Distribution and Fate of Ultraviolet Absorbents and Industrial Antioxidants in the St. Lawrence River, Quebec, Canada

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ABSTRACT: Ultraviolet absorbents (UVAs) and industrial antioxidants (IAs) are contaminants of emerging concern. In this study, we investigated the distribution and partitioning of these contaminants in surface water, suspended particulate matter (SPM), sediment, and various tissues of lake sturgeon (Acipenser fulvescens) and northern pike (Esox lucius) from the St. Lawrence River (SLR), Quebec, Canada. Results indicated that 2,6-di-tert-butyl-1,4-benzoquinone (BHTQ) was the dominant contaminant in the dissolved phase of the surface water, with median concentrations of 43, 15, and 123 ng/L for three sampling sites, respectively. Surface water collected downstream of a major city showed higher levels of various UVAs, BHTQ, and diphenylamine compared to the upstream, suggesting the influence of the urban activities on the contamination of these emerging contaminants in the SLR. SPM showed greater sorption capacities of most target contaminants compared to those of the sediment. Different contamination profiles were found in lake sturgeon and northern pike, implying that the accumulation of UVAs and IAs in fish depends on their feeding behavior. The field-based tissue-specific bioaccumulation factors (BAFs) for frequently detected contaminants (log BAF 1.5–4.2) were generally comparable to or lower than the Estimation Program Interface modeling results (1.4–5.0), indicating that some of these contaminants may be less bioaccumulative than previously expected.

KEYWORDS: organic ultraviolet filters, benzotriazole ultraviolet stabilizers, synthetic phenolic antioxidants, aromatic secondary amines, aquatic environment, partitioning, UV328

INTRODUCTION

Ultraviolet absorbents (UVAs) and industrial antioxidants (IAs) are additives used in various industrial and consumer products. Given the UV light-absorbing properties of UVAs, they are used in products such as personal care, sunscreens, rubbers, lubricants, and plastics to protect materials from UV light-induced degradation or color change. Once UV radiation is absorbed, UVAs can rapidly rearrange their intramolecular conformation, emit the radiation at a higher wavelength, and/or release the energy as heat. Organic UV filters (UVFs) and benzotriazole UV stabilizers (BZT-UVs) are two groups of UVAs. Organic UVFs typically contain a carbonyl group and absorb only a restricted spectrum of UV light, whereas BZT-UVs have a common 2-hydroxyphenyl benzotriazole structure and exhibit broad-spectrum absorption. Synthetic phenolic antioxidants (SPAs) and aromatic secondary amines (Ar-SAs) are IAs added in products such as plastics (including food packaging and storage), rubbers, fuels, lubricants, adhesives, and sealants to prevent materials from oxidative degradation. These antioxidants can donate their reactive hydrogen atoms (N–H, O–H) to scavenge free radicals and thus inhibit material degradation.

The multiple uses of these chemicals lead to their large production volumes, as summarized in Table S1. Most of these compounds are in the Toxic Substances Control Act Inventory, and some of them are listed in the High Production Volume Challenge Program by the United States or classified as Substances of Very High Concern in Europe (Table S1). The potential pseudo-persistent, bioaccumulative, and toxic properties of UVAs and IAs have garnered increasing environmental concern. For example, 2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol (UV328) has recently been considered to satisfy all criteria set out in Annex D to the

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Stockholm Convention on Persistent Organic Pollutants (POPs).8,10

Because UVAs and IAs are not covalently bonded to materials, they can leach into the environment from industrial/consumer products/waste, which contribute as nonpoint sources.17 Another major nonpoint source is urban runoff. For example, urban runoff during rainfall and snowmelt in Toronto (Canada) have been found to be sources of BZT-UVs to Lake Ontario.12 Wastewater treatment plant (WWTP) also releases these contaminants to the aquatic environment,2,13–16 and many of these contaminants do not significantly degrade during treatment processes; therefore, sludge and effluent become a route of contamination for UVAs and IAs to the environment.2,14 These contaminants have been detected in environmental matrices such as WWTP influent, effluent, and sewage sludge in China and Canada,15–17 dust (indoor and playground) in Asian countries and the United States,18–20 river sediment in Canada and Germany, marine sediment in Europe and China,21–23 fresh surface water in Canada, Germany, and China,24,25 tap water in Spain,26 and biota samples in the Great Lakes of North America and the Pearl River Estuary of China27,28 (a review of selected published results is presented in Table S2). A nontarget study also revealed that Ar-SAs were the main group of contaminants detected in the muscle, gonads, and eggs of European eel (Anguilla anguilla), with concentrations in the order of μg/g (wet weight, ww).29

The ecological risks of these contaminants are not certain, but there is some evidence showing their adverse effects on organisms. As summarized in the literature,4,30 benzophenone-type UVFs may lead to endocrine-disrupting effects in vitro and in vivo (e.g., rats and fish), while SPAS and their transformation products may be related to hepatic toxicity, endocrine-disrupting effects (e.g., in fish), and carcinogenicity (e.g., in mice). In vitro studies have reported that BZT-UVs are endocrine disruptors and may be associated with the aryl hydrocarbon receptor (AhR)-mediated effects in humans and fish,31–33 indicating the possibility for dioxin-like toxicity. Ar-SAs might lead to liver, blood, reproductive, and developmental toxicities in mammals, as summarized by Lu et al.13 Given these potential toxicities of UVAs and IAs, it is essential to understand the environmental exposure of organisms to these contaminants and the affecting factors.

Previous research has mostly focused on the distribution and partitioning of UVAs in limited matrices (e.g., water, sediment, and biota) in the aquatic system under investigation.5,34 Water-suspended particulate matter (SPM) partitioning, which is a crucial factor affecting the bioavailability and exposure pathway (e.g., via water or ingestion), is poorly understood for UVAs and IAs. In addition, the bioaccumulation of SPAs in the tissues of wild fish is unknown. Furthermore, recent laboratory exposure studies found that BZT-UVs can be biotransformed relatively quickly and had a short half-life in fish when compared to the Estimation Program Interface (EPI) Suite estimated results.35,36 The whole-body-based bioconcentration factor (BCF) of UV328, for example, was measured to be 490–2080 L/kg in zebrafish (Danio rerio),35 which was lower than the EPI-predicted 6006 L/kg. UV328 had a half-life of about 3 days in juvenile rainbow trout (Oncorhynchus mykiss) that are exposed to this contaminant via food,36 which was much shorter than the 14 days predicted by EPI. As a result, some of these contaminants may be less bioaccumulative in wild fish than previously thought.

To address these knowledge gaps, the present study aimed to investigate the concentrations, partitioning, and bioaccumulation of UVAs and IAs in various matrices, including water, SPM, sediments, and the tissues of two fish species, the northern pike (Esox lucius), a top predator, and the lake sturgeon (Acipenser fulvescens), a benthic omnivorous feeder, in the St. Lawrence River (SLR). The SLR is a large, high flow river that flows from the Great Lakes and discharges into the Atlantic Ocean. Montreal is the second-largest city in Canada
by population, and its wastewater treatment plant (WWTP) discharges the primary-treated effluent into the SLR. The SLR basin is one of Canada’s priority ecosystems, and it is an important source of drinking water for about four million people. Thus, understanding the sources and fate of these emerging contaminants in the SLR is crucial for protecting the health of its aquatic ecosystems. In the SLR, northern pike and lake sturgeon are also important for sportive and commercial fisheries. To the best of our knowledge, this is the first study to report the concentration of a suite of UVAs and IAs in the SLR and in the lake sturgeon, which is considered a threatened species by the Committee on the Status of Endangered Wildlife in Canada in this ecosystem. We hypothesized that (1) water, SPM, and sediments downstream of the WWTPs have higher levels of IAs and UVAs than those upstream; (2) SPM plays an important role in carrying IAs and UVAs in the water column; and (3) these contaminants are less bioaccumulative in the tissues of northern pike and lake sturgeon compared to the EPI-predicted results.

**MATERIALS AND METHODS**

**Study Sites and Sample Collection.** Water (n = 22), SPM (n = 19; prepared from water filtration), and sediment (n = 16) samples were collected in glass bottles/jars from Lake St. Louis (LSL), Îles de Boucherville (IB), and Îlet Vert (IV) between 2018 and 2020 (Figure 1). Lake sturgeons were captured by a commercial fisherman using gill nets in June 2018, in LSL, a widening of the SLR located upstream of Montreal. Paired muscle and liver tissues were collected on-site from 15 adult specimens and frozen in the field. Northern pike was collected using a beach seine, 4 km upstream (IB, n = 16) and 4 km downstream (IV, n = 16) of the point of discharge of Montreal’s primary WWTP in the SLR in May 2016 (Figure 1). Another WWTP is located near the city of Longueuil, nearby site IB (Figure 1). The paired tissues of muscle, liver, brain, and blood plasma of northern pike were collected and frozen in the field. Details for fish age determination are presented in the Supporting Information (SI). The biometric data of fish samples are summarized in Tables S3 and S4. All samples were stored at −20 °C until extraction.

**Materials and Sample Preparation.** The names, properties, and structures of target contaminants including 7 UVFs, 10 BZT-UVs, 6 Ar-SAs, and 2 SPAs are presented in Table S1 and Figure S1. Details of chemicals and materials used in this study are shown in the SI. The sample extraction and clean-up were based on previously published methods with some modifications. Briefly, water samples were prepared using solid-phase extraction (SPE), while sediment, SPM, and fish samples were processed using ultrasonic bath-assisted extraction. The extracts of sediment and SPM were cleaned by SPE.
cartridges, and the fish samples were cleaned using gel permeation chromatography. Details are described in the SI.

Instrumental Analysis. A gas chromatography-mass spectrometry (GC-MS) was used for all sample analyses based on published methods with some modifications. Details are presented in the SI, and the GC-MS parameters are shown in Table S5. Quantitation was done by the relative response to the surrogate standards using a solvent standard curve. BP3 was not quantifiable in SPM and sediment samples due to coelution issues.

Quality Control. High-performance liquid chromatography (HPLC) grade water and Ottawa sand were used to prepare one water field blank and one sediment field blank, respectively. Only BHTQ was detected from the field blank of water, and the concentration in the blank was subtracted from the water samples. Contact with plastics was limited whenever possible by using glass materials such as tubes, syringes, cartridges, and vessels. For every 6–10 samples, two procedure blanks and two spike-recovery samples were prepared and analyzed. The method detection limit (MDL) and method quantification limit (MQL) were defined as the concentration of standard that produces a peak in the matrix with signal-to-noise (S/N) ratios of 3 and 10, respectively. For analytes that were detectable in the method blanks, MQLS were based on 3 times the standard deviation (SD) of the procedural blanks. The concentrations of all quantifiable analytes were corrected by the average background contamination in blanks. Recoveries and MQLS of target contaminants are presented in Table S6.

Data Analysis. Field-based sediment—water distribution coefficients (Kd) (L/kg, dry weight (dw)) were derived from the equation $K_d = C_{\text{sediment}} / C_{\text{water}}$, where $C_{\text{sediment}}$ and $C_{\text{water}}$ are the contaminant concentration in paired sediment (ng/kg, dw) and water (ng/L) for each sampling site, respectively. Organic carbon-normalized sediment—water partitioning coefficients ($K_{oc}$) for each sampling site were estimated by the equation $K_{oc} = K_d \times 100 / f_{oc}$, where $f_{oc}$ is the organic carbon fraction for each sampling site by weight. Bioaccumulation factors (BAFs; L/kg, ww) were determined by BAF = $C_{\text{biota}} / C_{\text{water}}$, where $C_{\text{biota}}$ is the contaminant concentration (ng/kg, ww) in each organism sample and $C_{\text{water}}$ is the mean concentration of water samples from the corresponding site in ng/L.

Data were analyzed using GraphPad Prism 9.1 (La Jolla, CA). The statistics were conducted for target contaminants with detection frequency higher than or equal to 50%, and results under MQL or MDL were replaced by 1/2 MQL or 1/2 MDL, respectively. Concentration data are reported as based on dw for SPM and sediment and based on ww for fish tissues unless otherwise indicated. The normality and homogeneity of variances of data were tested using Shapiro–Wilk and Bartlett’s tests. The comparisons of concentrations were performed using the nonparametric Mann–Whitney test or Kruskal–Wallis test followed by Dunn’s multiple comparison test. The correlation hypotheses were tested by two-tailed Spearman or Pearson correlation analyses, depending on data distribution. The significant level was set as $p = 0.05$.

### RESULTS AND DISCUSSION

Spatial Distribution in Water. For the LSL site, the most frequently detected contaminants (>50%) were five UVFs (benzophenone (BP), 2-hydroxy-4-methoxybenzophenone (BP3), 2-ethylhexyl salicylate (EHS), 3,3,5-trimethylcyclohexyl salicylate (HMS), and ethylhexyl methoxycinnamate (EHMC)), one BZT-UV (UV328), and two SPAs (2,6-di-tert-butyl-4-methylphenol (BHT) and 2,6-di-tert-butyl-1,4-benzoquinone (BHTQ)) (Table S7 and Figure 2). In addition to these contaminants, the UFV 2-ethylhexyl 2-cyano-3,5-diphenylacrylate (OC) and the Ar-SA diphenylamine (DPA) were also frequently detected (>50%) in the samples from IB and IV (Table S7 and Figure 2). At each site, BHTQ showed the highest concentrations, with the median of 43 ng/L for LSL, 15 ng/L for IB, and 123 ng/L for IV. At site IB, BHTQ was positively correlated with HMS ($r = 0.912, p < 0.01$) and UV328 ($r = 0.814, p < 0.05$), while BP3 was correlated to OC ($r = 0.925, p < 0.01$) (Table S8). In addition, BP3 was positively correlated with BP ($r = 0.734, p < 0.05$) and EHMC ($r = 0.933, p < 0.01$) at site IV (Table S8). Positive correlation was also found for OC vs BP ($r = 0.805, p < 0.5$) and OC vs EHMC ($r = 0.900, p < 0.01$) at site IV (Table S8). The positive correlations suggest that these contaminants may have similar sources in the SLR.

In the present study, all of the six frequently detected UVFs (BP, BP3, EHS, HMS, EHMC, and OC), as well as BHTQ and DPA, were found at higher concentrations at the downstream site (Figure 2). For UV328, the concentration in water at site IB was significantly higher than the upstream site LSL, but the concentration decreased further at the downstream site of IV. These results suggest that the WWTP effluents of surrounding cities could elevate the dissolved concentrations of these target contaminants in the downstream water. Some of the target contaminants such as UV328 and BHT in this study have been previously detected in Canadian WWTP effluents. In addition, it has been reported that the WWTP processes could produce BHT metabolites (e.g., BHTQ) and increase their concentration in effluents. Since the BHTQ levels in the IV water were higher than those in other sampling sites, the WWTP at Montreal may be sources/vectors of these contaminants to the SLR. Another possible source of these contaminants is urban runoff. For example, Parajulee et al. reported that the concentrations of BZT-UVs in an urban watershed (Toronto, Canada) were about 4–90 times and 3–21 times greater during rainfall and snowmelt, respectively. However, there is currently no information about levels of UVAs and IAs in urban runoff along the SLR, which warrants future investigation. For BHT, there were no spatial differences among the three sampling sites, implying nonpoint sources of this contaminant along the SLR.

The concentrations of UVAs and IAs in the SLR surface water were generally at the lower end in the reported data worldwide. For BZT-UVs, UV328 was detected from <MQL to 40 ng/L with a median concentration of 4 ng/L for the SLR, which was comparable with the level of UV328 in a river in India (ND-5.2 ng/L) but lower than the concentrations detected in surface water of a river in Japan (30–583 ng/L). For UVFs, higher concentrations have been detected in marine water from other locations such as Hong Kong and Shantou (China) (BP3: 39–5429 ng/L; OC: 75–6812 ng/L; EHMC: 52–4043 ng/L), New York and Los Angeles (USA) (BP3: 23–601 ng/L; OC: 117–377 ng/L; EHMC: 89–150 ng/L), as well as freshwater from Romania (EHS: up to 139 ng/L (mean 48 ng/L)). However, concentrations of BP3 (up to 101 ng/L), OC (up to 93 ng/L), and EHMC (up to 17 ng/L) in the water of SLR were comparable with the levels in Japan (BP3 up to 86 ng/L; OC up to 108 ng/L; freshwater) and Spain (EHMC up to 16 ng/L; marine water). For IAs,
although BHT was detected in all SLR water samples, its level (<MQL-22 ng/L) was lower than what was detected in the freshwater from Spain (mean: 112 ± 12 ng/L) and Germany (25–365 ng/L).

**Concentrations in SPM and Sediment.** The median concentrations of SPM were 27, 8, and 148 mg/L for the samples from LSL, IB, and IV, respectively. Five UVFs (BP, EHS, HMS, EHMC, OC), five BZT-UVs (2-(2H-benzotriazol-2-yl)-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (UV326), 2,4-di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl) phenol (UV327), UV328, 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethyl butyl)phenol (UV329)), two SPAs (BHT, BHTQ), and three Ar-SAs (DPA, bis(4-tert-butylphenyl)amine (C4C4), bis(4-(2,4,4-trimethylpent-2-yl)-phenyl)amine (C8C8)) were detected in SPM samples (Table S7). The concentrations of most frequently detected (>50%) contaminants (EHS, HMS, EHMC, BHT, BHTQ, and C8C8) are shown in Figure S2. Akin to the surface water, the dominant contaminant was BHTQ with median concentrations of 119, 1180, and 495 ng/g for LSL, IB, and IV, respectively. Different from the rare detection of C8C8 in the water (0–13%), C8C8 was frequently detected (60–100%) in the SPM (median 4 ng/g for LSL; 59 ng/g for IB; 16 ng/g for IV), which is consistent with its high hydrophobicity (log K_{ow} = 10.8). The contaminant EHMC in the SPM at LSL (median: <2 ng/g) and IB (12 ng/g) was comparable to reported levels in the SPM from German rivers (median 13 ng/g in 2005–2006 and <2.7 ng/g in 2017) and Spain rivers (<6.5 ng/g), but the EHMC level at the SLR IV site (median: 209 ng/g) was much greater than the SPM from these European rivers. For BHT, concentrations detected in SPM from WWTP effluents in the United States were up to 122 μg/g dw, which is in the same order as that detected in SPM from the SLR surface water (up to 95 μg/g dw). The very high concentrations of UVAs and IAs suggest that SPM is a significant carrier of these contaminants in the SLR. Although the downstream sites IB and IV showed higher median concentrations than the upstream LSL site, overall there was no clear spatial trend of the target contaminants associated with SPM (Figure S2).

In sediments, the concentrations of detectable contaminants were generally much lower than the SPM (Table S7 and Figure S3). BHT (<5 (MQL)-181 ng/g) and BHTQ (<6 (MQL)-620 ng/g) were detectable (>MDL) in all sediment samples, but they were not quantified in some samples because the concentrations were between MDL and MQL. Higher levels of BHT and BHTQ were found for site IV (BHT: 2.5 ng/g; BHTQ: 98 ng/g; median) compared with that of LSL (BHT: 2.5 ng/g; BHTQ: 18 ng/g; median) and IB (BHT: 2.5 ng/g; BHTQ: <6 ng/g). These results follow the same trend as the dissolved concentrations in water. The concentrations were generally lower than that of the sediment from the coastal area of northern China (BHT: 197 ng/g; BHTQ: 188 ng/g; median). For BZT-UVs, UV234 was more frequently detected (20–80%) and at greater concentrations in sediment (median 7.5–24 ng/g) than in all other matrices studied, suggesting that sediment is a major sink of UV234. A higher median level of UV234 was found at the downstream site IV,
suggested a possible impact of Montreal’s WWTP release on the distribution of UV234 in sediment (Figure S3). In contrast, UV328 was detected more frequently in the sediment from LSL (67%) compared to the two other sites (40%) and the concentrations for all sites (<2−13 ng/g) were lower than that of UV234. For UVFs and Ar-SAs, BP, EHS, and C8C8 were frequently detected without clear spatial pattern (Figure S3). The concentrations of UV328 (up to 13 ng/g dw) and EHS (up to 15 ng/g dw) in the SLR sediment were higher than that of the Baltic Sea (UV328, up to 0.88 ng/g dw and EHS, up to 0.42 ng/g dw).23 But UV328 concentrations were lower than the levels reported in sediments from Japan (up to 320 ng/g dw).39 The levels for C8C8 in the SLR sediments (median <0.9−7 ng/g) were lower than the previously reported data in Ontario, Canada (an urban creek: median up to 31 ng/g;5 unknown locations: median 10 ng/g).50

The total organic carbon (TOC) content in the sediment was in the range of 0.15−0.93,1.73−3.30, and 0.17−2.13% for LSL, IB, and IV, respectively. The TOC of site IB was significantly higher than that of LSL and IV. However, no significant correlation was found between sediment TOC and any quantifiable contaminants at each site. This result is in line with previous observations of the sediment collected from Europe and east Asia,8,23,43 indicating that the distribution of these contaminants may be affected by many factors (e.g., composition of organic carbon, sources of contaminants) but not significantly by TOC.

Water−Particle Partitioning. The mean log Kd of BP, DPA, BHTQ, BHT, EHS, HMS, EHMC, and OC was in the range of 2.7−4.1 for sediment and 4.1−5.9 for SPM (Figure 3), indicating a higher affinity of SPAs and UVFs with SPM compared to sediment. There were no significant differences in log Kd among the three sampling sites. The measured sediment−water mean log Kow ranged from 4.4 to 6.2, which was generally higher than the EPI-predicted values and did not correlate with log Kow (Figure 3). It has been reported that the field-based sorption coefficients of some organic contaminants may be greater than that expected from the Kow-based equilibrium models.50,51 The sediment−water distribution of chemicals is not only a partition process but also controlled by organic carbon mineralization of the specific sampling sites.50,51

Tissue Distribution in Fish. Given the hydrophobicity of the target contaminants (log Kow: 3.0−10.8), the lipid content may affect their distribution in fish tissue, but no correlation was found between the concentrations of most target contaminants and the lipid content of fish tissues. This result implies that lipid content is not the dominant factor affecting the accumulation of these contaminants. Other factors such as biotransformation55 and binding with proteins52 may be involved in regulating the tissue distribution of these contaminants in the studied fish. Therefore, the data were not lipid-normalized and ww-based data were used for comparison.

Lake Sturgeon. Liver. In liver, the most frequently detected UVAs were UV328 for BZT-UVs (53%) and BP3 for UVFs (67%) (Table S9 and Figure S4). The levels of UV328 in the liver of lake sturgeon (3.2 ± 0.9 ng/g ww) were comparable with previously reported concentrations in white sucker (Catostomus commersonii) from an urban creek in Ontario, Canada (4.8 ± 1.5 ng/g ww),53 and the liver of sea bass from the Ariake Sea (Japan) (2.4−2.5 ng/g ww)55 but lower than the concentrations in the liver of eagle ray (Aetobatus flagellum) (8.1± 3.2 ng/g ww) and hammerhead shark (Sphyrna lewini) (55 ± 46 ng/g ww) from the Ariake Sea.54 Negative correlations were found between the concentration of BP3 in liver and the length of lake sturgeons (total length: r² = 0.43, p < 0.05 and fork length: r² = 0.45, p < 0.05) (Table S10). The negative correlation highlights a biodilution that could be induced by the phenomena of growth dilution.55 The concentration range and the 90th percentile level of BP3 in the liver of lake sturgeon (<30−783 ng/g; 657 ng/g ww) were comparable to the liver of Atlantic cod (Gadus morhua) in Norway (<20−1037; 700 ng/g ww), but the median levels of BP3 were much higher in the lake sturgeon (194 ng/g) than that of cod (<20 ng/g).56 In addition, BP3 levels in lake sturgeon were much higher compared to the liver of lebanceh mullet (Mugil liza) from Brazil (7.6−74.4 ng/g dw)57 and various freshwater fish species from Lake Chaohu in China (<0.25−100 ng/g dw),58 suggesting a relatively high contamination of BP3 in the lake sturgeon. For IAs, BHT (47%) and C8C8 (87%) showed the highest detection frequency for SPAs and Ar-SAs, respectively. Their concentrations were up to 9 ng/g ww for BHT and 17 ng/g ww for C8C8 in the liver of lake sturgeon. BHT levels in lake sturgeon liver were lower than that usually detected in other aquatic organisms, with a value in the order of μg/g dw.21 C8C8 levels in the liver of lake sturgeon (<0.2−17 ng/g; median: 3.0 ng/g ww) were greater than the concentrations measured in white sucker’s liver from the upstream (0.5−1.4 ng/g; median: 0.7 ng/g) of an urban creek in Ontario (Canada) but comparable with the white sucker from the same river downstream of a city/WWTP (0.7−6.8 ng/g; median: 3.9 ng/g ww).53

Muscle. For BZT-UVs, UV328 was the dominant compound and it was detected in 73% of muscle samples with the concentration as high as 117 ng/g ww (median: 19 ng/g ww). This concentration was much higher than previously reported UV328 in fish samples from the Great Lakes (<0.08−6.7 ng/g).5,28 BHT was detected in 60% of the samples with a maximum concentration of 41 ng/g ww (median: 2 ng/g ww; mean: 8 ng/g ww). The BHT concentrations in lake sturgeon muscle were lower than that of farmed salmon, trout, and halibut muscle from Norway with levels from 122 to 2607 ng/g ww but were in the range of farmed cod muscle with a mean concentration of 11 ng/g ww.59 C8C8 was the most frequently detected (73%) Ar-SA with a median concentration of 0.1 ng/g (ww). A positive correlation was found between age and the C8C8 concentration in muscle (r² = 0.33; p = 0.02) (Table S10), which indicated a tendency for this contaminant to accumulate in this tissue over time.

Northern Pike. Liver. In northern pike, the most frequently detected compounds in liver were UVFs and SPAs (Table S9 and Figure S5) including BP (50% IB and IV), BP3 (69% IB and 64% IV), BHT (69% IB and 43% IV), and BHTQ (81% IB and 78% IV). The contaminant BP3 (median: 317 ng/g ww) in the pike liver was higher than in liver of lake sturgeon from LSL (median: 194 ng/g ww) and many other fish previously reported, possibly because these fish were collected close to WWTPs. For SPAs, contrary to the results obtained in lake sturgeon, BHTQ was detected more frequently and in greater concentration than BHT. Since the BHTQ levels in the water of LSL and IB were similar and BHTQ is a metabolite of BHT, the high levels of BHTQ in pike may indicate a faster uptake of BHTQ or rapid biotransformation of BHT in this fish. It has been reported that BHT can be biotransformed to BHT-quinol
in the liver of mice, and BHT-quinol can be transformed into BHTQ following an oxidation reaction.59 BHTQ is known to induce greater toxicity than BHT, mainly due to its ability to damage DNA,60 which can potentially pose risks to pike. As a pelagic fish, northern pike may uptake BHTQ from the SPM, which is known to have much greater levels of BHTQ (median: 1180 ng/g for IB and 495 ng/g for IV, dw) compared to sediment (median: 18 ng/g for LSL, dw) (Figures S2 and S3). This could be another possible reason for higher levels of BHTQ in pike than in the lake sturgeon, which are mainly exposed to sediment.

Muscle. In the muscle of northern pike, the dominant contaminants were BP and BHTQ (Table S9) and they were more frequently detected in the samples from site IB.

Brain. Unlike liver and muscle, BHT was the dominant compound in the brain of northern pike (Table S9 and Figure S5), with concentrations up to 48 ng/g (ww) and 37 ng/g (ww) for IB and IV, respectively. BHTQ was also found in pike’s brain (up to 35 ng/g) (Table S9). These results suggest that BHT and BHTQ may cross the blood–brain barrier of fish. It has been reported that BHT accumulates in the brain of male Sprague-Dawley rats exposed to diet (1.2%) for 2 weeks61 and that BHT could lead to the increased number of dead cells in the cerebellum of pups suckled by the dosed female rats.62 However, the neurotoxicity of BHT and BHTQ in aquatic organisms is not clear and worth further investigation.

Plasma. In plasma, BP3, UV329, BHT, and BHTQ showed higher detection frequency in northern pike. It is known that UV329 can bind to serum albumin, which could be a possible reason for the higher detection frequency of UV329 in the plasma than other tissues.52 A positive correlation was found between the concentration of BHT and BHTQ measured in plasma ($r^2 = 0.31; p < 0.005$), indicating a similar partitioning process for BHT and BHTQ.

Comparisons between Lake Sturgeon and Northern Pike. Lake sturgeon and northern pike showed different contamination patterns of the target analytes. The most frequently detected contaminants in lake sturgeon tissues were BP3, UV328, BHT, and C8C8, whereas the dominant target contaminants in northern pike were BP, BP3, UV329, BHT, and BHTQ. These differences are probably related to the different habitats, feeding ecology, and life span of these two fish species. Northern pike is an opportunistic pelagic piscivore, whereas lake sturgeon is an omnivorous bottom feeder. The accumulation of these contaminants is considered to be diet-specific.40,55,63 Some studies have suggested that
bottom feeders tend to accumulate more BZT-UVs and Ar-SAs than fishes with other feeding habits.\textsuperscript{5,54,55} In addition, lake sturgeon from this study were older (16–25 years old) than northern pike (2–7 years old), suggesting different exposure histories to contaminants.

In northern pike, most detectable target contaminants (except for UV329) were mainly found in liver. This distribution pattern is in line with previous studies that reported higher affinity of these compounds to liver in different fish species.\textsuperscript{30,33,64} It is known that UV329 could bind to serum albumin,\textsuperscript{12} which might be related to the accumulation of these contaminants in the plasma. Similarly, BP3 and C8C8 in the liver of lake sturgeon were also greater than their levels in the muscle (Figure S4). In contrast, muscle accumulated more UV328 and BHT compared to the liver of lake sturgeon (Figure S4). To the best of our knowledge, the toxicokinetics data for these contaminants in lake sturgeon are currently not available. Previous \textit{in vivo} research discovered a higher accumulation level of decabrominated diphenyl ether (BDE 209) in the muscle of Chinese sturgeon (\textit{Acipenser sinensis}) compared to the liver during the spawning and stop feeding period.\textsuperscript{65} This result was attributed to the rapid biotransformation of BDE 209 in the liver, which result in a faster concentration decreasing rate in the liver than in the muscle.\textsuperscript{65} Lake sturgeon spawning typically begins in May and ends in June, and they stop feeding completely during this time (i.e., limited contaminant uptake and mainly a contaminant elimination phase).\textsuperscript{66} The lake sturgeon samples for this study were collected in June 2018, which might coincide with the clearance period for some of the sampled specimens. The mechanisms underlying such tissue distribution patterns for UV328 and BHT in lake sturgeon should be investigated further.

\textbf{Bioaccumulation Factors.} BAFs for fish liver and muscle are presented in Figure S6. While muscle can be more representative of whole-body accumulation, the high concentrations and more frequent detections in liver (Figures S4 and S5) provide rationale for also calculating the liver-based BAF. Overall, BP3 (log BAF 4.2 ± 0.3) in fish liver showed the highest bioaccumulation potential. The mean log BAFs for BHT, BHTQ, UV329, UV328, and C8C8 in fish tissues were in the range of 2.3–3.5, 1.5–2.2, 3.4–4.2, 2.6–3.4, and 1.6–2.3, respectively. These contaminants showed comparable or lower field-based log BAF compared to the predicted log BAF (with biotransformation; EPI suite) (Figure S6), implying a faster elimination rate of target SPAs, BZT-UVs, and Ar-SAs in these two species. These comparisons between the field-based log BAF and the EPI-predicted log BAF should be interpreted with caution because the EPI-estimated log BAF is based on the whole body of fish, whereas the present study only obtained tissue-specific log BAF. Additional uncertainty exists because water exposure varies continuously throughout the entire life span of these long-lived fish in the field; thus, the water concentration obtained by 1–2 times of sampling may contribute to error for the log BAF calculation.

Giraudo et al.\textsuperscript{68} reported that the measured half-life was 3.0 days for UV328 and 2.2 days for UV234 in the juvenile rainbow trout (\textit{O. mykiss}), which were much shorter than the EPI modeling results (14 days for UV328 and 13 days for UV234). Thus, these contaminants may be less persistent and bioaccumulative in the SLR compared to the modeling results. In contrast, the BAFs of BP and BP3 in fish liver were close/greater than the predicted BAF without considering biotransformation, suggesting the longer retention or lack of biotransformation of benzophenone-type UVFs in the liver of lake sturgeon and northern pike. It has been reported that part of BP3 can be biotransformed to BP1 (2,4-dihydroxybenzophenone) in adult zebrafish, but the biotransformation was undetected in embryos.\textsuperscript{67} The toxicokinetics and biotransformation potential of benzophenone UVFs in lake sturgeon and northern pike are important data gaps.

In the muscle of lake sturgeon, a parabolic relationship was found between log BAF and log $K_{ow}$ (Figure 4), demonstrating the low bioavailability or fast elimination of extremely hydrophobic C8C8. A similar relationship was previously found for substituted diphenylamine antioxidants in the crayfish (\textit{Orconectes spp.}), hornyhead chub (\textit{Nocomis biguttatus}), and common shiner (\textit{Luxilus cornutus}) in a creek in Ontario, Canada,\textsuperscript{7} as well as for organochlorine compounds (OCs) in juvenile rainbow trout in a laboratory-controlled experiment \textit{via} diet exposure.\textsuperscript{69} In the muscle and plasma of pike, log BAF and log $K_{ow}$ of BP, BP3, BHT, BHTQ, and UV329 showed positive correlations; thus, results suggest that log $K_{ow}$ may be a key factor influencing the partitioning of these contaminants in muscle and plasma. In contrast, there was no clear trend between log BAF and log $K_{ow}$ in fish liver, which might be due to the different biotransformation processes of these contaminants in this tissue, which warrant further investigation.

This study revealed the presence of UVAs and IAs in surface water, SPM, sediments as well as piscivorous pelagic and omnivorous bottom feeder fish from the SLR, indicating the accumulation of these contaminants of emerging concern in the SLR. In comparison to Ar-SAs and BZT-UVs, SPAs and UVFs were detected more frequently and at higher concentrations in the surface water. These results highlight the priority to assess the ecological risks of SPAs and UVFs in aquatic ecosystems and the potential risks that these chemicals may pose to humans. SPM had greater sorption capacities of these contaminants than that of the sediment, suggesting that the ingestion and gill uptake of SPM could be an important exposure pathway of aquatic organisms to UVAs and IAs. The accumulation pattern of these contaminants in fish was species-specific and may be affected by the age and size of fish. Lake sturgeon tended to accumulate BP3, UV328, BHT, and C8C8, whereas northern pike showed an accumulation of BP, BP3, UV329, BHT, and BHTQ. The field-based tissue-specific BAFs of detected SPAs, BZT-UVs, and Ar-SAs were generally lower than the EPI modeling results, implying that these contaminants may be less bioaccumulative than previously expected. Liver was a major tissue to accumulate most of these compounds in fish and BHT/BHTQ could distribute into fish brain. Future research should investigate the adverse effects of these contaminants on aquatic species.

\section*{ASSOCIATED CONTENT}

\subsection*{Supporting Information}

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c07932.

Additional information about target contaminants, experimental details, and results: properties, production, regulations, and structures of target contaminants; concentrations of target contaminants in environmental matrices reported in the literature; fish age determination; materials and sample preparation; instrumental
analysis; GC-MS parameters; recovery and quantification limits; TOC analysis; biological parameters of fish; concentrations and distribution of target contaminants in water, SPM, sediment, and fish tissues; correlation matrix for the concentrations of target contaminants in the water and fish; and field-based log BAF in different fish tissues (PDF)

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Notes
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