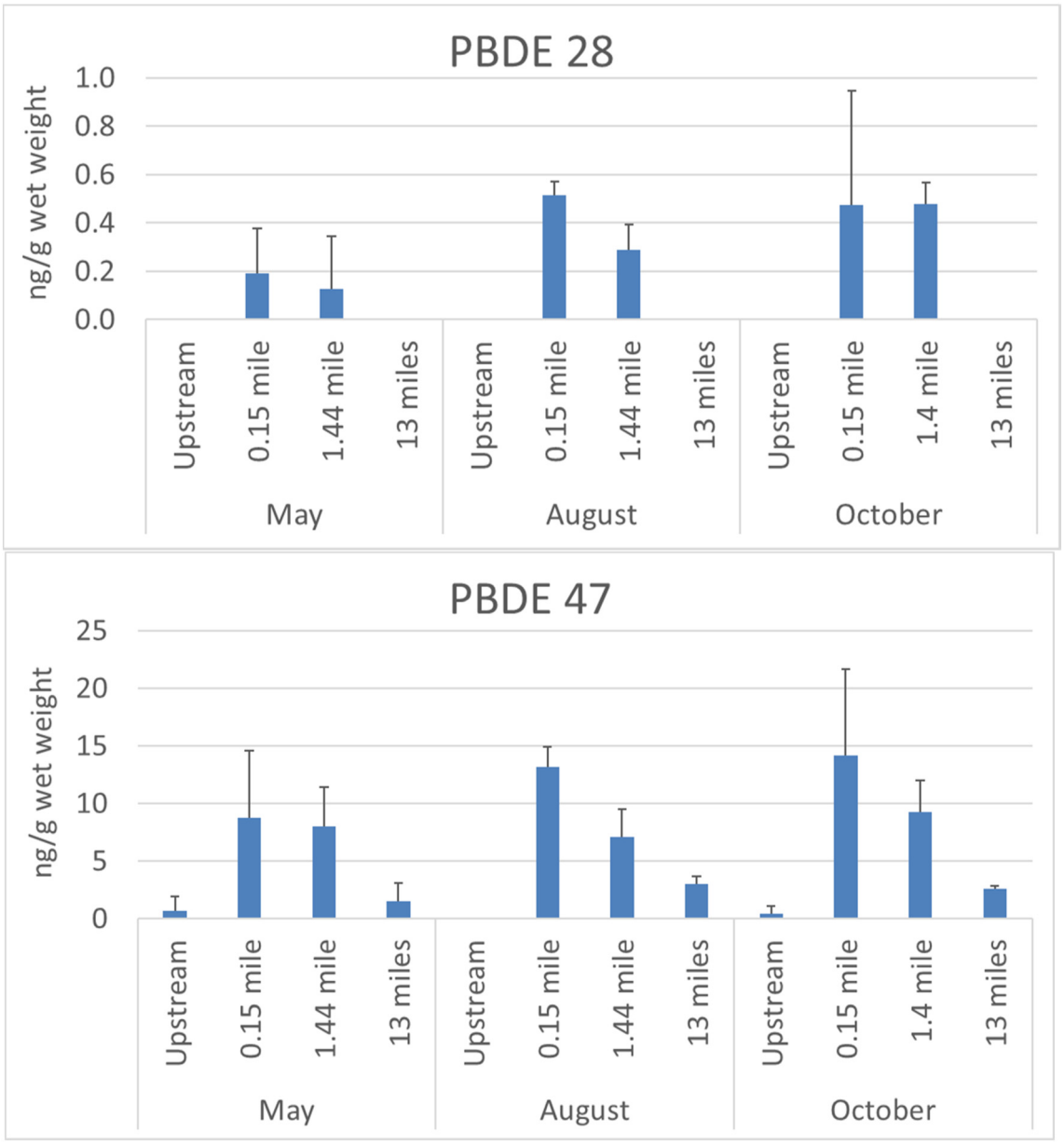


Fig. 3. Average concentrations (ng/g wet weight) of PBDE congeners detected in mottled sculpin tissues. Error bars represent standard deviation for n = 3 (three fish samples collected from the same sampling site).

trout, only 8 are currently listed in the IRIS database, highlighting the need for additional characterization of health effects, particularly for PBDEs and other emerging flame retardants, for which some of the highest tissue concentrations were observed.

Weekly fish consumption limits are presented in Table 3. Values presented represent the number of fish meals per week, assuming a serving size of 0.227 kg (or approximately 8 oz.) per meal. Related to association with noncarcinogenic health effects, only 6 of 17 detected chemicals are listed in the IRIS database, and include 2 pesticides (pentachlorobenzene, HCB), 2 PAHs (fluoranthene, pyrene), and 2 PBDE congeners (BDE-47 and -99). Adverse noncancerous health effects associated with oral exposure to these chemicals include hepatic and urinary systematic effects for the pesticides and PAHs, and nervous system effects for PBDEs. For noncancerous effects, weekly consumption limits ranged from as low as 3 fish meals per week to nearly 30,000 fish meals per week, indicating variable risks associated with consumption of brown trout. For example, the weekly consumption limits were lowest for PBDEs, indicating higher potential for development of noncancerous adverse effects from fish consumption for this class of contaminants, further highlighting the need to perform chronic effects studies for other flame retardants in the future. Weekly fish consumption limits for both pesticides and PAHs were higher than the PBDEs, and indicated that for at least for these compounds, there was low risk associated with tissue concentrations detected in this study.

When carcinogenic health effects were considered, detected chemicals in edible fish have a much lower weekly consumption limit, ranging from only 3 to 4 meals per week. However, it is important to note that only 3 of our 17 detected analytes have thresholds for carcinogenic adverse health effects listed in the EPA IRIS database: *p,p′*-DDE, HCB, and PCBs. For each of these chemicals, the oral cancer slope factor is associated with development of hepatic tumors. The remaining contaminants are either listed as noncarcinogenic due to a lack of testing or insufficient data on chemical carcinogenicity.

Weekly consumption limits were calculated with detected concentrations from whole body homogenates, and while all fish weighed >0.227 kg, future studies focused on concentrations in only the edible

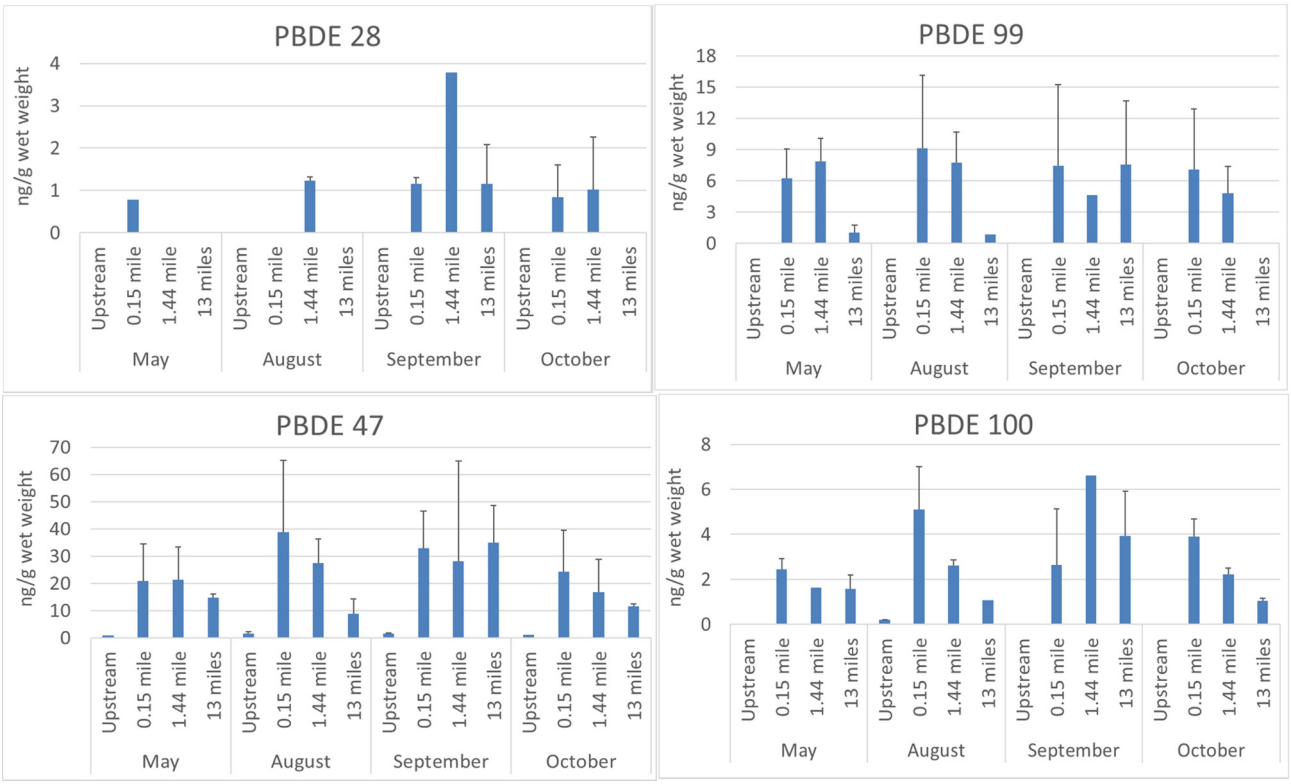


Fig. 4. Average concentrations (ng/g wet weight) of PBDE congeners detected in brown trout tissues. Error bars represent standard deviation for n = 3 (three fish samples collected from the same sampling site). *No detect values were substituted with a zero, resulting in no error bars.

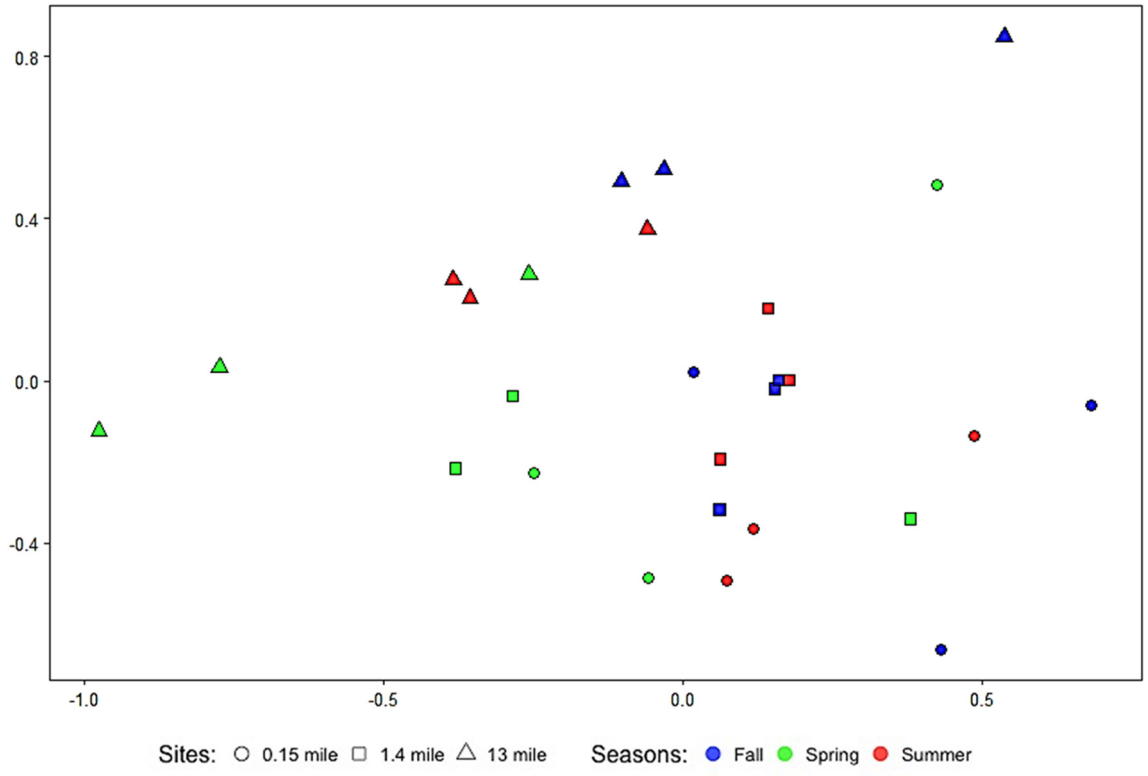


Fig. 5. Nonmetric multidimensional scaling (NMDS) ordinations of detected targeted analyte concentrations in mottled sculpin tissues at all distance during all seasons downstream of the East Canyon Water Reclamation Facility discharge to East Canyon Creek, Park City, Utah, USA.

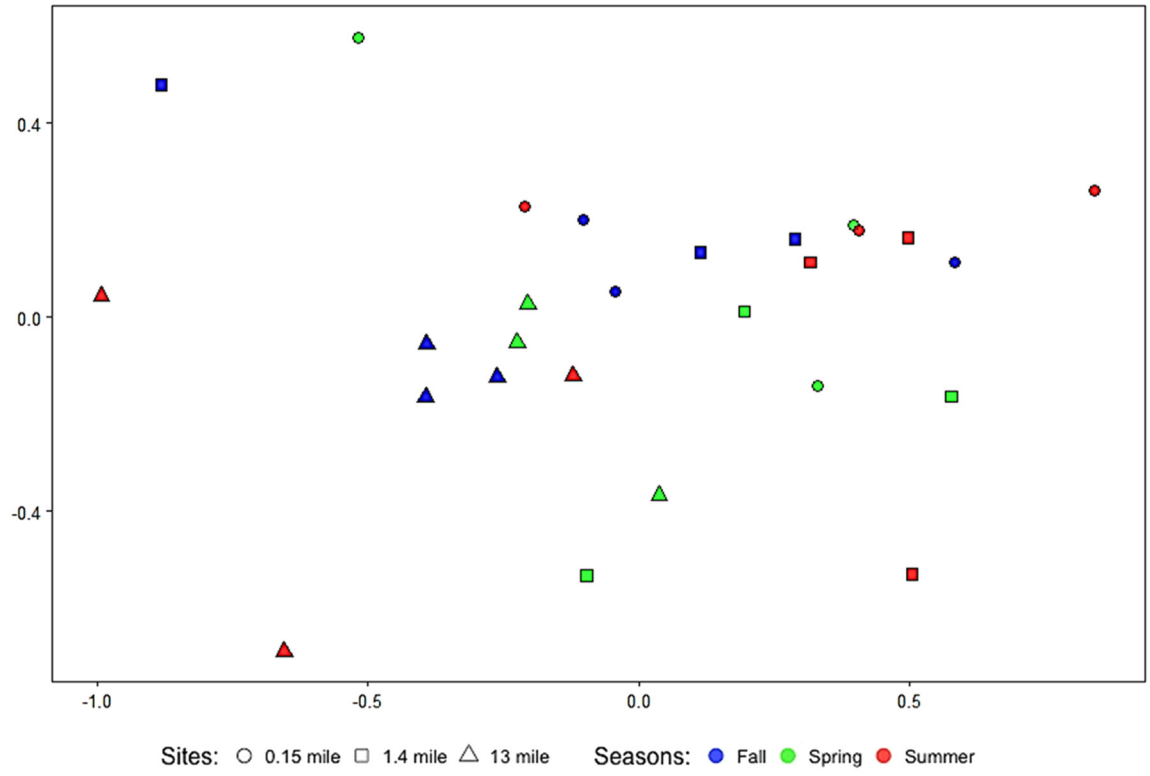


Fig. 6. Nonmetric multidimensional scaling (NMDS) ordinations of detected targeted analyte concentrations in brown trout tissues at all distance during all seasons downstream of the East Canyon Water Reclamation Facility discharge to East Canyon Creek, Park City, Utah, USA.

Table 2
Risk values used in risk-based consumption limit tables for target analytes detected in brown trout tissue.

Target analyte	Noncarcinogenic health effects[a]	Carcinogenic health effects[b]
	Chronic Rfd[c] (mg/kg-d)	CSF[c] $(mg/kg\text{-}d)^{-1}$
Pesticides and metabolites		
Pentachlorobenzene	0.0008	NA
Pentachloroaniline	NA	NA
p,p′-DDE	NA	0.34
HCB	0.0008	1.6
PAHs		
Phenanthrene	NA	NA
Fluoranthene	0.04	NA
Pyrene	0.03	NA
Cyclopenta(*cd*)pyrene	NA	NA
PBDEs		
BDE-28	NA	NA
BDE-47	0.0001	NA
BDE-99	0.0001	NA
BDE-100	NA	NA
OPEs		
TDCIPP	NA	NA
TPHP	NA	NA
TBA	NA	NA
TCIPP	NA	NA
PCBs		
PCB-180	NA	2

NA = no values available in EPA IRIS database.
[a] Chronic, systemic effects.
[b] Assuming a 1 in 100,000 risk level.
[c] Oral reference dose (RfD) and oral cancer slope factor (CSF) obtained from EPA IRIS database.

Table 3
Weekly fish consumption limits for carcinogenic and noncarginogenic health endpoints for target analytes detected in brown trout collected from East Canyon Creek in Utah, USA.

Target analyte	Risk based consumption limit	
	Noncarcinogenic health effects[a]	Carcinogenic health effects[b]
	Fish meals/week	Fish meals/week
Pesticides and metabolites		
Pentachlorobenzene	91	NA
Pentachloroaniline	NA	NA
p,p′-DDE	NA	3
HCB	454	4
PAHs		
Phenanthrene	NA	NA
Fluoranthene	8465	NA
Pyrene	29,435	NA
Cyclopenta(*cd*)pyrene	NA	NA
PBDEs		
BDE-28	NA	NA
BDE-47	3	NA
BDE-99	12	NA
BDE-100	NA	NA
OPEs		
TDCIPP	NA	NA
TPHP	NA	NA
TBA	NA	NA
TCIPP	NA	NA
PCBs		
PCB-180	NA	4

NA = no values available in EPA IRIS database.
[a] Chronic, systemic effects.
[b] Assuming a 1 in 100,000 risk level.

portion of the fish are needed to improve the screening level risk-based calculations reported here. Further, several assumptions are included in consumption limit calculations, including body weight, fish serving size, and weekly limits that are based on a 7-day timeframe, which may not account for more acute exposure if one or two large meals are consumed over a shorter period of time. These calculations also only consider risks associated with a single contaminant, which is often not representative of real-world conditions where a single fish might include several contaminants with low consumption limits. Still, this screening level approach can highlight contaminants of interest for future studies.

4. Conclusions

In the present study, we expanded our previous efforts in East Canyon Creek, Utah, USA, with polar ionizable contaminants to examine spatial and seasonal occurrence of 218 SVOCs, including pesticides and their metabolites of concern, PCBs, PAHs, PBDEs, and other flame retardants in mottled sculpin and brown trout. Unlike our previous observations of ionizable pharmaceuticals in these fish species, in which snowmelt altered accumulation (Haddad et al., 2018), for which accumulation appears to be governed by inhalational exposure from water and not diet, we did not observe consistent seasonal differences in accumulation of the lipophilic contaminants examined here. Such an observation indicates the importance of trophic transfer of these SVOCs. Out of 218 targeted contaminants, 11 and 17 were detected in mottled sculpin and brown trout, respectively. They included four PAHs (phenanthrene, acenaphthylene, fluoranthene, and cyclopenta[*cd*]pyrene); four pesticides and metabolites (pentachlorobenzene, pentachloroaniline, HCB, and *p,p′*-DDE); PCB 180, four PBDE congeners (BDE-28, -47, -99, and -100); and four OPE flame retardants (TPHP, TCIPP, TDCIPP, and TBA). Among pesticides and their metabolites, *p,p′*-DDE and HCB were detected in almost all of the fish samples. BDE-47 and TPHP were also detected in up to 100% of fish samples. BDE-47 and *p,p′*-DDE were measured at highest concentrations, reaching up to 73 and 19 ng/g ww, respectively.

Different patterns of contaminant accumulation were observed between mottled sculpin and brown trout, which occupy different trophic positions and have different life-spans (Haddad et al., 2018). Phenanthrene and TDCIPP were detected at higher concentrations in May compared to other seasons when instream flows were three fold higher, while pentachlorobenzene and *p,p′*-DDE were detected at higher levels in lowest instream flows months - August and September. PBDE congeners showed a spatial pattern with lowest concentrations measured at the reference upstream sampling site, and highest levels downstream close to the effluent discharge. Such longitudinal gradients of accumulation of these lipophilic contaminants in fish identify the importance of dietary exposure to SVOCs and incorporating site specific considerations of effluent dominated conditions during ecological and health bioaccumulation assessments.

Declaration of competing interest

The authors declare no conflict of interest.

Acknowledgements

Technical assistance of Tawana Simons and LiMei Yun, USDA/ARS, is appreciated. Support for this study was partially provided by the Snyderville Basin Water Reclamation District. We thank staff from the Snyderville Basin Water Reclamation District and the Utah Department of Natural Resources for assistance with collection of field samples.

Disclaimer

Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.140222.

References

Ali, N., Dirtu, A.C., Van den Eede, N., Goosey, E., Harrad, S., Neels, H., et al., 2012. Occurrence of alternative flame retardants in indoor dust from New Zealand: indoor sources and human exposure assessment. Chemosphere 88, 1276–1282.
Anderson, M.J., 2001. A new method for non-parametric multivariate analysis of variance. Austral. Ecol. 26, 32–46.
Anderson, T.D., MacRae, J.D., 2006. Polybrominated diphenyl ethers in fish and wastewater samples from an area of the Penobscot River in Central Maine. Chemosphere 62, 1153–1160.
Ankley, G.T., Brooks, B.W., Huggett, D.B., Sumpter, J.P., 2007. Repeating history: pharmaceuticals in the environment. Environ. Sci. Technol. 41, 8211–8217.
Bailey, R.E., van Wijk, D., Thomas, P.C., 2009. Sources and prevalence of pentachlorobenzene in the environment. Chemosphere 75, 555–564.
Brooks, B.W., Riley, T.M., Taylor, R.D., 2006. Water quality of effluent-dominated ecosystems: ecotoxicological, hydrological, and management considerations. Hydrobiologia 556, 365–379.
Burket, S.R., Sapozhnikova, Y., Zheng, J.S., Chung, S.S., Brooks, B.W., 2018. At the intersection of urbanization, water, and food security: determination of select contaminants of emerging concern in mussels and oysters from Hong Kong. J. Agr. Food Chem. 66, 5009–5017.
Choo, G., Lee, I.S., Oh, J.E., 2019. Species and habitat-dependent accumulation and biomagnification of brominated flame retardants and PBDE metabolites. J. Hazard. Mater. 371, 175–182.
Clarke, K.R., Somerfield, P.J., Chapman, M.G., 2006. On resemblance measures for ecological studies, including taxonomic dissimilarities and a zero-adjusted Bray-Curtis coefficient for denuded assemblages. J. Exp. Mar. Biol. Ecol. 330, 55–80.
Covaci, A., Harrad, S., Abdallah, M.A.E., Ali, N., Law, R.J., Herzke, D., et al., 2011. Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour. Environ. Int. 37, 532–556.
Deng, D., Chen, H.X., Tam, N.F.Y., 2015. Temporal and spatial contamination of polybrominated diphenyl ethers (PBDEs) in wastewater treatment plants in Hong Kong. Sci. Total Environ. 502, 133–142.
Du, B., Perez-Hurtado, P., Brooks, B.W., Chambliss, C.K., 2012. Evaluation of an isotope dilution liquid chromatography tandem mass spectrometry method for pharmaceuticals in fish. J. Chromatogr. A 1253, 177–183. https://doi.org/10.1016/j.chroma.2012.07.026.
Fairbrother, A., Muir, D., Solomon, K.R., Ankley, G.T., Rudd, M.A., Boxall, A.B.A., et al., 2019. Toward sustainable environmental quality: priority research questions for North America. Environ. Toxicol. Chem. 38, 1606–1624.
Goerke, H., Weber, K., Bornemann, H., Ramdohr, S., Plotz, J., 2004. Increasing levels and biomagnification of Persistent Organic Pollutants (POPs) in Antarctic biota. Mar. Pollut. Bull. 48, 295–302.
Haddad, S.P., Luek, A., Scott, W.C., Saari, G.N., Burket, S.R., Kristofco, L.A., et al., 2018. Spatio-temporal bioaccumulation and trophic transfer of ionizable pharmaceuticals in a semi-arid urban river influenced by snowmelt. J. Hazard. Mater. 359, 231–240.
Hammer, Ø., Harper, D.A.T., Ryan, P.D., 2001. PAST: paleontological statistics software package for education and data analysis. Palaeontol. Electron. 4, 1–9.
He, M.J., Lu, J.F., Wei, S.Q., 2019. Organophosphate esters in biota, water, and air from an agricultural area of Chongqing, Western China: concentrations, composition profiles, partition and human exposure. Environ. Pollut. 244, 388–397.
Krzeminski, P., Schwermer, C., Wennberg, A., Langford, K., Vogelsang, C., 2017. Occurrence of UV filters, fragrances and organophosphate flame retardants in municipal WWTP effluents and their removal during membrane post-treatment. J. Hazard. Mater. 323, 166–176.
Lehotay, S.J., Han, L., Sapozhnikova, Y., 2016. Automated mini-column solid-phase extraction cleanup for high-throughput analysis of chemical contaminants in foods by low-pressure gas chromatography—tandem mass spectrometry. Chromatographia 1–18.
Luthy, R.G., Sedlak, D.L., Plumlee, M.H., Austin, D., Resh, V.H., 2015. Wastewater-effluent-dominated streams as ecosystem-management tools in a drier climate. Front. Ecol. Environ. 13, 477–485.
Mankin, J.S., Viviroli, D., Singh, D., Hoekstra, A.Y., Diffenbaugh, N.S., 2015. The potential for snow to supply human water demand in the present and future. Environ. Res. Letters 10.
McCune, B., Grace, J.B., 2002. Analysis of Ecological Communities. MjM Software, Gleneden Beach, Oregon, USA.
Oksanen, J., Blanchet, F.J., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., et al., 2017. Vegan: Community Ecology Package.
R Core Team, 2013. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna http://www.R-project.org/.
Sapozhnikova, Y., 2018. High-throughput analytical method for 265 pesticides and environmental contaminants in meats and poultry by fast low pressure gas chromatography and ultrahigh-performance liquid chromatography tandem mass spectrometry. J. Chromatogr. A 1572, 203–211.

Sapozhnikova, Y., Lehotay, S.J., 2015. Review of recent developments and applications in low-pressure (vacuum outlet) gas chromatography. Anal. Chim. Acta 899, 13–22.
SWCA Environmental Consultants, 2010. East Canyon Reservoir and East Canyon Creek Total Maximum Daily Load (TMDL).
Tabe, S., Pileggi, V., Nowierski, M., Kleywegt, S., Yang, P., 2016. Occurrence, removal, and environmental impacts of emerging contaminants detected in water and wastewater in Southern Ontario-part I: occurrence and removal. Water Pract. Technol. 11, 298–314.
Teng, Y., Wang, X.M., Zhu, Y., Chen, W., Christie, P., Li, Z.G., et al., 2017. Biodegradation of pentachloronitrobenzene by Cupriavidus sp YNS-85 and its potential for remediation of contaminated soils. Environ. Sci. Poll. Res. 24, 9538–9547.
US EPA, 2000. Volume 2: risk assessment and fish consumption limits. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, third edition.
Vives, I., Grimalt, J.O., Ventura, M., Catalan, J., 2005a. Distribution of polycyclic aromatic hydrocarbons in the food web of a high mountain lake, Pyrenees, Catalonia, Spain. Environ. Toxicol. Chem. 24, 1344–1352.
Vives, I., Grimalt, J.O., Ventura, M., Catalan, J., Rosseland, B.O., 2005b. Age dependence of the accumulation of organochlorine pollutants in brown trout (Salmo trutta) from a remote high mountain lake (Redo, Pyrenees). Environ. Pollut. 133, 343–350.
Wang, X.W., Xi, B.D., Huo, S.L., Sun, W.J., Pan, H.W., Zhang, J.T., et al., 2013. Characterization, treatment and releases of PBDEs and PAHs in a typical municipal sewage treatment plant situated beside an urban river, East China. J. Environ. Sci. 25, 1281–1290.
Wickham, H., 2016. Ggplot2: Elegant Graphics for Data Analysis. 2nd ed. Springer, New York.
Zhou, C.L., Pagano, J., McGoldrick, D.J., Chen, D., Crimmins, B.S., Hopke, P.K., et al., 2019. Legacy polybrominated diphenyl ethers (PBDEs) trends in top predator fish of the Laurentian Great Lakes (GL) from 1979 to 2016: will concentrations continue to decrease? Environ. Sci. Technol. 53, 6650–6659.