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Concentrations, toxic equivalence, and age-corrected trends of legacy organic contaminants in Lake Champlain lake trout: 2012–2018

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ABSTRACT

Our study is the first comprehensive, multi-year assessment of polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), organochlorine pesticides (OCPs), polychlorinated naphthalenes (PCNs), polychlorinated dibenzo-p-dioxins, and polychlorinated dibenzofurans (PCDD/Fs) lake trout concentrations and trends in Lake Champlain (LC). Lake trout whole-fish, fillets, and eggs were collected over the 2012–2018 study period. Total PCB concentrations (395.7 ng/g wet weight (ww)) were the highest average concentration of any contaminant grouping reported in this study. Whole-fish lake trout modeling revealed highly significant ($p < 0.05$) log-linear correlations for all dioxin-like contaminants measured. Overall contaminant decreases for the 2012–2018 period ranged from 20.9% (total PCNs) to 39.3% (2378-TCDD). Contaminant decreases for total PCBs and total-5-PBDEs were 30.9% and 48.3%, respectively. Of particular significance were the measured total PBDE concentrations (74.3 ng/g ww) found in LC whole-fish lake trout. Log-linear forecasting indicates that whole-fish lake trout TEQs will be below the guidelines protective of wildlife thresholds during the periods 2035–2047 (TRG_{bird}) and 2062–2088 (TRG_{mammal}). Based on current USEPA guidelines, all lake trout fillets from Lake Champlain analyzed for this study exceed the human health cancer screening value of 0.15 pg-TEQ/g ww by a substantial margin (average = 8.61 pg-TEQ/g ww). Dioxin-like trend data collected for Lake Champlain indicates that the mechanisms of contaminant uptake, trends, and yearly percent decline reflect those found in the Great Lakes.

1. Introduction

There is an extensive collection of research documenting persistent organic contamination residing in the Great Lakes watershed going back nearly 60 years. Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), organochlorine pesticides (OCPs), polychlorinated naphthalenes (PCNs), polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), and non-ortho polychlorinated biphenyls (CP4-PCB) levels have been investigated and reported routinely by both American and Canadian researchers (SI WS-6). In large part, the current status of legacy contamination and trends in Lake Champlain has received comparatively little attention over the last 20 years.

Lake Champlain is a deep, near oligotrophic cold water lake in the northeastern United States. It is bordered by New York and Vermont, with a small portion residing in the Canadian province of Quebec (Fig. S1). Its drainage basin stretches 21,325 km^2, from Canada to the Hudson River and between the Adirondack and Green Mountains (Lake Champlain Basin Program, 2006). Lake Champlain is divided geographically into several distinct basins, each with unique bathymetric and limnological characteristics (Fig. S2, Myer and Gruendling, 1979). Lake trout generally inhabit the Main Lake basin which is the deepest sub-basin, although spawning occurs in the shallower North and South basins (Marsden et al., 2018). The Lake Champlain basin is heavily forested (64%) with 16% used for agriculture and 6% developed land use (Winslow, 2016). Fishing and recreation are a large economic factor in the region. In 2015, the Lake Champlain Basin Program (LCBP) released an economic report estimating that the tourist expenditures in the area surrounding Lake Champlain amounted to $300 million of revenue in 2013 to the State of Vermont (Voigt et al., 2015).

Human agricultural and industrial presence around Lake Champlain increased dramatically following the Revolutionary War and approximately 600,000 people currently live in the basin (Winslow, 2016). Industrial activity predates modern environmental protection measures and known legacy contamination exists at several former industrial sites. The old Ticonderoga Paper Mill and associated sludge beds (Mason et al., 1977; O'Keefe et al., 1994), Burlington Harbor (Lacey

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et al., 2001; McIntosh et al., 1997), and the delisted Cumberland Bay New York State Inactive Hazardous Waste Site (USDOI, 1968; NYSDEC, 2018a) are known sources of legacy contaminants to the LC ecosystem. Inferred legacy sources of agricultural pesticides include a robust agricultural belt in the watershed (Lacey et al., 2001; McIntosh et al., 1997) and the presence of waste water treatment facilities (WWTP), which are known sources of PBDEs (North, 2004; Ratola et al., 2012; Song et al., 2006).

The USEPA Great Lakes Fish Monitoring and Surveillance Program (GLFMSP) has monitored legacy contaminants in the Great Lakes since 1978. Lake Champlain has "similar hydrology, limnology, fisheries/age structure, and population pressures, allowing for proportional comparison to the Great Lakes" (Pagano and Garner, 2019). Understanding of contaminant dynamics in the Great Lakes and other similarly impacted waterbodies could be enhanced by comparison to contrasting lake systems (size, impacts, and human population pressures). Additionally, LC supports a healthy lake trout population with a similar food web structure to the Great Lakes. There is also evidence that lake trout population age-effects being investigated in the Great Lakes are also impacting Lake Champlain (Murphy et al., 2018; Pagano et al., 2018).

Lake Champlain holds an important historical, recreational, agricultural, and economic position in Vermont and New York (Voigt et al., 2015). Our 2012–2018 study presents a comprehensive assessment of legacy contaminants in Lake Champlain lake trout utilizing whole-fish, fillets, and egg tissues. Lake trout whole-fish were used to model log-linear trends for several select contaminants. As lake trout ages tend to vary widely due to ecological and food web perturbations, the Age Trend Model (ATM) was used to perform statistical trend analyses (Pagano et al., 2018). The purpose of this study was to assess the concentrations/trends of legacy contaminants, determine wildlife protection values, and evaluate human health screening values for Lake Champlain. Additionally, we will contrast LC lake trout contaminant concentrations and ratios to lake trout found in the Great Lakes. To our knowledge, this study is the first comprehensive, multi-year assessment of PCBs, PBDEs, PCDD/Fs, CP4-PCBs and PCN lake trout concentrations and trends in Lake Champlain.

2. Materials and methods

2.1. Sampling

Whole-fish lake trout (*Salvelinus namaycush*) were collected at Hatchery Cove, Grand Isle County, VT yearly by University of Vermont (UVM) and Vermont Fish and Wildlife Department (VTFWD) from 2012 to 2018, excluding 2014. Sampling methods followed those detailed in Pagano et al. (2018) and Pagano and Garner (2019). US EPA GLFMSP protocols were followed for sample collection and processing ("Great Lakes Fish Monitoring Surveillance Program Data | Great Lakes Monitoring | US EPA," n. d.). Briefly, 10 individual lake trout were collected per year, with paired egg samples from females when available. A DAYMIX egg sample was prepared from an equal amounts of eggs collected from all females. Lake trout were aged using maxillary structures by the Michigan Department of Natural Resources (MDNR) and Aquatec Environmental, Inc. (Aquatec, Williston, VT) and further confirmed by hatchery fin clips by J. Ellen Marsden - UVM (Wellenkamp et al., 2015). All individual fish were homogenized by Aquatec, and an equal subsample from every individual was additionally homogenized to form a composite (COMP) sample. Several individual fish collected in 2015 and 2016 were homogenized as skin-on fillet samples.

2.2. Chemical analysis

Detailed analytical procedures have been previously described fully (Pagano et al., 2018; Pagano and Garner, 2019). In brief, samples were extracted on an ASE 350 and spiked with labeled surrogate solutions before extraction. A FMS PowerPrep II Workstation was used for sample clean-up. Samples were analyzed using Method 1613 B for dioxins and furans (USEPA, 1994), Method 1668C for non-ortho coplanar PCBs (USEPA, 2010), and Method PCN-3431 for PCNs, respectively (Gewurtz et al., 2018; McGoldrick et al., 2018; Ontario Ministry of the Environment, 2010). OCPs and congener-specific PCBs were measured with GC-ECD using dual-column techniques (Chang et al., 2012; Zhou et al., 2018). PBDEs were analyzed by GC-MS-NCI (Zhou et al., 2019). Quality control samples were included and analyzed with each subset of samples. QA/QC was monitored both internally using SOP laboratory measures and externally by QA review from General Dynamics Information Technology (Alexandria, VA). Detailed QA/QC data for are included in SI-WS-1 and SI-WS-2.

2.3. Data treatment

Data treatment follows methods and rationales detailed in recent publications (Garner and Pagano, 2019; Pagano et al., 2018; Pagano and Garner, 2019). SPSS Version 21 and SigmaPlot Version 13 software were used for statistical analysis and modeling. As the data was not normally distributed, nonparametric statistical tests were used. Independent sample Mann-Whiney (M-W) U tests or Kruskal-Wallis Rank-Sum test (Kruskal and Wallis, 1952; Mann and Whitney, 1947) were used for global comparisons between Lake Champlain, Cayuga Lake, and Great Lakes data. Statistical significance was defined at the 95% confidence interval ($p < 0.05$). Outlier values were identified in SPSS using 1.5x the interquartile range (IQR) criteria. COMP samples are reported as the average age of all individual fish collected in a given annual sample. Trends were modeled as log-linear transformations of first-order decay models for clarity and consistency with recent publications (Garner and Pagano, 2019; Pagano et al., 2018; Pagano and Garner, 2019).

3. Results and discussion

3.1. Legacy contaminants

Select groupings of legacy contaminants are summarized for Lake Champlain (LC) lake trout eggs, fillets, and whole-fish in Table 1 and fully reported with associated descriptive statistics and physical data in the Supporting Information (SI) Worksheet (SI-WS-5). Overall, 190 legacy chemical components are reported. Select groupings or components of interest reported in SI-WS-3 and Table 1 are based on the highest concentration levels measured, historical production levels/current use, and/or toxicological importance in LC lake trout (SI-WS-6).

Polychlorinated biphenyls (PCB) are the most abundant legacy contaminant measured in all LC sample matrices measured, and is one of the persistent chemicals responsible for current fish health advisories in Lake Champlain. Overall total PCB concentrations (Σ140 congeners/coelutors) identified in LC lake trout whole-fish was 395.7 ng/g ww, the highest average concentration of any contaminant grouping reported in this study. The most abundant individual PCB congeners by average were 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB-153, 34.0 ng/g ww, 8.6%) followed closely by 2,2′,3,4,4′,5′-hexachlorobiphenyl (PCB-138, 28.2 ng/g ww, 7.1%). The top ten most abundant PCB congeners (SI-WS-7) found in LC lake trout are all well represented in the higher chlorinated PCB technical Aroclor™ mixtures, making up over 47% of the total PCBs measured in this study.

As noted earlier, several sources of PCB contamination to the Lake Champlain basin have been previously identified, including Cumberland Bay - Wilcox Dock, the Saranac River, and Burlington Harbor. Cumberland Bay, adjacent to Plattsburg, NY on the Main Lake basin was the site of lumbering and paper manufacturing operations in the mid-to late-1800's. Industrial operations as far back as the 1930's were carried out by the Diamond National Company and Georgia

Table 1
Lake trout whole-fish, eggs, and fillet select contaminants 2012–2018: legacy contaminant summary (ng/g – ww), dioxin-like contaminant summary (pg/g – ww and pg-TEQ/g –ww).

Legacy Contaminant Summary									
	Whole Fish			Eggs			Fillets		
	Average	Max	Min	Average	Max	Min	Average	Max	Min
Total PCBs	395.674	836.439	217.484	94.612	241.009	47.731	217.554	313.488	137.463
Total DDTs	166.267	286.719	85.728	38.676	105.132	14.998	89.497	125.196	45.092
Total Chlordanes	23.941	43.692	12.905	6.032	27.567	0.000	14.264	20.388	8.952
Total 5 PBDEs	69.190	197.066	32.388	11.926	21.887	4.975	33.410	58.383	19.760
Dioxin-Like Contaminant Summary									
	Whole Fish			Eggs			Fillets		
	Average	Max	Min	Average	Max	Min	Average	Max	Min
2378-TCDF	14.776	27.898	9.215	3.768	6.644	1.826	10.581	12.014	8.593
2378-TCDD	0.724	1.291	0.422	0.210	0.348	0.119	0.465	0.587	0.331
Total PCNs	635.395	966.623	439.430	153.910			486.686	544.265	411.202
PCB_077	34.394	72.375	15.349	9.377	18.812	3.902	18.032	21.547	12.844
PCB_081	613.472	1183.122	269.181	174.888	311.903	70.725	329.206	382.543	247.242
PCB_126	103.837	219.409	41.292	23.833	45.329	10.490	53.448	67.051	39.389
PCB_169	25.835	46.165	12.738	4.233	7.605	2.094	14.015	18.678	8.968
Dioxin-Like Contaminant TEQ Summary									
	Whole Fish			Eggs			Fillets		
	Average	Max	Min	Average	Max	Min	Average	Max	Min
PCDD/F TEQ	4.259	8.027	2.519	1.027	1.523	0.559	2.803	3.266	2.244
CP-PCB TEQ	11.230	23.466	4.543	2.531	4.798	1.120	5.804	7.278	4.236
PCN-TEQ	0.297	0.542	0.198	0.058			0.215	0.247	0.189
Total TEQ	15.490	31.493	7.709	3.558	6.263	1.679	8.607	10.439	6.480

Pacific Corporation at the Wilcox Dock site in Plattsburg, NY. The Imperial Paper Company and Plattsburg Air Force Base were also responsible for additional historical inputs to the Saranac River and Cumberland Bay (USDOI, 1968). In 1992, extensive PCB contamination was first identified in Cumberland Bay by United States Geological Survey (USGS) and University of Vermont (UVM) researchers (Callihan et al., 1998). After additional investigative studies, Cumberland Bay was added to the NYS Inactive Hazardous Waste Site (IHWS) list in 1995. Numerous studies further defined the complexities and outlined the scope of the Cumberland Bay – Wilcox Dock site, which eventually would encompass 57 acres of sludge beds with PCB concentrations found in excess of 13,000 mg/kg. New York State Department of Environmental Conservation (NYSDEC) completed a remediation of Cumberland Bay dredging nearly 140,000 tons of sludge between 1999 and 2001. As of 2013, the Cumberland Bay - Wilcox Dock site was delisted from the NYS IHWS registry (NYSDEC, 2018a). The most recent Cumberland Bay Phase IV sampling in 2000 indicated that average PCB sediment concentrations averaged 6–7 ppm, with only a few sample locations exceeding 10 ppm and none exceeding 18 ppm (USACE et al., 2003). No mass balance or total maximum daily load (TDML) modeling estimates were published as to the extent of chemical contamination that likely would have migrated into Lake Champlain before/during/or after the Cumberland Bay remediation. Results from this study indicates that PCB concentrations are declining in LC lake trout, although at a comparatively slower rate of decline (Fig. 2, SI-WS-10, SI-Fig. S3, Trends section, and GL section).

The total DDT grouping consists of some of the most environmentally recalcitrant contaminants found in the LC environment: including pp-DDE, pp-DDD, pp-DDT, and op-DDD. The pp-DDE isomer comprises the vast majority of the total-DDT (166.3 ng/g ww) measured in LC whole-fish lake trout (135.7 ng/g, 81.6%), followed by pp-DDD (10.6%), pp-DDT (6.7%), and op-DDD (1.1%) (SI-WS-7). In fact, pp-DDE alone was the largest individual chemical contaminant measured in LC lake trout (SI-WS-7). Interestingly, the relative percentage of the DDT isomers in LC are nearly identical to those recently reported in Cayuga Lake (Pagano and Garner, 2019).

The Lake Champlain Valley of New York and Vermont is an important agricultural area for the production of dairy, grains, fruit, and vegetables (Medalie, 2013). Chlordanes are a subset of the chlorinated cyclodiene pesticides and were used extensively until restricted for food production in 1978 and totally banned in 1988 by USEPA. The total chlordane grouping measured in this study includes cis- and trans-nonachlor, alpha- and gamma-chlordane, and oxychlordane moieties. The technical chlordane formulation consisted of about 5–11% trans-nonachlor (USEPA, 1997), whereas over ½ of the total chlordane (23.9 ng/g ww) measured in LC lake trout was trans-nonachlor (53.5%), followed by cis-nonachlor (19.3%), alpha-chlordane (16.9%), oxychlordane (5.4%), and gamma-chlordane (4.9%) (SI-WS-7).

Of significance to the LC ecosystem are the total PBDE concentrations found in LC whole-fish lake trout. In 2007, PBDE concentrations were measured by Canadian researchers in ten lake trout (3–7 years old) that were collected from the Main Lake basin reporting concentrations similar to those present in the Great Lakes at the time (Gewurtz et al., 2011). PBDEs were introduced into the environment as technical formulations (Great Lakes Chemical Corporation; DE-71™, DE-79™, and DE-83™) based on the degree of bromination and used in numerous commercial applications as flame retardants. The PBDE technical formulations were voluntarily phased-out from commercial use starting in 2004 and completed in 2013. The top five PBDE congeners found in LC lake trout are BDE-047 (44.0 ng/g ww, 59.3%), BDE-099 (14.3%), BDE-100 (13.2%), BDE-154 (3.3%), and BDE-153 (3.0%) representing 93.1% of the total PBDEs (Σ 26 congeners) measured in this study (SI-WS-7). On an average basis, BDE-047 (44.0 ng/g ww) is individually the second most common LC lake trout contaminant, behind only pp-DDE (SI-WS-7). The five major PBDE congeners (BDE-047 + 099 + 100 + 153 + 154 = total-5-PBDE) found in LC lake trout match those found in the DE-71™ formulation, although the actual concentration ranking of the total-5-BDE congeners is different in LC lake trout relative to the DE-71™ formulation (SI-WS-7). Of particular note is the enhancement of BDE-047 (2,2′,4,4′-TeBDE) and

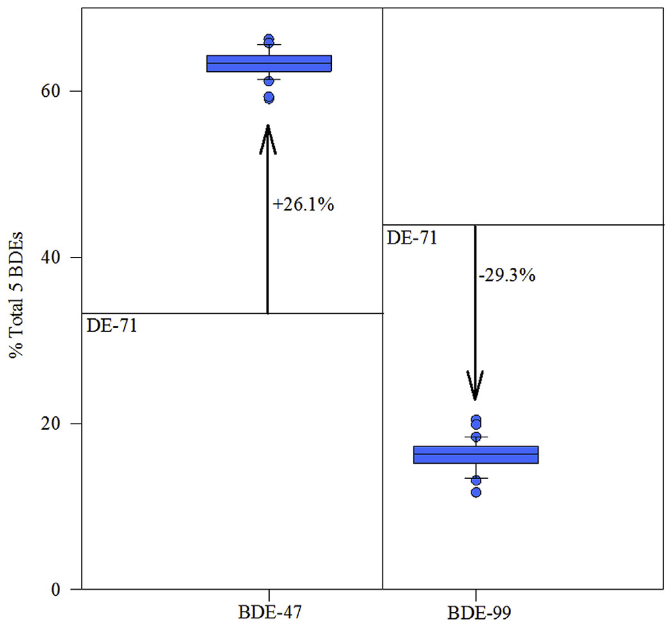

Fig. 1. PBDE-047 and PBDE-099 contributions to percent total-5-PBDEs in Lake Champlain whole-fish lake trout samples. Solid line indicates percent total-5-PBDE of PBDE-047 and PBDE-099 percentages found in the original DE-71™ technical formulation.

loss of BDE-099 (2,2′,4,4′,5-PeBDE) relative to percentages found in the DE-71™ formulation (Fig. 1, SI-WS-7). Stapleton and coworkers (2004) proposed that the debromination of a single meta-bromine (5′ position) on the BDE-99 molecule would result in the enrichment of BDE-47, although the debromination mechanism was not identified (Stapleton et al., 2004). Results from this study indicate the increase of BDE-47 (+26.1%) nearly matches the concomitant decrease in BDE-99 (−29.3%) relative to the percentages in the original DE-71 technical formulation (Fig. 1). In 1996, Smeltzer and Quinn estimated total direct wastewater treatment plant (WWTP) input volume to be 52 million cubic meters representing 0.2% of the total volume of Lake Champlain (Smeltzer and Quinn, 1996). WWTPs effluents are known contributing sources for PBDEs (North, 2004; Ratola et al., 2012; Song et al., 2006). The proportional distribution of PBDE sources to the LC environment have yet to be determined, but are likely due to a combination of waste water treatment plant (WWTP) discharges (Song et al., 2006), enhanced remobilization from sediment stores due to storm events, increased water temperatures (Hornbuckle et al., 2004), atmospheric transport/ deposition (Sofuoglu et al., 2013), and changes to the food web structure due to invasive species (Gewurtz et al., 2011; Marsden and Hauser, 2009). Further studies will be necessary in order to determine which sources can be mitigated to reduce PBDE loadings to the Lake Champlain ecosystem.

3.2. Dioxin and dioxin-like PBTs

The comprehensive dataset for all dioxin-like compounds and physical data measured in this study is provided in the SI (SI-WS-8 + 9), including 44 components for PCDD/F + CP4-PCB, and 42 for PCNs. Table 1 includes a summary of select Lake Champlain lake trout contaminant concentrations and descriptive statistics for whole-fish, fillets, and eggs. The average total concentrations and percent of total concentrations of CP4-PCBs (777.5 pg/g, 54.2%) and PCNs (635.4 pg/g, 44.3%) differ markedly as compared with total PCDD/F (22.9 pg/g, 1.6%) concentrations in whole-fish LC lake trout (SI-WS-13). Of greater importance in the assessment of the Lake Champlain ecological condition is the comparative toxicity of these dioxin-like contaminant groups relative to total concentrations. The most commonly used metric for the assessment of dioxin-like compounds is based on the activation of the aryl hydrogen receptor (AhR) or the toxic equivalence (TEQ) approach (WHO $_{2005}$), where each individual dioxin or dioxin-like compound is assigned a toxic equivalency factor (TEF) (Puzyn et al., 2007; Van den Berg et al., 2006). Importantly the TEQ approach is additive across all dioxin-like compound classes allowing for a comprehensive multi-chemical toxicological assessment in different environmental compartments and/or across trophic levels (CCME, 2001a, 2001b). As noted earlier, there are considerable differences in the concentration/abundance/toxicity of the various dioxin-like compounds found in LC biota based on assigned TEF values (Table 1 and SI-WS-13).

The largest difference in raw concentration (pg/g – ww) relative to the TEQ metric (pg-TEQ/g –ww) was noted for the PCDD/Fs and PCNs (SI–WS-13). Overall PCN concentrations as compared with dioxin-like concentration totals (PCDD/F + CP4-PCB + PCN) are reported at 44.3% as compared to 1.9% in toxic equivalence, whereas PCDD/F concentrations were only 1.6% of the dioxin-like concentration total relative to 27% of the TEQ measured in LC whole-fish lake trout.

Overall the dioxin-like compound concentrations (pg/g) are generally an order of magnitude lower than legacy compounds (ng/g) such as PCBs, PBDEs and OC pesticides measured in this study. The contribution from CP4-PCBs provided over 71% of the average TEQ for whole-fish LC lake trout, followed by 27% for PCDD/F, and only 1.9% for PCNs (SI-WS-13). PCB-126 (3,3′,4,4′,5-pentachlorobiphenyl, TEF = 0.1000) is the most toxicologically important of the non-ortho CP4-PCBs measured representing over 92% of the total CP4-PCB TEQ (SI-WS-13). Individually, four PCDD/F isomers provided nearly 96% of the TEQ (pg-TEQ/g) measured in LC whole-fish lake trout (SI-WS-13). The largest contribution was from 2378-TeCDF (34.7%) followed by 12378-PeCDD (27.2%), 2378-TeCDD (17.0%), and 23478-PeCDF (16.8%). On a concentration (pg/g) basis, the total furan contribution was 81.8% of the total as compared to total dioxin at 18.2%. The raw concentration (pg/g) contribution from the individual PCDF isomer 2378-TeCDF accounted for 64.7% of the total PCDD/F measured in whole-fish LC lake trout.

The elevated concentrations of 2378-TeCDF in LC lake trout are likely attributed to large concentrations of 2378-TeCDF and other dioxin-like compounds found in the Kraft mill sludge in the Southern Basin near Ticonderoga, New York (O'Keefe et al., 1994; Whittemore and Environmental Protection Agency, 1988). The Ticonderoga Paper Mill operated in the southern portion of LC for 70 years emptying Kraft mill sludge through Ticonderoga Creek and into the Southern LC basin. The resulting sludge covers an area of 1,000,000 m^2 and up to 6 m deep (Mason et al., 1977). A case was litigated before the Supreme Court of the United States (SCOTUS) over the pollution in the early part of the 1970's (*Vermont v. New York, 1974*). The *per curiam* decision held that it is not in the public interest to remediate the Southern Basin sludge deposit. In 1994, a New York State Department of Health – Wadsworth Laboratory study of PCDD and PCDF in the sediments of the affected area reported concentrations between 14 and 24,000 pg/g dry weight (dw) and 29–41,000 pg/g dw, respectively (O'Keefe et al., 1994). To our knowledge, no state or federal remedial activities have since been conducted in the Ticonderoga Creek - Southern Basin of Lake Champlain after the SCOTUS decision. The environmental fate of contaminants residing in the shallow Southern Basin sludge beds are particularly important as they are likely subject to periodic remobilization events (Hornbuckle et al., 2004; Nadal et al., 2015). It has been demonstrated that biota collected from sites near pulp and paper mills exhibit elevated levels of dioxins and furans, with furans generally having higher concentrations (Muir et al., 1992; Whittle et al., 1992). Hodsen and coworkers (1992) reported elevated levels of 2378-TeCDF and associated increased levels of AhR activity in white sucker (*Catostomus commersoni)* immediately downstream of an Kraft mill outfall (Hodson et al., 1992). According to a current State Pollutant Discharge Elimination System (SPDES) discharge permit (NY0004413), International Paper Company – Ticonderoga Mill (IPC-TM) is allowed a daily

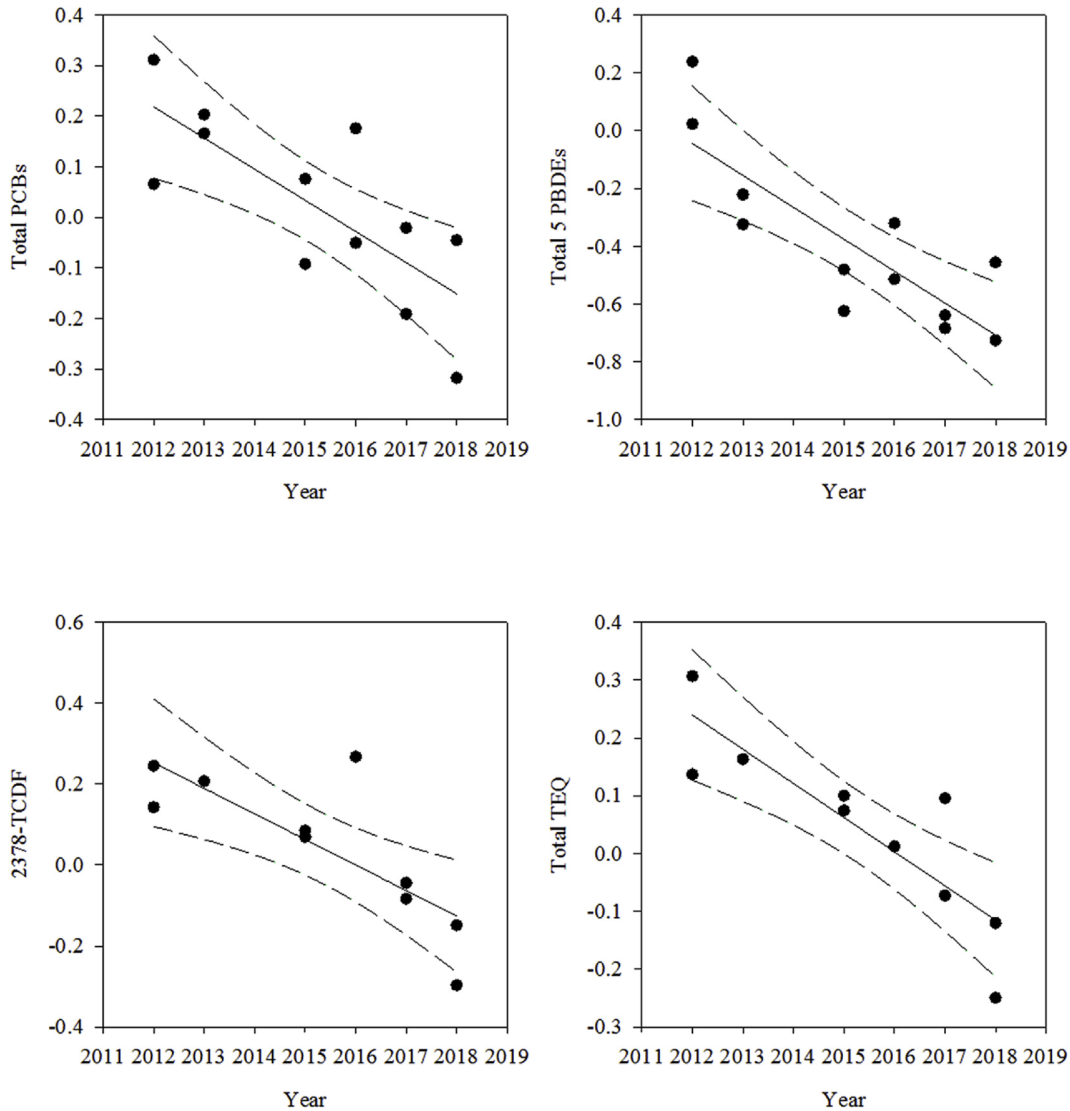

Fig. 2. Log-Linear first-order decay Age-trend models (ATM). It should be noted that the Y-axis does not represent a concentration.

maximum effluent limit release of 2378-TeCDD (10 pg/L) and 2378-TeCDF (39 pg/L) to an Internal Outfall 01 A holding pond (NYSDEC, 2018b). USEPA Toxics Release Inventory (TRI) pollution prevention reports indicates that IPC-TM releases approximately 1.8 g of dioxin and dioxin-like compounds per year ("Facility Profile Report | TRI Explorer | US EPA," n. d.).

Additional atmospheric inputs of dioxin-like compounds to the Lake Champlain basin have potentially been produced at the McNeil Generating Station (MGS) in Burlington, Vermont. In operation since 1984, the MGS burns biomass (wood chips) to produce electricity and steam. A critical review of prior bio-fuel incineration stack gas emission publications found a concentration range of 0.002–1.1 ng-TEQ/m^3, although wood chip combustion was determined to be very low (0.003 ng-TEQ/m^3) in comparison to other biomass categories (Schleicher et al., 2002; Zhang et al., 2017). Lavric et al. found similar emission levels in wood chip combustion power plants and reported flue gas emission rates between 0.026 and 0.095 ng-TEQ/kg - dry wood (Lavric et al., 2004). Other potential sources of chlorinated furans (including 2378-TeCDF) to the LC basin, which are thermodynamically favored combustion byproducts from uncontrolled waste incineration (including burn barrels and agricultural waste) and high-temperature industrial processes (Dopico and Gómez, 2015; Imagawa and Lee, 2001; Lee et al., 2005; Zhang et al., 2011).

Research describing the current (long-term database) and future (modeled) effects of climate change has blossomed in recent years. For example, the average August water temperature of Lake Champlain has increased nearly 3.8 °C since 1964 using a long-term monitoring database (Dalton et al., 2015; Smeltzer et al., 2012). Any modern comprehensive environmental assessment must take into account the potential remobilization of sequestered legacy contaminant sediment/soil stores due to the effects of stronger storms, fluctuating high and low water levels, enhanced wave action, and elevated water/air temperatures. Climate change derived scenarios (long-term database and modeled) are especially germane to the relatively shallow Southern and Northern basins in the LC watershed (SI Fig. S2). As noted earlier, the extensive Kraft mill sludge beds associated with the industrial waste stream of the International Paper Company (IPCO) dating back to 1880's were the point of legal action between New York State and the State of Vermont in the 1970's (*Vermont v. New York, 1974*). As a direct result of the SCOTUS *per curiam* decision, no remedial activity has ever been conducted on the LC Southern Basin sludge beds. It should be emphasized that the degree, types, and environmental impacts of the highly persistent environmental legacy contaminants likely contained in the Kraft mill sludge beds were unknown at the time of the SCOTUS decision. Additional research is needed to identify, quantify, and proportion the varied sources of biologically-available dioxin-like compounds partitioning to the LC water column and biota, especially those associated with the Kraft mill sludge beds in the Southern Basin of LC.

PCN concentrations measured in LC whole-fish lake trout averaged 635.4 pg/g – ww with a range of 439.4–966.62 pg/g – ww (Table 1). The major congeners reported (SI-WS-13) are mainly tetra- (43.5%), penta- (34.8%), and hexa-chlorinated naphthalenes (14.6%) comprising approximately 93% of the average total PCNs measured in LC whole-fish lake trout. Two congeners alone (tetraCN-42 and pentaCN-52/60) contributed over 46% of the overall raw PCN total, 23.5% and 22.6% respectively. Enrichment of the co-eluting PCN congeners pentaCN-52/60 (12,357-pentaCN/12,467-pentaCN) have been previously associated with incineration and industrial thermal processes (Helm et al., 2006). Alternatively, PCN-42 (1357-tetraCN) is not considered an environmental combustion marker and is only represented as a small percentage in the original PCN technical mixtures (Helm et al., 2006; Yamashita et al., 2000). Both PCN-042 (0.00001) and PCN-52/60 (0.0001) have relatively low TEF values (Puzyn et al., 2007). Similar PCN congener abundances were reported by Gewurtz and coworkers (2018) in several Great Lake fish species, including lake trout (Gewurtz et al., 2018). It is likely that the selective bioaccumulation of PCN-42, PCN-52/60, and other highly chlorinated PCNs are due to environmental persistence and resistance to metabolic degradation due to the structural (vicinal) position of chlorine substitution (Falandysz, 1998). Liu et al. (2014) suggested that impurities in technical PCB Aroclor™ formulations are the major source of PCNs to the environment, rather than contributions from industrial combustion processes (Liu et al., 2014). The sources of PCNs are likely a combination of combustion products and impurities in the PCB Aroclor™ solutions historically released from known industrial sources in the LC basin at Cumberland Bay, Saranac River, and Burlington Harbor (Callihan et al., 1998).

4. Trend modeling

4.1. Whole-fish lake trout

For this study, Lake Champlain whole-fish lake trout were modeled as log-linear correlations of first-order decay models fully described in recent publications (De Vault et al., 1986; Garner and Pagano, 2019; Grandjean et al., 2008; Huestis et al., 1997, 1996; Pagano et al., 2018; Paterson et al., 2005) (Figs. 2 and SI Fig. S3 – S6, Table 2). It is widely understood that lake trout accumulate contaminants as they age in a linear fashion, thus older and larger lake trout will contain enhanced concentrations of contaminants (Huestis et al., 1997, 1996; Pagano

Table 2
Model statistics for Lake Champlain whole fish COMP and individual fish ATM models.

LCLT 2012–2018 Whole COMP and INDIVIDUAL - ATM MODEL					
Contaminant	r2	k2	$t1_{/2}$	p	% Decrease
Total PCBs	0.538	−0.06	−11.3	0.004	30.9%
Total-5-PBDEs	0.661	−0.11	−6.3	< 0.001	48.3%
Total DDTs	0.002	−0.02	−38.5	0.336*	10.2%
Total Chlordanes	0.223	−0.03	−20.0	0.069*	18.8%
2378-TCDF	0.579	−0.06	−11.0	0.006	31.5%
2378-TCDD	0.529	−0.08	−8.3	0.010	39.3%
PCDD/F TEQ	0.526	−0.07	−9.9	0.011	34.3%
PCB_077	0.368	−0.05	−15.2	0.037	24.0%
PCB_081	0.638	−0.07	−10.5	0.003	32.7%
PCB_126	0.536	−0.06	−12.1	0.010	29.0%
PCB_169	0.512	−0.04	−16.2	0.012	22.7%
CP-PCB TEQ	0.539	−0.06	−12.4	0.009	28.5%
Total PCNs	0.572	−0.04	−17.8	0.018	20.9%
PCN TEQ	0.713	−0.07	−9.6	0.005	35.1%
Total TEQ (PCDD/F + CP)	0.709	−0.06	−11.7	0.001	29.9%

"*" indicates $p > 0.05$, relationship not statistically significant

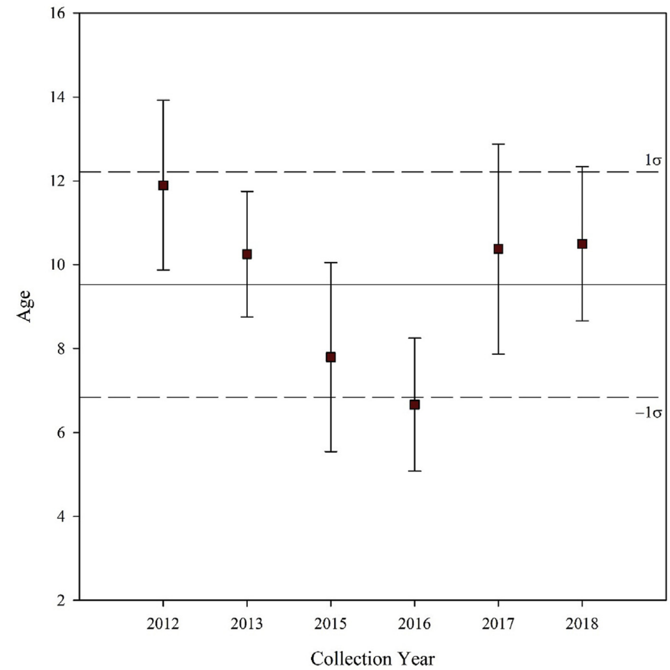

Fig. 3. Lake Champlain whole-fish lake trout average composite age - collection year assessment which indicates that age-correction was necessary for contaminant trend modeling.

et al., 2018; Skinner et al., 2010). As noted in recent publications, a critical variable that needs to be considered in all contaminant trend assessments is the overall uniformity of fish ages collected for trend assessments (Murphy et al., 2018; Pagano et al., 2018). Based on GLFMSP sampling and collection protocols, lake trout are collected in the 600–700 mm range to mitigate concentration effects due to changes in lake trout age population structure/reproductive recruitment. Fig. 3 illustrates that lake trout collected over the 2012–2018 period were biased by variable ages (criteria = 1σ), thus age correction was required for LC statistical trend modeling. Pagano and coworkers (2018) developed an Age-Trend Model (ATM) specifically to deal with significant changes in the Great Lakes lake trout age structure. The ATM utilized for this study "uses a lake-specific age-contaminant regression to mitigate the effect of a fluctuating lake trout age structure to directly improve the log-linear regression model" (Pagano et al., 2018). The ATM generates an elimination rate constant for each contaminant based on the ratio of the raw-model concentration and the concentration determined from the age-concentration regression. Although successfully modeled on the Salmon River (Garner and Pagano, 2019) and Cayuga Lake (Pagano and Garner, 2019), DAYMIX egg trend modeling was not possible on LC due to a lack of sufficient data points (N = 7, SI-WS-8). Where available, averages of individual fish were included in the model to increase statistical power. Rank Sum comparisons between the COMP and individual sample data show no statistical differences (SI-WS-4).

Whole-fish lake trout modeling revealed highly significant ($p < 0.05$) log-linear correlations for all dioxin-like contaminants measured (Figs. 2 and SI Fig. S3 – S6, Table 2, SI-WS-10). Statistical trend r^2 values ranging from 0.368 to 0.713 with the average $r^2 = 0.566$. Select dioxin-like contaminant half-lives ($t_{1/2}$) averaged 12.2 years, and ranged between 8.3 and 17.8 years generated from the apparent elimination rate constant (k_2). Overall contaminant decreases for the 2012–2018 period ranged from 20.9% (total PCNs) to 39.3% (2378-TCDD) (Table 2, SI-WS-10).

Two of the most important legacy compounds commonly found in the LC ecosystem, total PCBs and total-5-PBDEs demonstrated significant ($p < 0.05$) log-linear trend model correlations (Table 2, SI-

WS-10). The model fit for total PCBs and total-5-PBDEs were $r^2 = 0.538$, $p = 0.004$ and $r^2 = 0.661$, $p = < 0.001$, respectively. Total PCB and total-5-PBDE half-lives ($t_{1/2}$) were 11.3 and 6.3 years, respectively. At 6.3 years, the total-5-PBDE half-life was the shortest of any select contaminant measured in this study. Contaminant decreases for the 2012–2018 period for total PCBs and total-5-PBDEs were 30.9% and 48.3%, with total-5-PBDEs demonstrating the largest overall decrease over the 2012–2018 study (Table 2, SI-WS-10). No discernible trends were apparent for both total DDT ($r^2 = 0.002$, $p = < 0.336$) and total chlordanes ($r^2 = 0.223$, $p = < 0.069$). Although not statistically valid, trend analyses revealed longer half-lives for total DDT and total chlordanes (38.5 and 20.0 years) and smaller percent decreases (10.2% and 18.8%), respectively. The authors surmise that inputs of total DDT and total chlordane degradation products to the LC ecosystem are likely due to enhanced remobilization of residual soil agricultural contaminant runoff and resuspension of in-place sediment contaminant deposits due to climate change storm effects (Guilbert et al., 2014; McKnight et al., 2015; Rasmussen et al., 2015). A similar outcome was noted in a recent Cayuga Lake, New York publication which displayed slower rates of total DDT and total chlordane decline (Pagano and Garner, 2019).

4.2. Wildlife protection values (whole-fish, fillets, and eggs)

An essential aspect of any comprehensive lake study is to assess the effects of dioxin-like contaminants on sensitive wildlife populations. Tissue residue guidelines (TRG) "protective of wildlife consumers of aquatic biota" were developed by the Canadian Council of Ministers of the Environment (CCME, 2001a, 2001b). The CCME guidelines were developed based on the toxic equivalence (TEQ) approach which resulted in the "establishment of wildlife protection values (WPV) for sensitive populations" (Pagano and Garner, 2019). PCDD/F, CP-PCB, and PCNs are known aryl hydrocarbon receptor (AhR) agonists. WPV based on TEQ is the most comprehensive and inclusive approach for assessing the effects of dioxin-like chemicals on wildlife consumers of aquatic biota. TRG_{mammal} and TRG_{bird} have been established at 0.71 and 4.75 pg-TEQ/g/ww-diet respectively by the CCME. Values below the TRG_{mammal} and TRG_{bird} indicates "no adverse effect would be expected on sensitive wildlife consuming these tissues" (CCME, 2001a, 2001b). The most recent year of data (2018 and 2016) was utilized for the Lake Champlain WPV assessment (SI-WS-11). TEQ concentrations for 2018 COMP lake trout whole-fish sample (11.168 pg-TEQ/g) measured in Lake Champlain currently exceed both TRG_{mammal} and TRG_{bird}. Lake Champlain lake trout TEQ concentrations for 2016 COMP lake trout fillets (7.75 pg-TEQ/g) measured currently exceed both TRG_{mammal} and TRG_{bird}. DAYMIX lake trout egg samples collected in 2018 only exceed the TRG_{mammal}. The most realistic feeding scenario would be the consumption of the higher-energy portions of a lake trout carcass by opportunistic scavengers, although smaller mammals or birds may feed selectively on portions of the lake trout fillet and eggs. Utilizing the LC ATM model from this study, log-linear forecasting indicates that whole-fish lake trout TEQs will be below the TRG_{bird} and TRG_{mammal} guidelines protective of wildlife thresholds during the periods 2035–2047 and 2062–2088, respectively (SI-WS-11). The assumptions of this forecast are described fully in a previous publication (Pagano et al., 2018).

4.3. Human health screening values (fillets)

Currently each US state develops individual fish consumption advisories for anglers. Many state-based consumer guidance health advisories are based on the concentration of single contaminants, such as PCBs, Hg, and dioxins without consideration of potential additive toxicological effects (Gandhi et al., 2017). US states bordering the Great Lakes have formed the Great Lakes Consortium for Fish Consumption Advisories to develop cooperative standards for fish consumption advisories and the associated beneficial aspects of omega-3 fatty acid consumption (Williams et al., 2017). Separate Canadian fish advisories have also been promulgated for the adjoining Great Lakes waters (OMOE, 2005).

USEPA developed criteria establishing human health screening values for PCDD/F and CP-PCB utilizing the most inclusive multi-chemical toxic equivalence approach to generate fish consumption advisories (USEPA, 2009, 2000). The human health screening value was determined by USEPA and is expressed as total TEQ = 0.15 pg-TEQ/g-ww (USEPA, 2009, 2000). This is the "concentration in fish tissue that should not be exceeded with a potential cancer endpoint based on a total fish consumption-weighted rate. The following conditions apply: four 8-ounce fish meals per month, human adult body weight default value of 70 kg, cancer slope factor of 1.56 × 10–5 [mg/kg-d]-1, and 1 in 100,000 cancer risk level" (USEPA, 2009, 2000). Dioxin-like contaminant total TEQ results from 2015 to 2016 for Lake Champlain skin-on lake trout fillet samples are presented in Table 1. Based on current USEPA guidelines, all lake trout fillets from Lake Champlain analyzed for this study (average age = 7 years, average length = 612 mm or 24.1 inches) exceed the human health cancer screening value of 0.15 pg-TEQ/g-ww by a substantial margin (average = 8.61 pg-TEQ/g – ww). The overall percentage of total TEQ provided by the PCDD/Fs measured for this study was 32.5%, although the majority (67.5%) of total TEQ (PCDD/F + CP-PCB) associated with these fillet samples is due to the abundance of non-ortho CP-PCBs with the highest WHO_{2005} toxicity equivalence factors (TEF). Current New York State Department of Health (NYSDOH) and Vermont Department of Health (VTDOH) guidelines for fish consumption encompass several age/gender/reproductive age/location/length based restrictions to simplify consumption advisories for anglers (NYSDOH, 2019; VTDOH, 2013). A comparative assessment of USEPA, NYSDOH, and VTDOH consumption guidelines is beyond the scope of this research.

4.4. Lake Champlain - comparison to Great Lakes

Lake Champlain was chosen as a reference study lake for the USEPA GLFMSP based on known similarities with the Great Lakes in the areas of limnology, hydrology, fisheries/age structure, introduction of invasive species, climate change scenarios, and proportional population pressures (Denkenberger et al., 2007). As noted earlier, Lake Champlain has a long history of recorded legacy industrial chemical inputs similar to the Great Lakes. Long-term studies assessing contaminant dynamics in the Great Lakes are problematic due to scale and costs, but can be simulated by utilizing a "comparative and proportional approach among smaller but contrasting lake systems" (Baskaran et al., 2019; Pagano and Garner, 2019). Lake trout populations in Lake Champlain have a similar food web structure (trophic position/length of food web) as the Great Lakes (Guildford et al., 2008; Masset et al., 2019; Williams and Martinez, 2004). The similarities of Lake Champlain with the Great Lakes allows for a comparative assessment relative to contaminant concentrations (SI-WS-12).

Lake Champlain divides the northern portions of New York and Vermont and includes a population of about 600,000 people in the LC watershed. Lake Champlain has a very large drainage basin (DB) to lake surface area (SA) ratio (17.7:1) as compared to the DB:SA range of ratios (3.4–1.6:1) reported for the Great Lakes (SI-WS-12, (USDOC and NOAA, n. d.). The large drainage basin of LC would likely lead to enhanced agricultural and watershed runoff associated with documented climate change weather scenarios (increased rainfall and severe storm events) and contribute to greater legacy contaminant remobilization and loading from agricultural soils, atmospheric deposition, and sediments (Dalton et al., 2015; Guilbert et al., 2014; McKnight et al., 2015; Rasmussen et al., 2015).

As noted in an earlier study (Pagano and Garner, 2019), "lake trout are of special importance in comparative contaminant studies since they occupy the top predator position in all large bodies of water in the

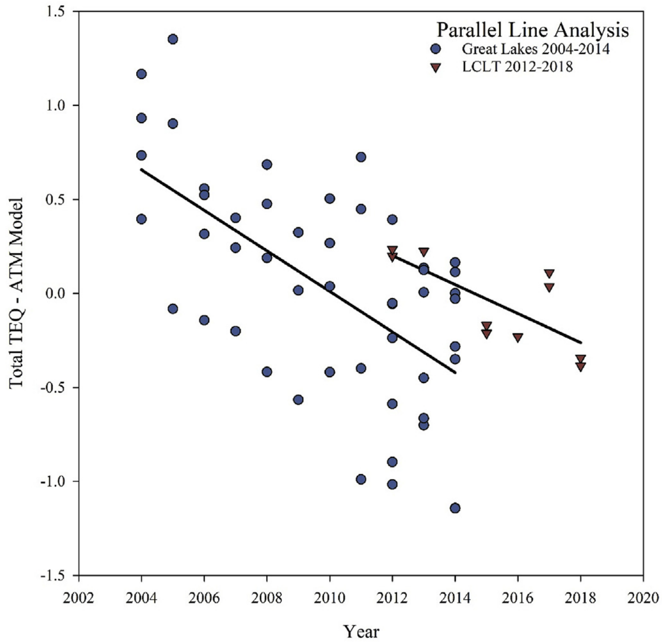

Fig. 4. Combined Great Lakes (2004–2014) and Lake Champlain (2012–2018) Total TEQ – Age Trend Model comparison. Parallel line analysis indicates no significant difference ($F_{1,57}$ = 7.71, p = 0.007). Y-axis units are arbitrary and do not constitute TEQ concentration. Great Lakes data was adapted from Pagano et al. (2018).

Great Lakes watershed". Utilizing GLFMSP sampling length protocols, comparative Von Bertalanffy growth function plots demonstrate that lake trout growth rates for the Great Lakes are similar to those found in Lake Champlain. PCDD/F and CP-PCB lake trout data collected between 2012 and 2018 from Lake Champlain "indicates that the general mechanisms of contaminant uptake, trends, and yearly percent decline reflect those recently described in the Great Lakes" (Pagano et al., 2018) (Fig. 4, SI-WS-12). The arbitrary units of the y-axis in Fig. 4 represents output from the ATM, since slope is the only directly comparable parameter. In the case of contaminant dynamics, another indication of LC direct comparability with the Great Lakes is the relative

Table 3
Age-restricted (7–13 years) rank sum select legacy Lake Champlain lake trout comparison with whole-fish lake trout in the Great Lakes and Cayuga Lake.

Kruskal-Wallis ANOVA on Ranks - lake trout ages 7–13[a] (significance $p < 0.05$)

	Cayuga	Erie	Huron	Michigan	Ontario	Superior
N	7	9	46	42	12	52
Age	0.164	0.178	1.000	0.538	0.142	1.000
Lipids %	1.000	0.027[b]	1.000	0.515	0.061	0.129
Total PCBs (ng/g - ww)	0.170	1.000	1.000	0.289	1.000	0.011[b]
Total DDTs (ng/g - ww)	0.330	0.358	0.136	1.000	1.000	< 0.001[b]
Total Chlordanes (ng/g - ww)	1.000	1.000	1.000	< 0.001	0.724	1.000
Total PBDEs (ng/g - ww)	0.016[b]	< 0.001[b]	0.017[b]	1.000	1.000	0.004[b]

[a] 7–13 is age range of lake trout COMP samples collected from Lake Champlain (N = 6).
[b] Significantly different than Lake Champlain lake trout.

percent changes of BDE-047 and BDE-099 as compared to congener percentages found in the original DE-71™ formulation. As noted earlier (legacy contaminant section), the percent contribution of BDE-047 and BDE-99 to the total-5-BDE are significantly different relative to technical formulation DE-71™, as determined by rank sum test ($p < 0.05$). A notable exception is Lake Huron lake trout, which appears to have an enlarged range of values (Fig. 5 + SI Fig. S7 + S8).

Of concern are the relative LC whole-fish lake trout concentrations of total-5-PBDE and total DDT as compared to the Great Lakes (Chang et al., 2012; Zhou et al., 2019, 2018). Controlling numerous/unknown variables in such comparisons is problematic, although many of the environmental conditions that exist in the Great Lakes are also found in LC as noted earlier in this section. Previous research has demonstrated the necessity of controlling the age variable as the most critical factor in trend or comparative assessments (Pagano et al., 2018; Pagano and Garner, 2019). For this study an age-restricted comparison of select legacy chemicals was tested for Great Lakes and LC whole-fish lake trout. The age range (7–13 years) utilized was the full range of ages of LC lake trout measured over this study. Results from the Kruskal–Wallis ANOVA on Ranks test for each select contaminant group, age, and lipids

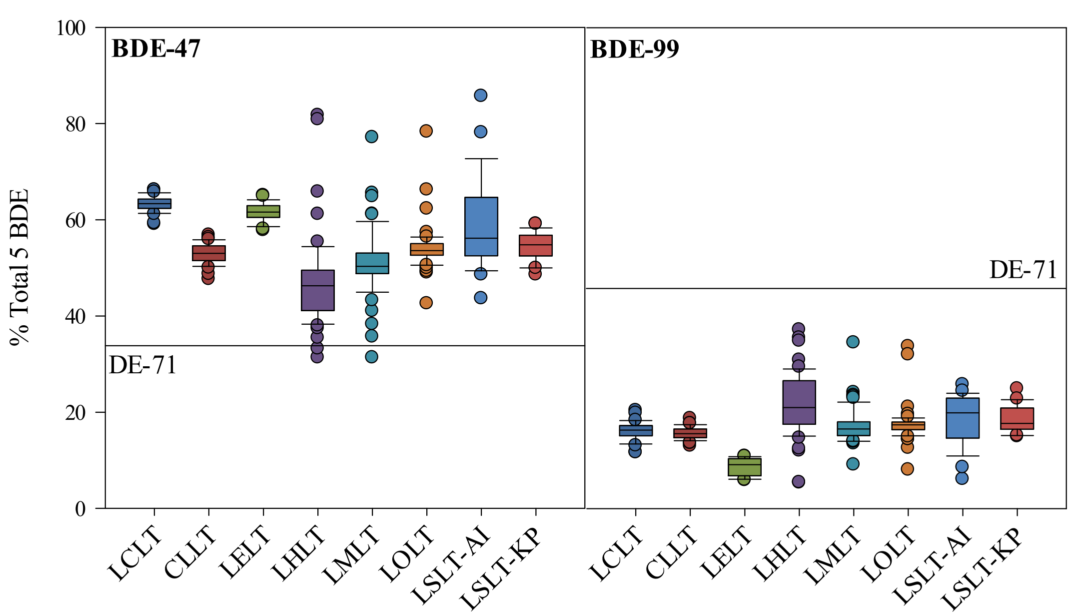

Fig. 5. PBDE-047 and PBDE-099 contributions to percent total-5-PBDEs in Lake Champlain, Cayuga Lake, and Great Lakes whole-fish lake trout samples. Solid line indicates percent total-5-PBDE of PBDE-047 and PBDE-099 percentages found in the original DE-71™ technical formulation.

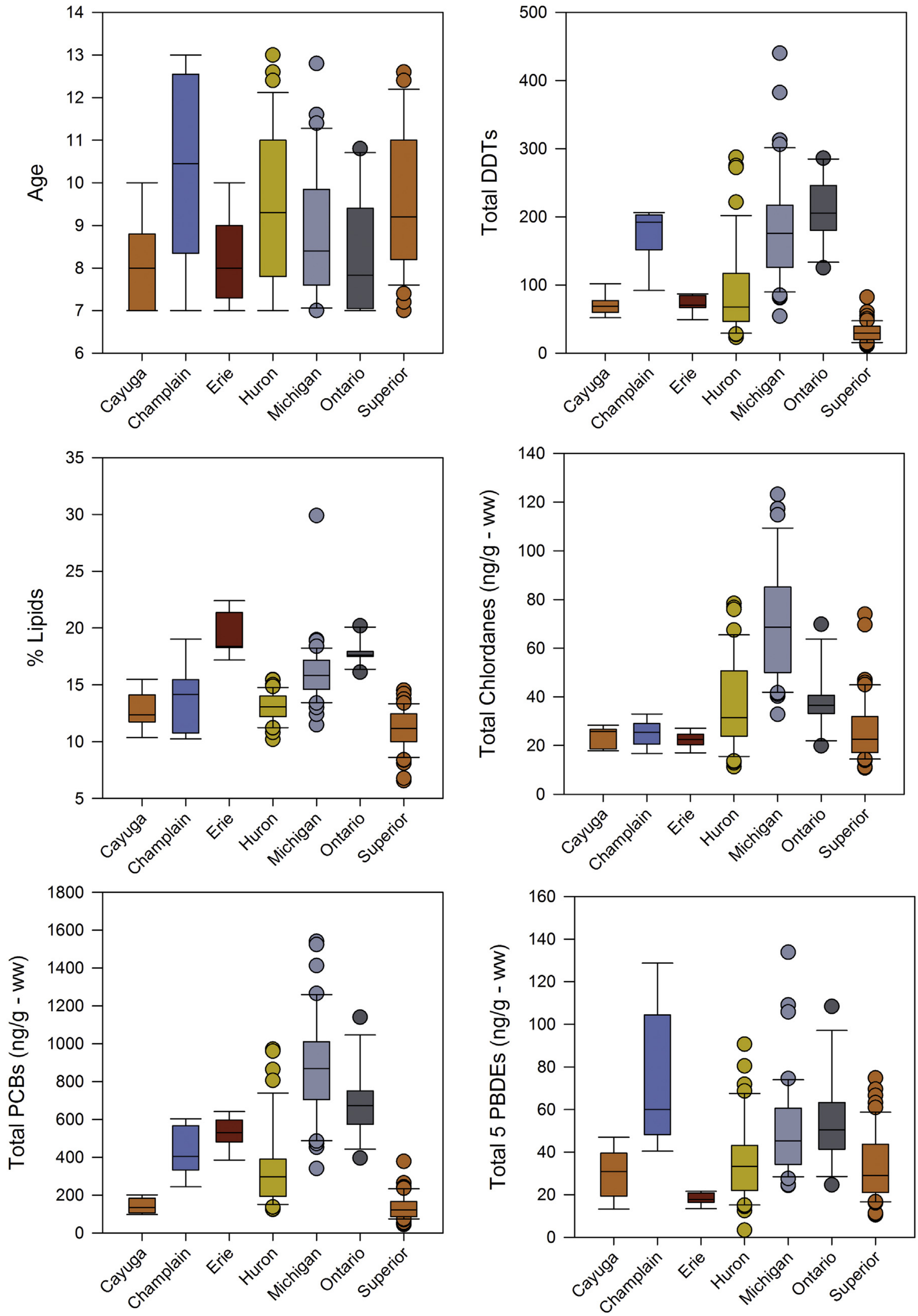

Fig. 6. Select legacy contaminant comparison (ng/g – ww) of Lake Champlain, Cayuga Lake, and Great Lakes whole-fish lake trout. Great Lakes data was adapted from Chang et al. (2012) and Zhou et al. (2018), 2019. Cayuga Lake data was adapted from Pagano and Garner (2019).

across the Great Lakes are reported in Table 3. Notably elevated LC contaminant concentrations, which are comparable to the GL and are illustrated for total-5-PBDEs, total-DDT, and total PCBs (Fig. 6). Of particular note is the relative concentration of total-5-PBDE to those found across the GL, which indicates LC as having the highest average total-5-PBDE concentration over the 2012–2018 period.

5. Conclusions

Lake Champlain has a long history of legacy industrial pollution similar to the Great Lakes. Our research provides further evidence that incremental progress has been made mitigating the effects of contaminant inputs to Lake Champlain through state and federal regulatory actions. Average total PCB concentrations over the 2012–2018 sampling period in LC whole-fish lake trout was 395.7 ng/g ww, the highest average concentration of any contaminant grouping reported in this study. Total DDT, total chlordane, and total-5-PBDEs concentrations were 179.3, 25.1, and 71.9 ng/g-ww, respectively. Of particular concern is the relative concentration of total-5-PBDE to those found across the GL, which indicates LC as having the highest average total-5-PBDE concentration over the 2012–2018 period. Our study demonstrated that Lake Champlain lake trout collected over the 2012–2018 period were biased by age, and an Age-Trend Model (ATM) was used to “mitigate significant lake trout population age-structure changes” (Pagano et al., 2018). Whole-fish lake trout ATM modeling revealed highly significant ($p < 0.05$) log-linear correlations for all dioxin-like contaminants measured. Overall contaminant decreases for the 2012–2018 period ranged from 20.9% (total PCNs) to 39.3% (2378-TCDD). The dioxin-like contaminant concentrations in Lake Champlain show similar rates of year by year decline when compared to the Great Lakes rates over similar periods. Log-linear forecasting indicates that whole-fish lake trout TEQs will be below the guidelines protective of wildlife thresholds during the periods 2035–2047 (TRG_{bird}) and 2062–2088 (TRG_{mammal}). The timeframes of these forecasts exceed those recently reported in the Great Lakes and Cayuga Lake, NY, indicating slower rates of LC contaminant decline for dioxin-like contaminants. Based on current USEPA guidelines, all lake trout fillets from Lake Champlain analyzed for this study exceed the human health cancer screening value of 0.15 pg-TEQ/g-ww by a substantial margin (average = 8.61 pg-TEQ/g – ww). Based on currently available long-term weather and water monitoring trends in Lake Champlain, additional studies are necessary to assess the effects of current and future climate change weather scenarios on Lake Champlain contaminant dynamics. Additional research is also needed to determine and mitigate the sources of legacy contaminants to the LC ecosystem, especially as it relates to the source apportionment of PBDEs and total-DDT. Based on previously reported Kraft mill process sludge research and concurrent with the reported effects of climate change, studies should be conducted in the Southern Lake Basin to characterize and determine if stores of dioxin-like contaminants are biologically available to the food web in Lake Champlain.

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CRediT authorship contribution statement

James J. Pagano: Conceptualization, Methodology, Writing - original draft. **Andrew J. Garner:** Conceptualization, Methodology, Writing - review & editing.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2020.109329.

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