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Characterization and spatial distribution of organic-contaminated sediment derived from historical industrial effluents

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Abstract Organic sediment contaminants [polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans (PCDD/Fs), and polycyclic aromatic hydrocarbons (PAHs)] were assessed using secondary monitoring data from a former tidal estuary (Boat Harbour) impacted by historical industrial effluents. Spatiotemporal characterization of PCDD/Fs and PAHs in sediments was conducted to inform a sediment remediation program designed to return this contaminated aquatic site back to a tidal lagoon. Spatiotemporal variations of sediment PCDD/F and PAH concentrations across Boat Harbour and off-site reference locations were assessed using secondary monitoring data collected between 1992 and 2015. Sediment PCDD/F toxic equivalency (TEQ) and PAH concentrations were compared to sediment quality guidelines. Sediment PCDD/F concentrations exceeded the highest effect thresholds posing severe ecological health risks. High sediment PCDD/F concentrations have persisted in Boat Harbour despite implementation of *Pulp and Paper Mill Effluent Chlorinated Dioxins and Furans Regulations* in 1992. PAH concentrations varied greatly. Five individual PAH compounds frequently exceeded severe effect thresholds, in contrast to total PAHs, which were below severe effect thresholds. Forensic analysis using PAH diagnostic ratios suggests pyrogenic PAHs derived from wood processes or coal combustion were likely sources. Twenty-five years of monitoring data revealed large data gaps in our understanding of sediment characteristics in Boat Harbour. Gaps included spatial (vertical and horizontal) and temporal variations, presenting challenges for remediation to accurately delineate sediment contaminants. Deeper horizons were poorly characterized compared to shallow sediments (0–15 cm). Historical secondary monitoring data showed that spatial coverage across Boat Harbour was inadequate. Due to severe ecological health risks associated with high sediment PCDD/F concentrations, remediation of the entire sediment inventory is recommended. Detailed vertical and horizontal sampling within Boat Harbour, establishment of local baseline concentrations, and additional sampling in down-gradient-receiving environments for a suite of contaminants are required to better characterize sediments prior to remediation.

Keywords Industrial effluent · Sediment monitoring · Organic contaminants · Polychlorinated dibenzo-*p*-dioxins · Polychlorinated dibenzofurans [PCDD/Fs] · Polycyclic aromatic hydrocarbons (PAHs) · Remediation

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Introduction

Pulp mill effluents can deleteriously impact aquatic ecosystems (Sunito et al. 1988; Colodey and Wells

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1992; Ali and Sreekrishnan 2001) caused by inorganic and organic loadings (Pokhrel and Viraraghavan 2004; Hewitt et al. 2006; Soskolne and Sieswerda 2010; Munkittrick et al. 2013; Hoffman et al. 2015, 2017a, b). Deleterious releases to aquatic ecosystems from pulp mills in Canada are governed under *Pulp and Paper Effluent Regulations* (PPER) pursuant to the *Fisheries Act* (1985) (PPER 1992; Roach and Walker 2017). In Canada, *Pulp and Paper Mill Effluent Chlorinated Dioxins and Furans Regulations*, issued under the Canadian Environmental Protection Act (1999), require mills using chlorine for bleaching to discharge effluent with dioxin and furans below measurable levels (EC 2013, 2014).

A bleached kraft pulp mill and chlor-alkali facility in Pictou County, Nova Scotia, has discharged wastewater effluent into the Boat Harbour Treatment Facility (BHTF) and subsequently into a 140-ha former tidal lagoon (Boat Harbour) since 1967. Boat Harbour lies within the Mi'kmaq Pictou Landing First Nation (PLFN) community (Fig. 1). The chlor-alkali facility used the BHTF and Boat Harbour to treat effluent from 1971 to 1992. The mill has undergone several ownership changes since 1967, as well as several changes to the pulping process. Previous owners used elemental chlorine in the bleaching process which was changed to chlorine dioxide in 1997 (Northern Pulp 2017) to meet PPER requirements for dioxins and furans (PPER 1992). Effluent treatment has been previously described in greater detail by Hoffman et al. (2017a). The treatment process has undergone several upgrades in aeration capacity since original inception of the plant. Currently, effluent is pumped to settling ponds, then to an aerated stabilization basin for treatment prior to discharge into Boat Harbour and subsequent discharge through a dam at the mouth of the former estuary (JWEL and Beak Consultants 1992; Fig. 2, top). Residence time (~20–30 days) of treated effluent in Boat Harbour has deposited large volumes of unconsolidated sediments, impacted with inorganic and organic contaminants, raising concerns for the Pictou Landing First Nation and nearby local communities (Hoffman et al. 2015; Pictou Landing Native Women's Group et al. 2016). The province of Nova Scotia owned and operated the BHTF from 1967 to 1995, after which the mill owners took over operation.

The province of Nova Scotia committed to ceasing use of Boat Harbour as an effluent-receiving lagoon by January 30, 2020, to enable remediation of contaminated sediments under the Boat Harbour Act (2015). However, before remediation can begin, detailed characterization of sediments is required to inform remedial decisions. Despite dozens of ad hoc historical studies conducted in and around Boat Harbour, the only holistic characterization of sediment contaminants has been performed by Hoffman et al. (2017a) who reported widespread metal(loid) sediment contamination. No comparable study exists for organic contaminants which is the focus of this study. Previous studies (e.g., JWEL 1997, 1999, 2001, 2005; JWEL and Beak Consultants 1992, 1993; Stantec 2013, 2016) reported a suite of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) along with p*olycyclic aromatic hydrocarbons* (*PAHs*) distributed throughout Boat Harbour sediments. PCDD/Fs are unintentional by-products of combustion processes and various industrial activities (Sunito et al. 1988). Industrial chlorinated organic chemical processes that produce PCDD/Fs include effluent wastewater from pulp mills (McLeay 1987; Richman et al. 2016) and chlor-alkali facilities (Svensson et al. 1991, 1993; Kannan et al. 1998; Yamamoto et al. 2018). Although naturally occurring, *PAH* contamination largely originates from anthropogenic activities, including combustion processes (MacAskill et al. 2016; Walker et al. 2017; Davis et al. 2019a, b) and pulp processing, especially those involving elemental chlorine (Hoffman et al. 2017a, b).

Sediments impacted by industrial activity can accumulate organic contaminants and pose unacceptable ecological risks to aquatic biota (Hope 2006; El-Shahawi et al. 2010; Walker and MacAskill 2014). Although some PAHs are carcinogenic, they generally have lower risk of acute *toxicity* to humans (CCME 2008; ATSDR 2009). However, PCDD/Fs are of a primary concern, because they are highly persistent, lipophilic, and bioaccumulative and can be acutely toxic and carcinogenic to biota and humans (Norstrom 2006; Hites 2011). Long-term sediment contamination exceeding sediment quality guidelines (SQGs) often requires intensive remediation and site-specific disposal procedures (Walker et al. 2013a, 2015a, b).

A comprehensive assessment of organic contamination has not been conducted for Boat Harbour but is essential prior to remediation to accurately delineate sediment contaminant characteristics (e.g., depth, spatiotemporal extent, and magnitude of impacts). This paper expands on previous work by Hoffman et al. (2017a) to conduct a comprehensive sediment

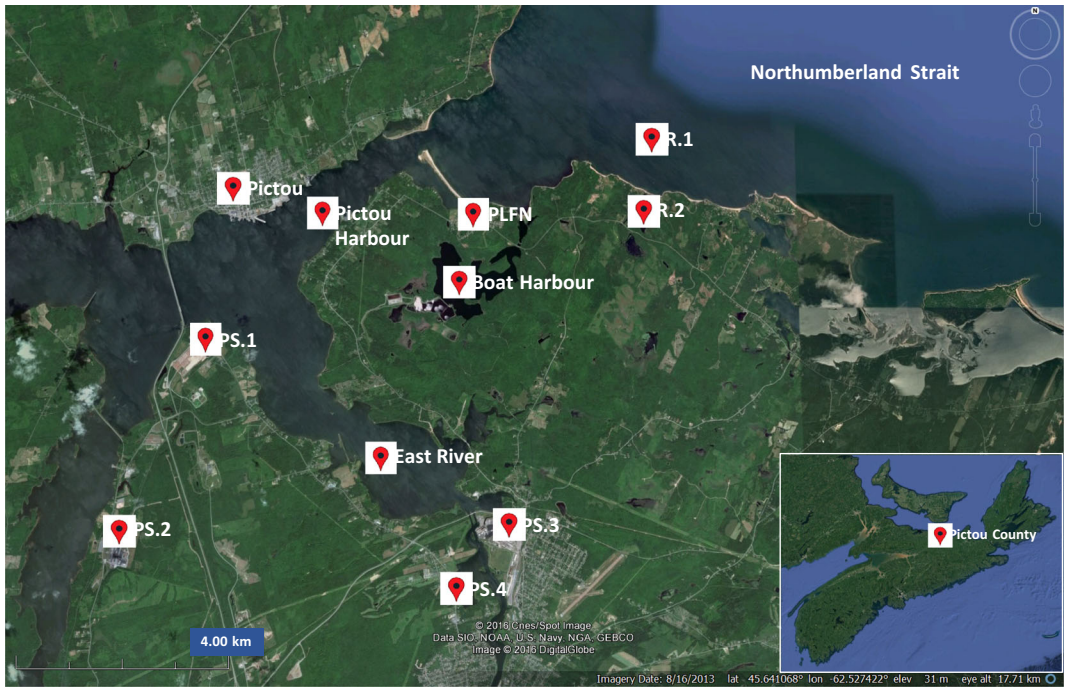


Fig. 1 Location of Boat Harbour in Pictou County, Nova Scotia, relative to communities (e.g., Pictou and Pictou Landing First Nation (PLFN)), two previously studied reference sediment sampling sites (i.e., offshore and Fergusons Pond (R.2)), and local point source emitters [e.g., pulp and paper mill (PS.1), tire manufacturing facility (PS.2), coal-fired thermal electrical generating station (PS.3), and former chlor-alkali facility (PS.4)] (©Google Earth)

characterization examining a suite of organic contaminants, focusing on PCDD/Fs and PAHs, using secondary monitoring data. Specifically, this study examines long-term sediment monitoring data between 1992 and 2015, using geographic information system (GIS) techniques. Distribution of organic sediment concentrations was examined spatiotemporally. A discussion of findings in relation to potential contamination sources and gaps in long-term monitoring data is provided to better inform future remedial action plans for Boat Harbour.

Materials and methods

Review of secondary monitoring data

Relevant sediment organic chemistry secondary monitoring data related to Boat Harbour was obtained from government reports and peer-reviewed articles based on approaches reported by Hoffman et al. (2017a). Organic sediment concentrations (including PAHs; PCDD/Fs; volatile organic compounds; benzene, toluene, ethylbenzene, and xylenes; total petroleum hydrocarbons; polychlorinated biphenyls; and total organic carbon) using standardized laboratory analytical methods were relevant for this study. Sample locations had to be georeferenced. Details about sediment sampling methods and depth were also a requirement. This resulted in only eight relevant studies used for this review (JWEL 1997, 1999, 2001, 2005; JWEL and Beak Consultants 1992, 1993; Stantec 2013, 2016).

Sediment sampling

Sediments were collected using cores or grabs between 1992 and 2015. Assumptions made regarding georeferencing sampling locations (entered in ©ArcMap) and sampling techniques can be found in Hoffman et al. (2017a). Relevant criteria included PCDD/F and PAH concentrations, location of the sample (decimal degrees x, y coordinates), sample identification, date, depth (cm), and characteristics such as marine sediment and unconsolidated sediment/deposits. Sample location coordinates were generated by overlaying report maps in ©Google Earth to attain a unified coordinate system (Hoffman et al. 2017a).

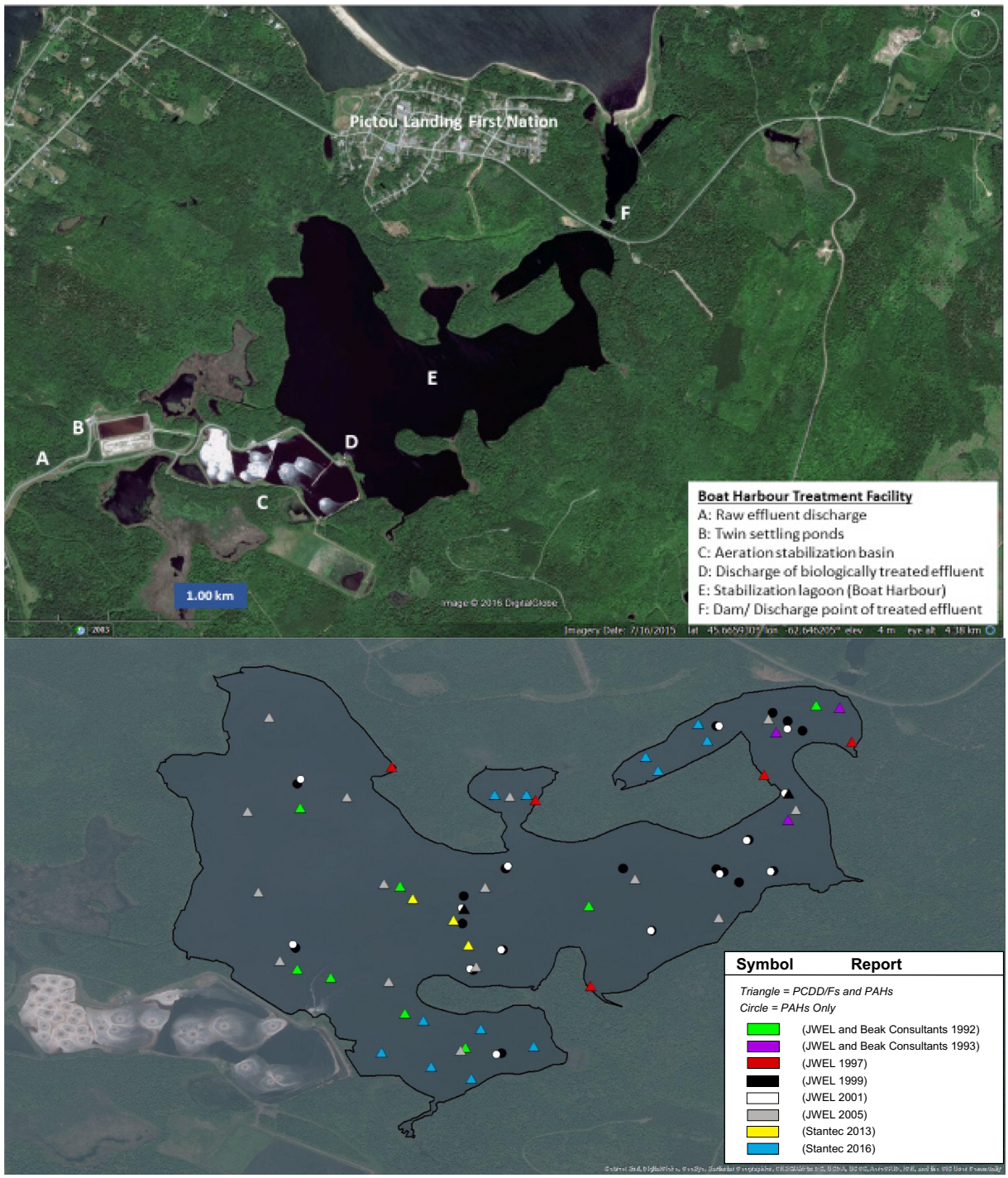


Fig. 2 Components of the Boat Harbour Treatment Facility (BHTF) and Pictou Landing First Nation (PLFN) community (top). Spatiotemporal coverage (1992–2015) of the sediment sampling stations in Boat Harbour (bottom). Colored triangles indicate sampling and analysis of PCCD/Fs and PAHs, and colored circles indicate sampling and analysis of PAHs only (©Google Earth; from Hoffman et al. 2017a)

Quality control

Individual reports are cited where the use of method blanks, spike blanks, matrix spikes, and duplicate samples varied (Hoffman et al. 2017a). As reported by Hoffman et al. (2017a), commercial laboratories accredited by Standards Council of Canada were used for analysis of samples using Environment Canada EPS 1/RM/19 standard methods (Trudel 1991; Environment Canada 1992). Unless otherwise indicated, samples and field duplicates were analyzed on a dry weight (dw) basis. Detection limits (DLs) for PCDD/Fs varied between 0.0987–46 pg/g and 0.005–0.06 mg/kg for PAHs. Recovery rates for PCDD/Fs varied between 30 and 120%. Censored data (½DL) were used for all <DL data (MacAskill et al. 2016; Davis et al. 2018). Total PAH values were derived by using summed concentrations plus ½DL values for all <DL. Boat Harbour sediment PCDD/F and PAH data were compared to two reference sites in the down-gradient-receiving marine environment (R.1) (JWEL 1994) and Fergusons Pond (R.2) (Fig. 1) (JWEL 1997, 1999, 2001).

Data analysis

Currently, Boat Harbour is a *freshwater* habitat but it will be returned to tidal conditions post-remediation (Hoffman et al. 2017a). For this study, similar approaches were used as Hoffman et al. (2017a). For example, PAH concentrations of 103 samples from 85 stations were compared to both current freshwater and marine Canadian Council of Ministers of the Environment (CCME) SQGs (CCME 2016). Contaminant concentrations below low-effect level CCME interim sediment quality guidelines (ISQGs) have little chronic or acute effect on aquatic biota, whereas contaminant concentrations above severe-effect level CCME probable effect levels (PELs) are highly likely to negatively impair aquatic biota (Walker et al. 2015a, b). In this study, sediment concentrations were assessed as *severely contaminated* if PELs were exceeded, *moderately contaminated* between ISQGs and PELs, and *uncontaminated* if sediment concentrations <ISQGs (Walker et al. 2015a). No CCME guidelines for total PAHs exist, so total PAH sediment concentrations were compared to effects range low (*ER-L)* (4.02 mg/kg) *and effects range median* (ER-M) (44.8 mg/kg) (Long et al. 1998; NOAA 1999).

Toxic equivalency (TEQ) concentrations of 60 PCDD/F samples from 48 stations were calculated by multiplying the PCDD/F concentrations with associated toxic equivalency factors (TEFs), representing a weighted quantity measure based on the toxicity of each PCDD/F congener. Boat Harbour PCDD/F TEQ concentrations were determined using WHO-established TEFs applied to fish, birds, and humans/mammals (van den Berg et al. 1998) and then compared to related CCME guidelines (CCME 2001a, b, 2002). Temporal PCDD/F congener patterns and percent contributions (Σ17PCDD/Fs) in the sampled Boat Harbour sediment were illustrated using stacked bars. In the down-gradient-receiving marine environment, PCDD/F congener concentration data was limited to a single sample at R.1 (JWEL 1994) (Fig. 1).

PAH diagnostic ratios were used to determine source apportionment for PAH compounds, as PAH mixtures maintain their proportional integrity (ratio of compounds present) following release, regardless of changes in PAH bulk concentration (Tobiszewski and Namiesnik 2012). PAH ratios are particularly useful for determination of PAH source apportionment using historical datasets (MacAskill et al. 2016; Walker et al. 2017; Davis et al. 2019a, b). PAH ratios were applied using anthracene, fluoranthene, phenanthrene, and pyrene, due to high levels of detection: fluoranthene/pyrene to phenanthrene/anthracene (adopted from Maxxam 2016) and fluoranthene/fluoranthene + pyrene to anthracene/anthracene + phenanthrene (Yunker et al. 2002). Box and scatter plots were used to display temporal (1992–2015) and spatial (vertical) variations of PCDD/F and PAH sediment concentrations, respectively. Significant temporal differences ($p < 0.05$ level) were determined by one-way analysis of variance (ANOVA) followed by a Tukey's test using Minitab.

Organic sediment concentrations from reports were presented unmodified (except censored data). Statistical analysis of independent temporal differences in organic contaminant concentrations used ANOVA. Inter-annual data independence was assumed because of a variation in sampling techniques (abiotic variation) and bioturbation conditions (biotic variation). Mid-range sample depths were used to assess the vertical variation of PCDD/F and PAH concentrations. Like Hoffman et al. (2017a), spatio-temporal variation of PAH and PCDD/F concentrations and sampling locations was assessed using ©ArcMap over three periods (1992–1996, 1998–

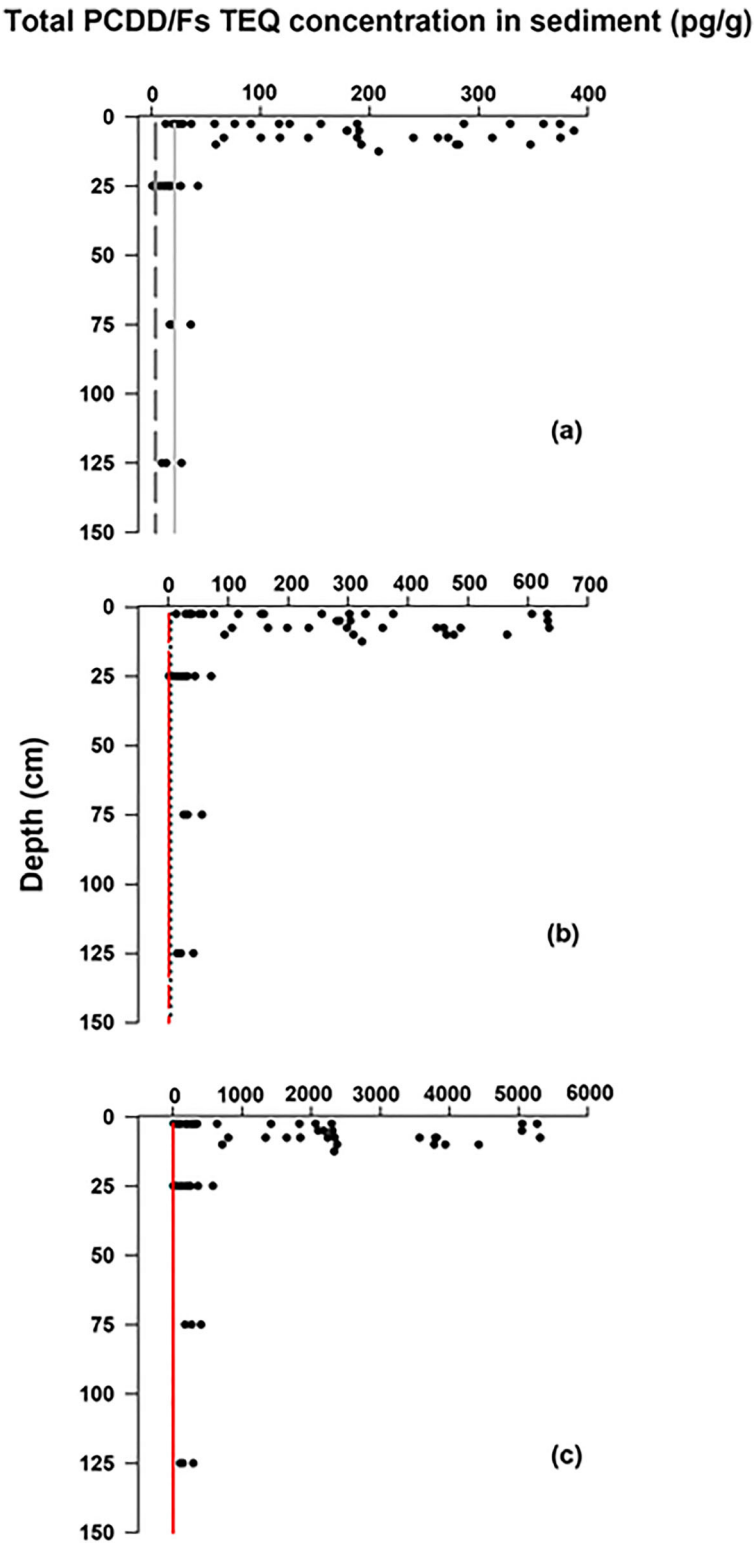
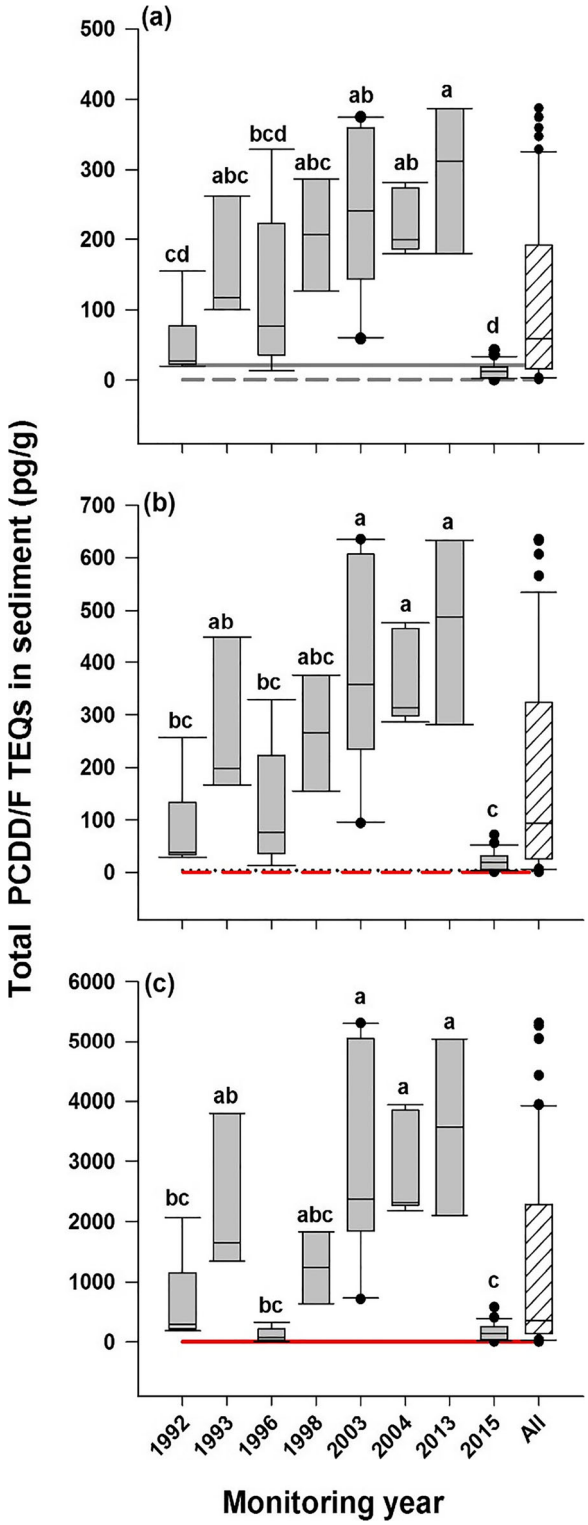


Fig. 3 Vertical variation of the total PCCD/F TEQ sediment concentrations ($n = 60$) with depth (cm) for different receptors. **a** Fish. **b** Human/mammals. **c** Birds. *Black circles* indicate individual sediment concentrations. CCME freshwater and marine sediment quality guidelines are the same for fish category and indicated using *solid horizontal line* for PEL value (21.50 pg/g) and *dashed line* for ISQG value (0.85 pg/g) (CCME 2001a). Soil quality guideline for the protection of environmental and human health for all land uses is shown using *black dotted horizontal line* (4.00 pg/g) (CCME 2002). CCME tissue residue guidelines for the protection of wildlife consumers of aquatic biota are indicated using *red dashed line* for mammals (0.71 pg/g) and *red solid line* for birds (4.75 pg/g) (CCME 2001b)



◀ **Fig. 4** Temporal variation (~25 years) of the total PCCD/F TEQ sediment concentrations (n = 60) in Boat Harbour for different receptors. **a** Fish. **b** Human/mammals. **c** Birds. *Black circles* indicate outliers; *error bars* indicate minimum and maximum values that are not outliers; *gray rectangles* indicate concentrations for a given year; *patterned rectangles* indicate concentrations for all years combined. CCME freshwater and marine sediment quality guidelines are the same for fish category and indicated using *solid horizontal line* for PEL value (21.50 pg/g) and *dashed line* for ISQG value (0.85 pg/g) (CCME 2001a). Soil quality guideline for the protection of environmental and human health for all land uses is shown using *black dotted horizontal line* (4.00 pg/g) (CCME 2002). CCME tissue residue guidelines for the protection of wildlife consumers of aquatic biota are indicated using *red dashed line* for mammals (0.71 pg/g) and *red solid line* for birds (4.75 pg/g) (CCME 2001b). Significant temporal differences were determined by one-way ANOVA followed by Tukey's test; years attributed with the same letters were not significant and those with different letters were significantly different ($p < 0.05$ level)

2003, and 2004–2016) against which future studies post-remediation can compare against the study of Hoffman et al. (2017a).

Results and discussion

Hoffman et al. (2017a) reported that secondary monitoring data varied widely in sampling techniques (e.g., using grabs, cores, discrete or composite sampling) and sample depth (e.g., shallow vs. deep). For this study, approximately 17% and 38% of PCDD/F and PAH samples, respectively, were grab samples, while 83% and 62% of PCDD/F and PAH samples were cores. This variability created challenges for inter-annual comparisons. Overall, sediments were highly organic (4–27% mean total organic carbon). Generally, the highest PCDD/F and PAH concentrations corresponded with high total organic carbon contents and are an important factor governing the occurrence of persistent organic contaminants (Alimohammadi et al. 2017). Although total organic carbon data is not presented herein, it has previously been reported in greater detail by Hoffman et al. (2017a). A review of previous sediment sampling programs in Boat Harbour showed that subsurface conditions consisted of anthropogenic black freshwater organic sediment (12–26 cm deep), underlain by marine clay (Spooner and Dunnington 2016; Stantec 2016). Temporal georeference analysis of sampling locations revealed that overall spatial coverage was lacking (Fig. 2, bottom), corroborating Hoffman et al. (2017a), who

Table 1 Sediment quality guideline (SQG) exceedances for select PAH compounds, total PAHs, and PCDD/F TEQs in Boat Harbour between 1992 and 2015

	Freshwater				Marine					
	ISQG		PEL		ISQG				PEL	
	SQG limit	Number of exceedances (%)	SQG limit	Number of exceedances (%)	SQG limit	Number of exceedances (%)			SQG limit	Number of exceedances (%)
Anthracene (mg/kg; n = 103)	0.047	52 (50.5)	0.245	31 (30.1)	0.047	52 (50.5)			0.245	31 (30.1)
Fluoranthene (mg/kg; n = 103)	0.111	77 (74.8)	2.355	8 (7.8)	0.113	77 (74.8)			1.494	29 (28.2)
Fluorene (mg/kg; n = 103)	0.021	76 (73.8)	0.144	7 (6.8)	0.021	76 (73.8)			0.144	7 (6.8)
Phenanthrene (mg/kg; n = 103)	0.042	86 (83.5)	0.515	60 (58.3)	0.087	77 (74.8)			0.544	59 (57.3)
Pyrene (mg/kg; n = 103)	0.053	81 (78.6)	0.875	42 (40.8)	0.153	72 (69.9)			1.398	29 (28.2)
Total PAHs (mg/kg; n = 103)	ER-L				ER-M					
	SQG limit	Number of exceedances (%)			SQG limit				Number of exceedances (%)	
	4.02	46 (44.7)			44.80				0 (0)	
PCDD/Fs (pg/g; n = 60)	Freshwater and marine (fish)				Canadian tissue residue guidelines				Canadian soil quality guidelines for the protection of environmental and human health	
	ISQG		PEL		Mammals		Birds		Human	
	0.85	60 (100)	21.50	40 (66.6)	0.71	60 (100)	4.75	60 (100)	4.00	56 (93.3)

ISQG indicates CCME interim sediment quality guidelines and PEL indicates CCME probable effect levels (CCME 2016). There are no CCME guidelines for total PAHs, so these were compared to effects range low (ER-L) and effects range median (ER-M) (Long et al. 1998; NOAA 1999). The total sediment samples (n) are indicated under each parameter and include sediment collected from all depth horizons

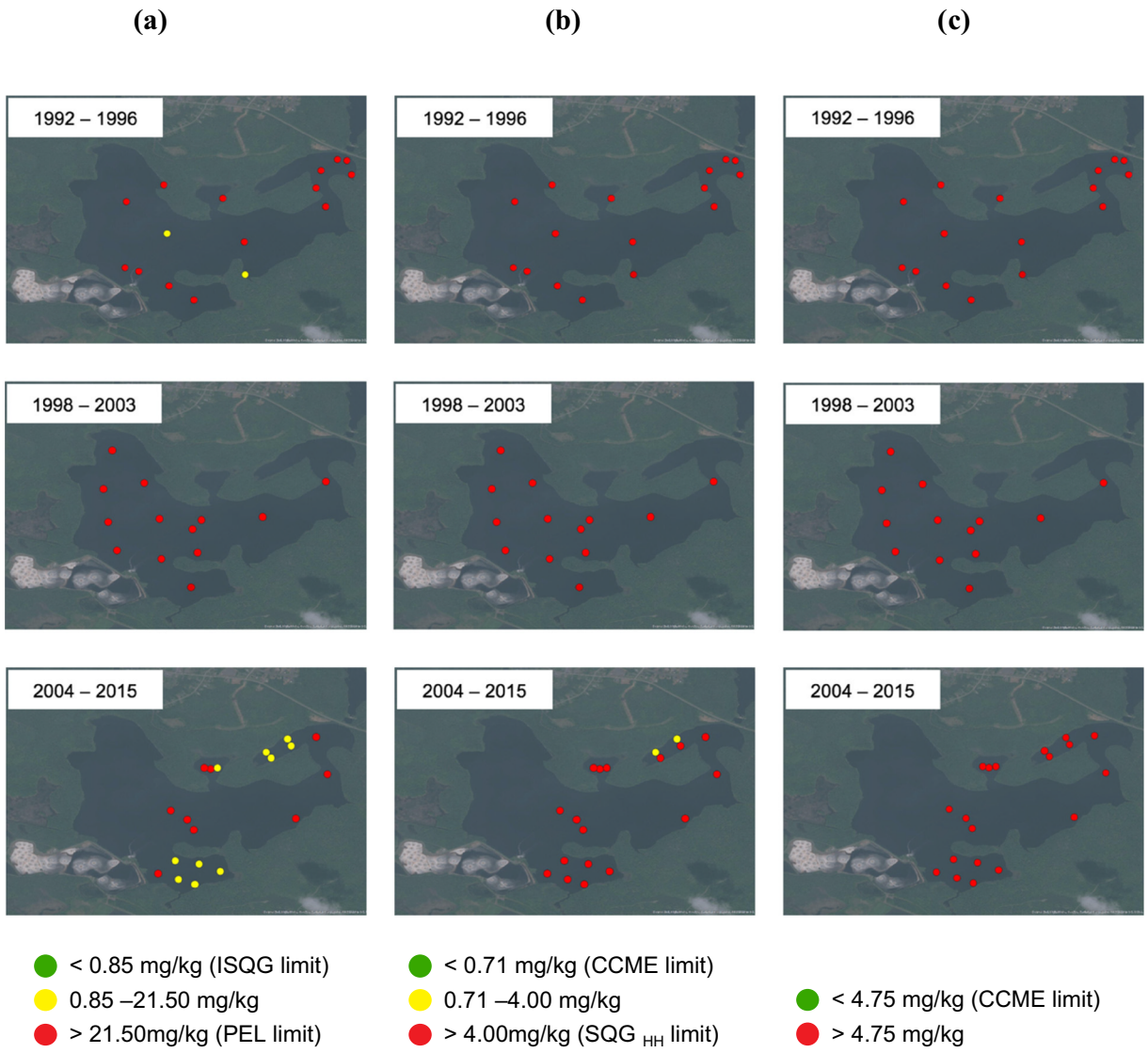


Fig. 5 Spatiotemporal variation of PCCD/F TEQ sediment concentrations (n = 60) for different receptors. **a** Fish compared to CCME freshwater and marine sediment quality guidelines [green, < 0.85 pg/g (ISQG); yellow, 0.85–21.50 pg/g; red, > 21.50 pg/g (PEL)]. **b** Human/mammals compared to CCME tissue residue guidelines for the protection of wildlife consumers of aquatic biota and soil quality guideline (SQG) for the protection of environmental and human health for all land uses [green, < 0.71 pg/g (CCME); yellow, 0.71–4.00 pg/g; red, > 4.00 pg/g (SQG_{HH})]. **c** Birds compared to CCME tissue residue guidelines for the protection of wildlife consumers of aquatic biota (green, < 4.75 pg/g; red > 4.75 pg/g) over three periods: top, 1992–1996; middle, 1998–2003; and bottom, 2004–2015

reported a lack of spatial coverage for metal(loid)s. Half of 54% Boat Harbour sediment samples analyzed for PCDD/F concentrations (from 60 samples and 49 locations) and PAH concentrations (69%) (from 103 samples and 81 locations) were from shallow horizons (0–15 cm), leaving deeper horizons undercharacterized. This presents challenges for accurate horizontal and vertical delineation of impacted sediment for future remedy decisions (Fig. 3; Supplementary material Fig. S1 and Tables S1 and S2).

Despite a wide variation in sampling methods, there was widespread PCDD/F sediment contamination reported across Boat Harbour for the entire period (Fig. 4). Temporal analysis of PCDD/F TEQs differed from that of PAHs. Temporal sediment PAH concentrations peaked around 1998 and mirrored peaks in sediment metal(loid)

concentrations reported by Hoffman et al. (2017a). In contrast, PCDD/F TEQs did not peak in 1998, although concentrations were significantly higher compared to those in 1996 in all TEF categories during this year. PCDD/F patterns were consistent across sampling years, except for 1998, when a substantial spike in 2,3,7,8-tetrachlorodibenzo-*p*-dioxin concentrations occurred. The change in pattern of PCDD/F in 1998 suggests that previous aerated stabilization basin improvements or dredging caused a change of chemical composition in Boat Harbour sediments. PCDD/F TEQs peaked between 2003 and 2013, declining significantly in 2015 to concentrations below those reported in the 1990s. However, the number of samples collected in 2015 was limited and included composite samples which presumably attenuated overall concentrations. Despite this significant decline, all (n = 60) PCDD/F TEQs exceeded low-effect CCME fish ISQGs, 66.6% (n = 40) exceeded severe-effect CCME fish PELs, and 93.3% (n = 56) exceeded soil quality guideline for human health (SQG_{HH}), indicating severe contamination and risk to biota (Table 1). The results were replicated in the spatiotemporal analysis displaying discrete locations and relative PCDD/F TEQ concentrations (Fig. 5). Of the samples detected below upper-effect PELs (33.4%; n = 20) and SQG_{HH} (6.7%; n = 4), most were from isolated coves (Stantec 2016; Fig. 5).

Percent contributions of PCDD/F congeners indicate higher proportions of 2,3,7,8-tetrachlorodibenzofuran (68.6–97.3%) and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (10.7–63.8%) in Boat Harbour sediment for all TEF categories. Congener patterns in Boat Harbour sediment differ from R.1 reference samples, where higher proportions of 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (20–33%) and 2,3,4,7,8-pentachlorodibenzofuran (17–24%) were present (Supplementary material Fig. S3). Additionally, there was no SQG exceedance of PCDD/F concentrations at R.1. However, PCDD/F chemistry data in down-gradient-receiving waters was limited to a single sampling event (JWEL 1994) and, thus, may not represent current conditions. Findings suggest inputs of PCDD/Fs result from sorption to organic-rich Boat Harbour sediments and are not released in appreciable amounts to down-gradient-receiving marine waters. This is consistent with the original design objectives of utilizing Boat Harbour as a sedimentation lagoon. Furthermore, differences in congener signatures may suggest different inputs of PCDD/Fs in the marine environment from anthropogenic sources. Further investigation both within Boat Harbour sediments and down-gradient-receiving environments within marine sediments and biota is required to adequately characterize local PCDD/F contamination and to address uncertainty regarding off-site migration of PCDD/F-contaminated sediment (Romo et al. 2019).

High sediment PCDD/F concentrations, with limited inter-annual variation, have persisted in Boat Harbour over the entire period (25 years). This is despite implementation of *Pulp and Paper Mill Effluent Chlorinated Dioxins and Furans Regulations* in 1992, which prohibits the release of measurable PCDD/Fs in effluent wastewater (EC 2013, 2014). This was supported by data reported under the National Pollutant Release Inventory (NPRI) program. According to recent substance reports submitted to NPRI from 2011 to 2016, no on-site releases of dioxins and furans (total) to water were reported by the mill (EC 2017). High PCDD/F concentrations measured in Boat Harbour sediments after 1992 reflect highly persistent properties of these bioaccumulative, acutely toxic organic compounds, which were presumably present before sediments were collected and reported in studies reviewed herein. Sediment PCDD/F concentrations were presumably derived from nearby historical pulp mill effluents, prior to 1997 when the bleaching process was changed to meet PPER requirements, or from a former chlor-alkali facility, between 1971 and 1992 when the BHTF and Boat Harbour were used to treat effluents. Pulp mill effluent wastewater has long been associated with legacy PCDD/F sediment contamination (Norstrom 2006; Hites 2011; Richman et al. 2016), but chlor-alkali facilities, normally associated with mercury releases (Walker 2016), are well-known point sources for PCDD/Fs in effluent wastewater (Svensson et al. 1991, 1993; Kannan et al. 1998; Yamamoto et al. 2018).

Although most individual PAHs were <DLs, five individual PAHs (anthracene, fluoranthene, fluorene, phenanthrene, pyrene) frequently exceeded low-effect freshwater and marine ISQGs and PELs (Table 1, Figs. 6 and 7). Again, SQG exceedances for PAHs were mostly measured in surface (0–15 cm) horizons, leaving deeper horizons undercharacterized. Total PAHs frequently exceeded ER-L (45%), but due to the relatively large quantity of individual PAH compounds <DLs, total PAH concentrations did not exceed ER-M. However, total PAH concentrations were still higher than those reported by Davis et al. (2018), who characterized total PAH concentrations in nine small craft harbors along the Northumberland Strait covering roughly the same temporal period (2001–2017). Total PAH

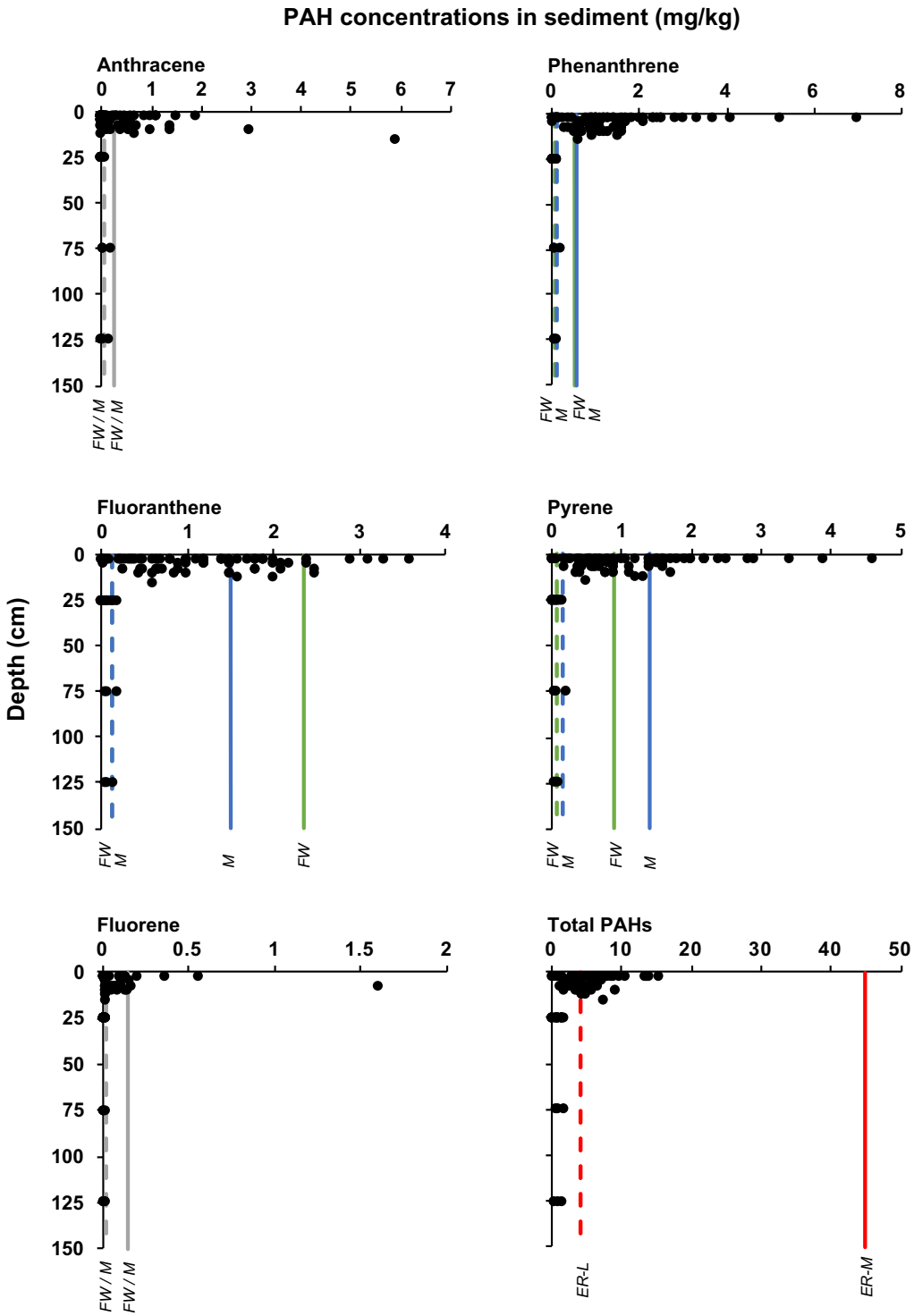


Fig. 6 Vertical variation of the select individual PAH compounds and total PAH sediment concentrations ($n = 103$) with depth (cm). *Black circles* indicate individual sediment concentrations. For individual PAH compounds, CCME freshwater (dark green) and marine (blue) sediment quality guidelines (SQGs) are indicated using *solid horizontal lines* for PEL and *dashed lines* for ISQG values. Gray represents when marine and freshwater SQGs are equal (CCME 2016). For total PAH concentrations, *dashed line* indicates the ER-L (4.02 mg/kg) and *solid line* indicates ER-M (44.80 mg/kg) (Long et al. 1998; NOAA 1999)

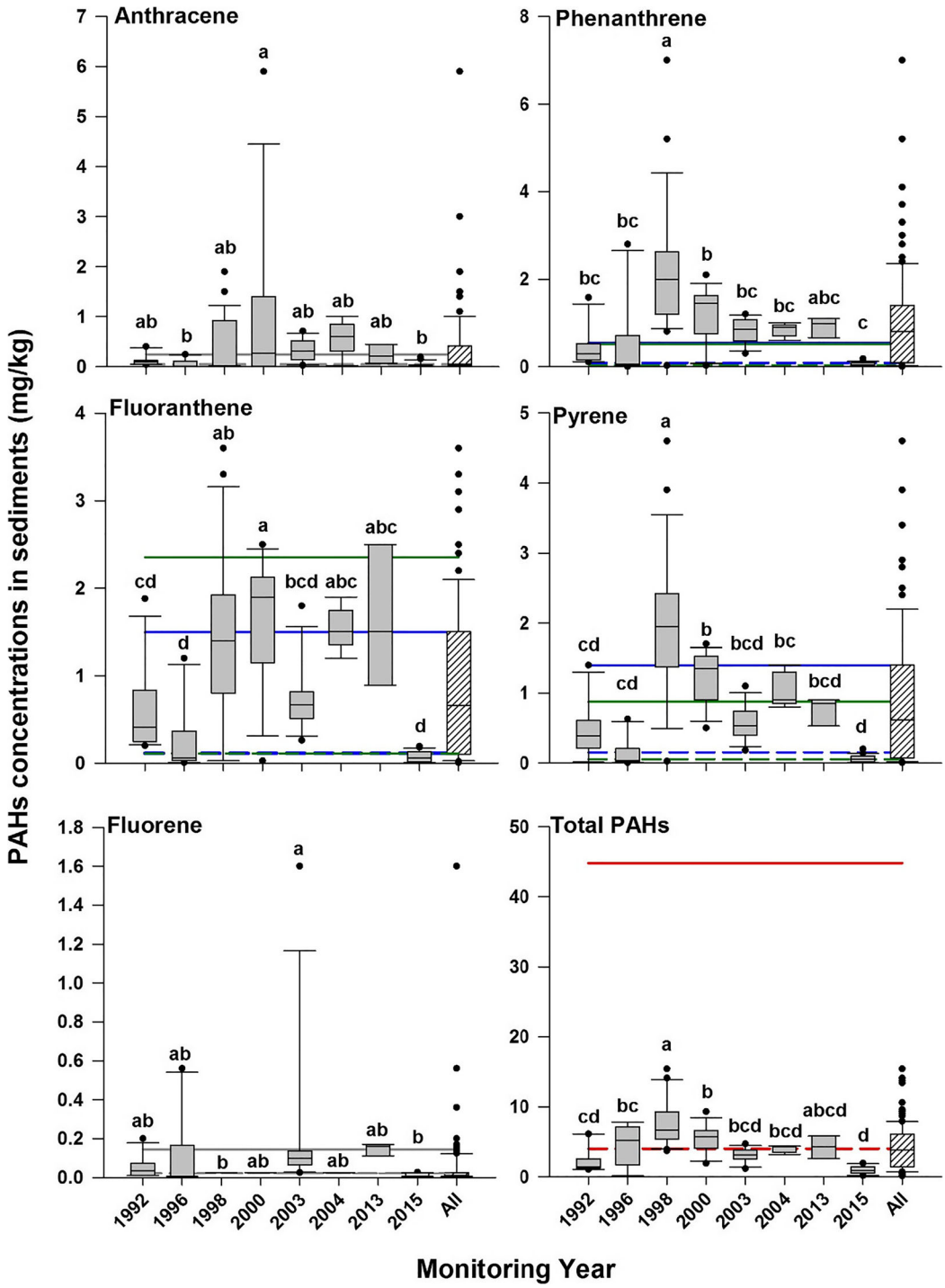


Fig. 7 Temporal variation (~25 years) of the select individual PAH compounds and total PAH sediment concentrations ($n = 103$) in Boat Harbour. *Black circles* indicate outliers. For individual PAH compounds, CCME freshwater (dark green) and marine (blue) sediment quality guidelines are indicated using *solid horizontal lines* for PEL value and *dashed lines* for ISQG value. Gray represents when marine and freshwater SQGs are equal (CCME 2016). For total PAH concentrations, *solid horizontal red lines* indicate ER-M (44.80 mg/kg) and *dashed lines* indicate ER-L (4.02 mg/kg) (Long et al. 1998; NOAA 1999). Significant temporal differences were determined by one-way ANOVA followed by Tukey's test; years attributed with the same letters were not significant and those with different letters were significantly different ($p < 0.05$ level)

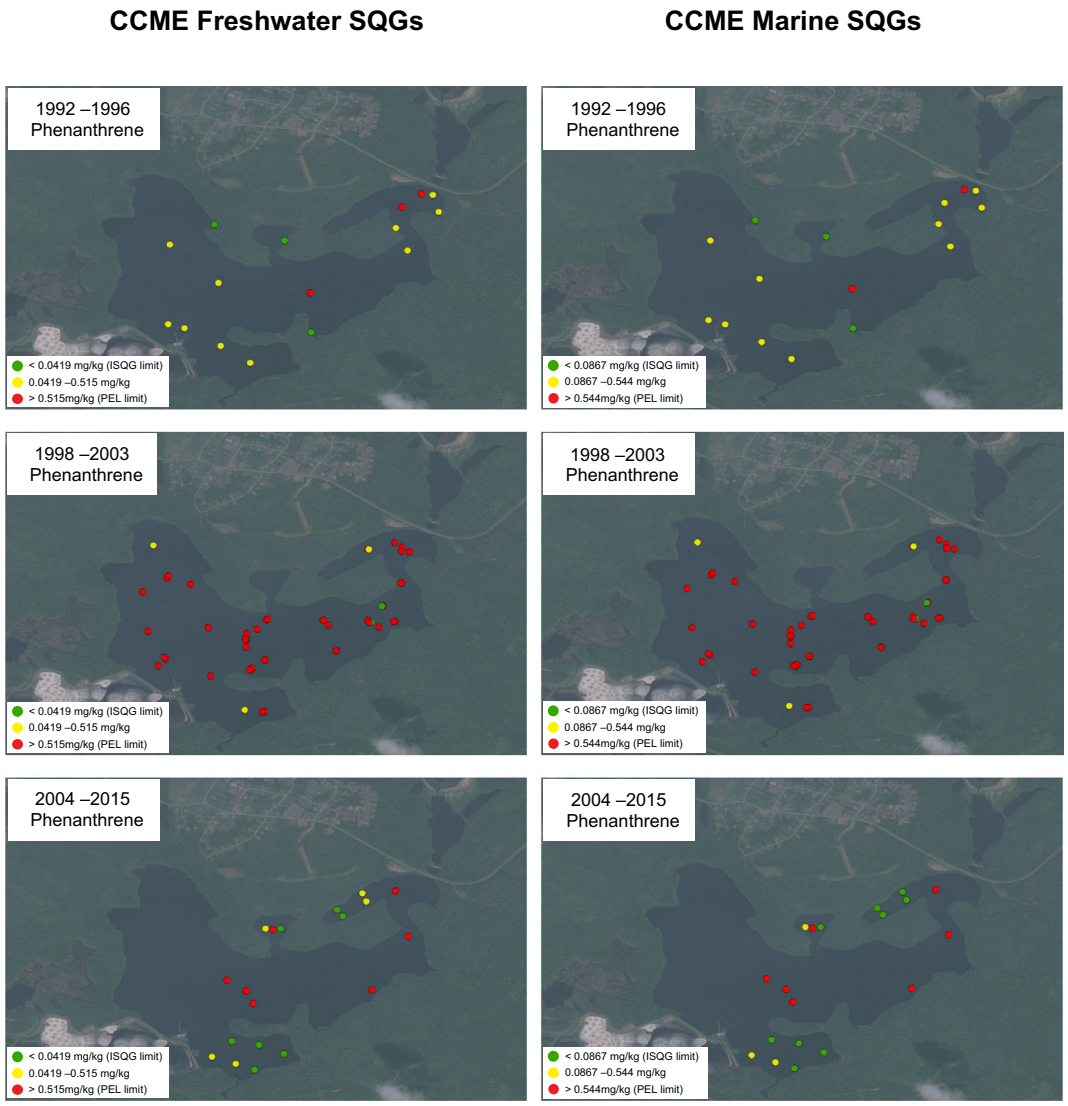


Fig. 8 Spatiotemporal variation of sediment phenanthrene concentrations (n = 103) compared to CCME freshwater [green, < 0.0419 mg/kg (ISQG); yellow, 0.0419–0.515 mg/kg; red, > 0.515 mg/kg (PEL)] and marine [green, < 0.0867 mg/kg (ISQG); yellow, 0.0867–0.544 mg/kg; red, > 0.544 mg/kg (PEL)] SQGs in Boat Harbour sediment over three periods: top, 1992–1996; middle, 1998–2003; and bottom, 2004–2015

concentrations varied widely between 0.10 and 15.4 mg/kg over 25 years (Fig. 7). Significantly higher total PAH concentrations were measured in 1998 compared to those measured before or after, consistent with temporal trends found with metal(loid) concentrations (Hoffman et al. 2017a). There appears to have been a gradual decline of individual PAH compounds and total PAH concentrations after 1998, presumably due to weathering or degradation of PAHs associated with increased oxygen concentrations following aerated stabilization basin improvements in 1996 (JWEL 1999). The results were also mirrored spatiotemporally for some individual PAH sediment concentrations. For example, there were higher frequencies of both freshwater and marine PEL exceedances for phenanthrene between 1998 and 2003 (Fig. 8). To a lesser extent, this spatiotemporal pattern was observed in fluoranthene and total PAH sediment concentrations (Supplementary material Figs. S2 and S4). However, decreasing PAH concentrations after 1998 may not indicate improving conditions. Apparent decreases in PAH concentrations since 1998 may also be attributable to bioturbation (Nedwell and

Walker 1995), burial from less contaminated sediment (Walker et al. 2013b, c), undersampling, more stringent provincial industrial approvals (NSE 2015), improvements to effluent wastewater treatment combined with increased federal regulatory oversight (EC 2013, 2014), or changes to deposition rates. These factors may have attenuated PAH concentrations temporally (Hoffman et al. 2017a).

Ratios of fluoranthene/pyrene to phenanthrene/anthracene indicate coarse clustering, suggesting a common source (Supplementary material Fig. 5a). Furthermore, double PAH diagnostic ratios of fluoranthene/fluoranthene + pyrene to anthracene/anthracene + phenanthrene suggest ~ 67% of PAH samples were derived from pyrogenic PAH sources (e.g., wood and coal combustion processes), based on transition values proposed by Yunker et al. (2002) (Supplementary material Fig. 5b). Less than 20% of the samples suggest petroleum combustion, while only a small fraction (13.6%) suggests direct petroleum sourcing. Similar ratio values (> 0.5) for the ratio of fluoranthene/fluoranthene + pyrene were observed from pulp mill effluent samples and surrounding sediment samples in Kitimat Harbour, British Columbia (Yunker et al. 2011). Likely sources for pyrogenic PAHs could be derived from local industrial combustion point source emitters (e.g., pulp and paper mill, a tire manufacturing facility, and a coal-fired thermal electrical generating station) (Hoffman et al. 2015, 2017a, b) or long-range atmospheric transport. Nova Scotia is known as the *tail pipe of North America*, due to being within the trajectory of long-range transport of emissions from transboundary sources along the Eastern Seaboard, plus central and eastern Canada (NSE 2014). Despite the pyrogenic PAH signature observed, it is suggested that plant-derived PAHs (terpenes and other hydrocarbon constituents) may be dominant in pulp mill effluent, while parent and alkylated PAHs may not be emitted in large proportions, and that plant-derived PAHs emitted by pulp mill effluent may pose a large risk to biota as they demonstrated increased bioavailability and toxicity in biological assessments at Kitimat Harbour (Yunker et al. 2011).

Volatile organic compounds and benzene, toluene, ethylbenzene, and xylenes were other organic contaminant classes reported in two reports (JWEL and Beak Consultants 1992; Stantec 2016). All volatile organic compounds (n = 27; DL = 0.01–0.05 mg/kg) and benzene, toluene, ethylbenzene, and xylenes (n = 16; DL = 0.01–0.05 mg/kg) concentrations were <DL. Modified total petroleum hydrocarbon concentrations (resembling lube oil) in all Stantec (2016) samples (n = 9) collected from the cove south of point D exceeded Nova Scotia Tier 1 standards for a sediment of 43 mg/kg for protection of freshwater and marine aquatic life (Atlantic RBCA 2012). Highest concentrations of 3800 mg/kg and 1400 mg/kg were detected at 0.5–1.0 m and 1.0–1.5 m, respectively. Samples with the highest concentrations were rerun for TPH with silica gel to assess whether naturally occurring hydrocarbons were present, but no significant difference between samples were detected, suggesting hydrocarbons were likely from anthropogenic sources. Additionally, from two Boat Harbour reports analyzing polychlorinated biphenyls (n = 10; DL = 0.05 mg/kg), all concentrations were <DL (JWEL and Beak Consultants 1992; JWEL 1999). However, due to limited spatiotemporal sediment sampling, volatile organic compounds; benzene, toluene, ethylbenzene, and xylenes; total petroleum hydrocarbons; and polychlorinated biphenyls were historically underassessed and lack adequate characterization.

Although mill effluents are likely the primary source of organic contaminants in Boat Harbour, other local sources may have contributed to organic inputs. In addition to the former chlor-alkali plant, a nearby coal-fired thermal generating station reported releases of atmospheric emissions of PCDD/Fs, ranging from 0.273 g TEQ in 2002 to 0.012 g TEQ in 2015, under the NPRI program (EC 2016). Atmospheric emissions of PCDD/Fs from mill smoke stacks ranged from 0.011 g TEQ in 2002 to 0.008 g TEQ in 2015 (EC 2016). This is supported by PAH ratios in sediments, indicating wood or coal combustion as primary sources, but this warrants further investigation for other possible sources. PCDD/F and PAH sediment concentrations using various sampling and subsequent sub-sampling techniques showed a wide spatiotemporal variation between 1992 and 2015. Although PAH concentrations varied greatly (likely due to inconsistent sampling techniques), PCDD/F sediment concentrations did not follow this trend and exceeded high effect thresholds for 25 years and are therefore contaminants of concern for future remediation.

Exceedances of organic contaminants indicate potential ecological risk to biota. A recent fish survey by Oakes (2016) found mummichog and ninespine sticklebacks in Boat Harbour. Aside from pulp and paper environmental effects monitoring events, there have been few studies conducted in the down-gradient-

receiving marine environment to determine potential ecological impacts (St-Jean et al. 2003; Romo et al. 2019). For example, Fergusons Pond (located 2.5 km northeast of Boat Harbour on the Northumberland Strait) was previously used as a reference site (i.e., JWEL 1997, 1999, 2001) and considered a priori unimpacted by industrial activities (R.2) (Fig. 1). All individual PAHs were <ISQGs in Fergusons Pond (n = 4). Over the past 25 years, Boat Harbour sediment total PAH concentrations were up to 12 times higher than the samples collected from Fergusons Pond, assuming total PAH values were summed concentrations plus ½DL values for <DL (0.01 mg/kg and 0.05 mg/kg). Of the five priority individual PAHs, phenanthrene concentrations were up to 1400 and 280 times higher than the samples collected in Fergusons Pond for 0.01 mg/kg DL and 0.05 mg/kg DL, respectively. Coastal sediments near industrial facilities around Nova Scotia have been widely reported as sinks for organic contaminants (King and Chou 2003; Walker et al. 2013a, b, c, d, 2015a, b), but limited background data exist. Therefore, Fergusons Pond and other suitable estuaries nearby require further investigation to better understand local baseline conditions and to help guide remedial objectives.

More sediment characterization is required to predict ecological risks associated with contaminated organic sediments in Boat Harbour and down-gradient-receiving marine environments prior to implementing costly remediation activities (Walker et al. 2013a, b; Walker 2014; Alimohammadi et al. 2017; Hoffman et al. 2017a; Romo et al. 2019). Assessment of contaminated aquatic sites in Canada follows federal and provincial ecological risk frameworks to guide remediation decisions (e.g., Chapman 2011; Contaminated Sites Regulations 2013; Hoffman et al. 2017a). Engineering considerations and stakeholder engagement (e.g., with knowledge holders and elders in the Mi'kmaq Pictou Landing First Nation community) will be a key to help establish local historical pre-mill conditions (Bennett 2013). According to Hoffman et al. (2017a), to return Boat Harbour to pre-mill tidal conditions, collection and measurement of local baseline data, combined with stakeholder engagement, are required to establish remediation end-point goals. Remediation will require ex situ or in situ sediment treatment to attain concentrations comparable to local or regional baseline conditions or below low effect levels (Hoffman et al. 2017a).

Gaps in vertical and spatial sediment characteristics were revealed by this review and consistent with findings by Hoffman et al. (2017a) related to metal concentrations. This study and those by Alimohammadi et al. (2017) and Hoffman et al. (2017a) suggest detailed vertical sediment core sampling and greater spatial coverage are required to accurately determine the depth and volumes of unconsolidated sediment prior to remediation. Adequate vertical and horizontal coverage is required for spatial analysis of hotspots vs. depth (Hoffman et al. 2017a). Accurate delineation of impacted sediments would allow for treatment or removal and proper disposal of sediments (Walker et al. 2013a). As reported by Hoffman et al. (2017a), sampling by Spooner and Dunnington (2016) using 14 cores reported that effluent-impacted organic sediments reached <30 cm across all stations helping to establish pre-mill *background* conditions. Confirmatory sampling of underlying marine clay sediments in Boat Harbour is required prior to remediation.

Baseline monitoring using multiple reference sites is crucial to establish background conditions to compare contaminated sediment sites to pre- and post-remediation (Walker 2014). Hoffman et al. (2017a) indicated few studies assessed Fergusons Pond or comparable reference sites (JWEL 1997, 2001), so warrants further study for comparison. An ecological risk assessment across different media and trophic levels in the area is recommended due to the extent and magnitude of PCDD/F TEQ concentrations in Boat Harbour sediments and potential ecological and human health effects (Hites 2011; Richman et al. 2016). Sediment and water quality along with biota (lobster, rock crab, and mussel tissue chemistry) in the Northumberland Strait is required to understand potential ecological risks associated with contaminated sediments transported from Boat Harbour (Walker et al. 2013d; Walker and MacAskill 2014; Roach and Walker 2017). According to Hoffman et al. (2017a), follow-up studies beyond the physical boundaries of Boat Harbour pre- and post-remediation are also recommended with several studies already completed or underway. These ongoing and future studies will allow local Pictou Landing First Nation community members, engineers, and environmental managers to document this unique Canadian cleanup and remediation of this impacted wastewater treatment lagoon, as it is restored to a tidal estuary for future use by the Pictou Landing First Nation.

Conclusions

Previous pulp mill (from 1967 to present) and chlor-alkali (from 1971 to 1992) effluent discharge into Boat Harbour has deposited large quantities of unconsolidated sediment requiring remediation. Despite a wide variation in sampling techniques, PCDD/F sediment concentrations consistently exceeded highest effect thresholds for CCME SQGs, posing ecological risk, making them the main contaminant of concern. Conversely, total PAH concentrations showed a wide temporal variation between 1992 and 2015, apparently peaking between 1998 and 2000, but these did not exceed severe effect thresholds. However, some individual PAH compounds (anthracene, fluoranthene, fluorene, phenanthrene, pyrene) frequently exceeded low effect thresholds. PAH diagnostic ratios suggest pyrogenic PAH sources (wood/coal combustion) are the primary source of PAH loadings.

A review of secondary data revealed gaps in sediment characteristics (vertical and spatial coverage). The Mi'kmaq Pictou Landing First Nation communities' desire to return Boat Harbour to a pre-mill tidal estuary supported by the *Boat Harbour Act* requires remediation of sediments to concentrations comparable to local baseline conditions or below low effect levels. The following studies are recommended: (i) detailed sediment sampling in and around Boat Harbour including vertical and horizontal delineation of contaminants; (ii) establishment of local baseline concentrations for a suite of organic and inorganic contaminants, which should also be complimented by discussions with local knowledge holders to elucidate pre-1967 conditions within Boat Harbour; and (iii) additional sampling of organic and inorganic contaminants, particularly PCDD/Fs, in up-gradient- and down-gradient-receiving environments to better characterize these sediments prior to remediation.

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