

**The atmospheric fate of 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH):
Spatial patterns, seasonal variability, and deposition to Canadian coastal regions**

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Abstract

Brominated flame retardants (BFRs) that are gradually phased out are being replaced by emerging BFRs. Here, we report the concentration of the α - and β -isomers of 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH; also known as DBE-DBCH) in over 300 air, water, and precipitation samples collected between 2019 and 2022 using active air and deposition sampling as well as networks of passive air and water samplers. The sampling region includes Canada's most populated cities and areas along the St. Lawrence River and Estuary, Quebec, as well as around the Salish Sea, British Columbia. TBECH was detected in over 60% of air samples at levels comparable to those of 2,2',4,4'-tetrabromodiphenyl ether (BDE-47). Concentrations of TBECH and BDE-47 were typically higher in urban areas, with stronger correlations with population density during warmer deployments. Uniform α/β -TBECH ratios across space, time and environmental media indicate highly similar atmospheric fate of the two isomers. Although TBECH air concentrations were strongly related to temperature in urban Toronto and a remote site on the East coast, the lack of such dependence at a remote site on the West coast can be explained by the small seasonal temperature range and summertime air mass transport from the Pacific Ocean. Despite there being no evidence that TBECH has been produced, or imported for use, in Canada, it is now one of the most abundant gaseous BFRs in the Canadian atmosphere. The recorded spatial and temporal variability of TBECH suggest that its emissions are not constrained to specific locations but are generally tied to the presence of humans. The most likely explanation for its environmental occurrence in Canada is the release from imported consumer products containing TBECH. Chiral analysis suggests that despite its urban origin, at least some fraction of TBECH has experienced enantioselective processing, i.e., has volatilized from reservoirs where it has undergone microbial transformations. Microbial processes in urban soils and in marine waters may have divergent enantioselectivity.

1. Introduction

Starting from the 1970s, brominated flame retardants (BFRs) have been used extensively in commercial products to reduce ignition and increase their resistance to fire. To date, at least 75 different kinds of BFRs have been commercially produced, with polybrominated diphenyl ethers (PBDEs) being historically the most used class (Alaee et al., 2003). However, their toxicity, potential for bioaccumulation, and persistence in the environment soon became apparent (Christensen et al., 2005; De Wit et al., 2006; Palm et al., 2002; Ruan et al., 2019), and PBDEs, along with other traditional BFRs, were eventually classified as persistent organic pollutants (POPs) (POPRC, 2009). As usage and production of these BFRs were restricted internationally in 2009 under the United Nations Environment Programme Stockholm Convention on POPs (UNEP-SC-POPs) (UNECE, 2018), emerging brominated flame retardants (EBFRs) entered into the market (Betts, 2008), which are touted to be less persistent than their traditional BFR counterparts. However, studies on their environmental behaviours have been limited.

1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH) is an EBFR that is widely used in plastics, fabric adhesives, and building insulation materials (Alaee et al., 2003). TBECH exists as four diastereomers (α , β , γ , and δ -TBECH). Furthermore, TBECH exhibits chirality and thus each diastereomer consists of a pair of enantiomers. While commercial TBECH comprises mostly the α - and β -isomers (57.3% and 42.5%, respectively) (Ruan et al., 2018), TBECH has been reported to thermally isomerize to the γ and δ isomers when heated to 123 °C (Arsenault et al., 2008). Although global production volumes or emissions of TBECH are difficult to establish, reports on its detection in the environment have been increasing over the years, attributed to the rising demand for EBFRs (Bohlin et al., 2014; Cequier et al., 2014; Drage et al., 2016; Genisoglu et al., 2019; Gentes et al., 2012; Newton et al., 2015; Pasecnaja et al., 2021; Tao et al., 2017; Zacs et al., 2021). TBECH was first detected in sediment samples collected in 1996 near a discharge pipe of the Frutarom plastics plant near Haifa, Israel (Santillo et al., 1997). Since then, TBECH was found in various environmental media worldwide, such as biota and water, with α - and β -TBECH being the dominant isomers. TBECH concentrations appear to be particularly high in indoor settings, such as offices and residences (Melymuk et al., 2016; Newton et al., 2015; Wong et al., 2018).

There is evidence that TBECH displays toxic effects at low concentrations both *in vitro* and *in vivo*. All TBECH isomers have shown to be strong androgen agonists, where TBECH competitively binds to the androgen receptor active site in varying degrees, first determined *in vitro* in human cell lines (Khalaf et al., 2009; Larsson et al., 2006). Moreover, several studies suggest that all isomers are capable of

multimodal endocrine disruption which involves estrogenic (Asnake et al., 2014), anti-androgenic (Wong et al., 2016), and thyroidal processes (Porter et al., 2014). This disrupting potential of TBECH is also seen in the *in vivo* studies reporting changes in circulating hormones (Curran et al., 2017; Gemmill et al., 2011), organ structure (Park et al., 2011), and reproduction (Marteinson et al., 2012a; Marteinson et al., 2012b) after exposure to low concentrations of TBECH. More details on the reported toxicological effects of TBECH from both *in vivo* and *in vitro* studies are discussed in Marteinson et al. (2021).

Presumably because no Canadian company reported the manufacture and importation of TBECH on a commercial scale (ECCC, 2017), it has been deemed a non-priority for assessment under Canada's Chemicals Management Plan (ECCC, 2019). As a result, TBECH remains unregulated at both national and international levels, despite being judged to be persistent and bioaccumulative. There is evidence, however, of its presence in the Canadian environment, as TBECH has been detected in different environmental media, ranging from urban outdoor air in Toronto (Shoeib et al., 2014) to whale blubber in the Arctic (Tomy et al., 2008). Only three studies have published on the enantiomeric composition of TBECH in the environment (Ruan et al., 2018; Ruan et al., 2019), with one study on Canadian urban soils (Wong et al., 2012). Therefore, concerted efforts to understand the sources, atmospheric behaviour, and enantiomeric profile of TBECH have been limited, not only in Canada, but also worldwide.

With the objective to gain insight in the atmospheric fate of α - and β -TBECH in general and in Southern Canada specifically, we sought to characterise the spatial and seasonal variability in their air concentrations and to explore their potential for atmospheric deposition. We also compare the atmospheric fate of TBECH with that of the PBDEs, in particular 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), one of the traditional BFRs that has been internationally banned under the UNEP-SC-POPs but can still be detected in the environment. Spatial patterns were investigated with two passive air sampler (PAS) networks in the coastal regions of Quebec (QC) and British Columbia (BC). Seasonal trends in air concentrations were studied using active air samplers (AAS) at an urban site in Toronto and two remote sites on either coast. The input to aquatic systems was studied by measuring year-round wet deposition and by taking passive water samples (PWS) at selected coastal sites.

2. Materials and methods

2.1 Sampling

2.1.1 Passive air sampling network

Networks of XAD-2 resin-based PASs (Wania et al., 2003) were installed in QC along the ca. 1000-km stretch of the St. Lawrence River and Estuary between Montreal and the Gulf of St. Lawrence, as well as in BC on the coast of the Central Salish Sea. PAS housings, containing two XAD-resin filled mesh cylinders each, were deployed at a height of ca. 3 to 5 m above ground on trees or other structures at 118 unique sites between 2019 and 2022. Because PASs were deployed at some sites more than once, there was a total of 169 PASs. Maps of the networks are shown in Figure S1, while coordinates of the sampling sites, dates of deployment and retrieval, and deployment duration are provided in Table S1 in the Supporting Information. By revealing the spatial variability in the air concentration of TBECH and other BFRs across a wide region, the networks can identify the location of emissions to the atmosphere. The networks included sites in highly urbanized and industrialised area, but also rural and remote sites. Additional details are provided in Text S1. After retrieval, the PASs were stored in metal shipping containers sealed with Teflon tape coated stoppers at -20°C until analysis.

2.1.2 Active air sampling and precipitation collection

To quantify the seasonal variability in the air concentration of TBECH and other BFRs in an urban source region, 48 consecutive week-long AASs were taken on the campus of the University of Toronto Scarborough in the eastern suburbs of Toronto, Ontario between June 2020 and May 2021 (Li et al., 2023). These measurements were complemented by 24-hour AAS taken once a month for one year at two remote coastal sites far from large urban centres and therefore, less likely to be influenced by local emission sources. These were on Saturna Island, BC (L43 on Figure S1; ca. 42 km NNE of Victoria; pop. ~300; Dec. 2019 - Nov. 2020; n=11) and Tadoussac, QC (near S57 on Figure S1; ca. 190 km NE of Quebec City; pop. ~800; Dec. 2020 and Nov. 2021; n=12). Contaminants in the particle and gas phase were collected on a glass-fiber filter (GFF) and a polyurethane foam (PUF)/XAD-2/PUF sandwich, respectively. The sampling periods are listed in Table S2.

At Saturna Island and Tadoussac, monthly-integrated wet deposition samples were taken during the same twelve-month period as the AAS. Precipitation samples were collected for one month each in sample bottles containing 0.2 L dichloromethane, which were connected to overflow bottles to capture any overflowing precipitation from the sample bottles. The sampling periods are listed in Table S3.

2.1.3 Passive water sampling network

Passive water samplers consisting of low-density polyethylene (LDPE) sheets in a metal mesh cage were deployed in 20 unique locations in BC and QC during the late spring and summer of 2021 (Table S9). Figure S2 provides maps with the sampling sites. Before deployment, the LDPE sheets were infused with several performance reference compounds (PRCs) to determine sampling rates. Details are provided in Text S2.

2.2 Sample analysis

The gas phase sorbent from the AAS at Saturna Island and Tadoussac was Soxhlet extracted. All other air samples underwent pressurised liquid extraction using an accelerated solvent extractor. The precipitation samples were filtered through 0.7 μm GFFs and the filtered samples were then subjected to liquid-liquid extraction. The LDPE sheets were simply soaked in solvent overnight. Fourteen ^{13}C -labelled surrogates were spiked into all samples prior to extraction. All extracts were reduced in volume and dried with Na_2SO_4 . Injection standards (^{13}C -PCB-105 and 180) were added to the final extracts. Details on the extraction solvents, conditions, and the standards are provided in Text S3.

All samples were analyzed for a suite of 28 BFRs, including 15 PBDE congeners (BDE-17, 28, 47, 49, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and 209), α -TBECH, β -TBECH, allyl 2,4,6-tribromophenyl ether (ATE), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), pentabromobenzene (PBBz), hexabromobenzene (HBBz), pentabromotoluene (PBT), pentabromoethyl benzene (PBEB), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DBTE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEHTBP), and decabromodiphenyl ethane (DBDPE). Four additional halogenated flame retardants (Dec-602, Dec-604, *syn*-DP, *anti*-DP) were also analyzed. Details of the instrumental analysis are provided in the Text S4. This is also where information on the QA/QC procedures can be found, which includes many procedural and field blanks. Limit of Detection (LOD) and Limit of Quantitation (LOQ) for different types of samples are provided in Table S12.

Both α - and β -TBECH are chiral molecules but can be expected to enter the environment as a racemate, i.e., with their two enantiomers being equally abundant (mean enantiomeric fraction $\text{EF}_{\text{standards}} = 0.502 \pm 0.001$). The unequal abundance of two enantiomers in environmental samples has been used to identify the occurrence of enantioselective processing, such as microbial transformation reactions. The enantiomeric composition of α - and β -TBECH was determined in samples with TBECH concentrations > LOQ from the PAS network in BC and QC, from the AAS in Toronto, and in a few PWS. The amounts of β -

TBECH in the extract were generally too low for reliable chiral analysis, therefore, only results on the enantiomeric analysis of α -TBECH are presented. A description of the analytical method for enantiomeric analysis is provided in Text S4.

2.3 Air and water concentration calculations

Volumetric air concentrations were derived from the amounts quantified in the PAS sorbent using sampling rates reported by Li et al. (2023). Volumetric water concentrations were calculated from the amount quantified in the LDPE sheets using the dissipation of PRCs and the approach by Booij and Smedes (2010). Details are again in Text S5. For statistical purposes, the measurements below the LOD are represented by the value of the compound specific LOD (Table S12).

2.4 Partitioning properties calculations using COSMO-RS and other prediction tools

Equilibrium partition ratios between octanol and water (K_{ow}), octanol and air (K_{oa}), and air and water (K_{aw}) of TBECH were estimated using quantitative structure-activity relationship (QSAR) models integrated in several chemical property prediction tools (EASE-Suite, EPI Suite, OPERA). Because these QSARs cannot distinguish between the properties of α - and β -TBECH, we also applied COSMOtherm, which is based on quantum chemistry and statistical thermodynamics. Details of these approaches have been described previously (Baskaran et al., 2021). More details on COSMOtherm are also given in Text S6. In general, the predicted partition ratios of TBECH from the different models are in good agreement, i.e., are typically within 0.30 log units of each other (Table 1). COSMOtherm tends to give slightly lower log K_{ow} and log K_{aw} values, suggesting a higher solvation in the aqueous phase than the QSARs. COSMOtherm-predicted properties for the two isomers are also very similar, with α -TBECH being slightly more volatile than β -TBECH.

Table 1 Equilibrium partition ratios and atmospheric degradation rate constant k (with respect to OH radical) of α - and β -TBECH calculated by various physical-chemical property prediction tools at 0°C and 25°C.

		Log K_{ow}		Log K_{aw}		Log K_{oa}		$k \times 10^{-12}$ (cm ³ /s)
		0°C	25°C	0°C	25°C	0°C	25°C	25°C
COSMOtherm	α -TBECH	4.49	4.45	-4.67	-3.82	8.93	8.36	1.92
	β -TBECH	4.39	4.35	-4.92	-4.07	9.08	8.51	1.86
EAS-E Suite	TBECH	5.70	5.43 ± 0.52	-4.41	-3.34 ± 0.36	10.14	8.80 ± 0.81	
OPERA			5.24 ± 0.03		-3.72 ± 1.20		8.42 ± 0.13	
EPI Suite			5.24		-2.77		8.00	
								4.86

3. Results

3.1 Air concentrations

3.1.1 Absolute concentrations ranges, isomer composition, and comparison with previous measurements

α - and β -TBECH and BDE-47 were the most consistently detected BFRs in air samples taken across Canada, detected in 69%, 59%, and 80% of samples from the PAS network, respectively. Table 2 summarises the results, whereas data for each individual sample are documented in Tables S1 and S2. To a lesser extent, several other EBFRs and PBDE congeners were also detected in the samples of this study, with their detection frequencies or concentrations summarized in Tables S4 to S8. Several legacy BFRs (BDE-190 and 85) and EBFRs (HBBz and PBBz) were occasionally detected in the PAS network samples, with detection frequencies ranging between 7 to 26%. These compounds, however, were not detected in the active air samples. Moreover, other BFRs that were detected frequently in water samples (BDE-17, 28, 99, and 100) were rarely detected in the other sample types. Because of their much higher detection frequencies in all samples, the remainder of the manuscript is focused on TBECH and BDE-47.

Table 2 Detection frequency, median, mean, and maximum of the concentrations and wet deposition fluxes of the three most frequently detected BFRs in air samples (gas phase) and water samples (dissolved) in Canada. For statistical purposes, measurements below the LOD were represented by the value of the compound specific LOD.

	n	α-TBECH				β-TBECH				BDE-47			
		n > LOD	med.	mean	max	n > LOD	med.	mean	max	n > LOD	med.	mean	max
Concentrations in Passive Air Samples in pg/m³													
QC	86	39	<LOD	0.22	1.21	30	<LOD	0.22	0.99	60	0.84	1.0	6.1
BC	83	77	0.44	0.54	2.20	70	0.38	0.46	2.1	76	1.5	1.9	10
Concentrations in Active Air Samples in pg/m³													
Tadoussac	12	10	0.09	0.13	0.29	9	0.06	0.08	0.17	11	0.13	0.23	0.69
Saturna	11	8	0.06	0.07	0.13	6	0.04	0.03	0.12	11	0.57	0.55	1.1
Toronto	48	48	0.30	0.40	1.34	48	0.20	0.26	0.87	48	0.66	1.5	9.3
Concentrations in Passive Water Samples in pg/L													
QC	12	0	<LOD	<LOD	<LOD	0	<LOD	<LOD	<LOD	12	1.5	2.0	6.2
BC	36	25	0.19	0.40	2.2	19	0.10	0.26	1.4	36	1.2	1.4	3.8
Concentrations in Precipitation Samples in pg/L													
Tadoussac	11	11	67	103	302	11	49	83	251	11	32	42	90
Saturna	12	12	233	464	1416	12	183	377	1125	11	23	36	102
Wet deposition fluxes in pg/m²/day													
Tadoussac	11	11	96	154	628	11	82	124	487	11	66	71	153
Saturna	12	12	697	759	2099	12	574	622	1731	11	53	127	468

To place these concentrations into context, Table S13 summarises all atmospheric concentrations of TBECH previously reported in the literature. A review of the occurrences of TBECH in other environmental media (e.g., soil, water, sediment) can be found in Marteinson et al. (2021). The concentrations of TBECH recorded here are at the lower end of the range of levels detected in urban outdoor air elsewhere. In particular, levels in Canadian urban locations are similar to those reported for outdoor air in Stockholm, Sweden (Newton et al., 2015; Wong et al., 2018), but somewhat lower than those measured in Birmingham, UK (Drage et al., 2016), Brno, Czech Republic (Bohlin et al., 2014; Melymuk et al., 2016) and previous measurements taken in Toronto (Shoeib et al., 2014). Much higher values had been reported for indoor air (Cequier et al., 2014; Genisoglu et al., 2019; Melymuk et al., 2016; Newton et al., 2015; Newton et al., 2016; Tao et al., 2016; Wong et al., 2018), an electronic waste facility in China (Hong et al., 2018) and - somewhat incongruously - in Longyearbyen, Svalbard (Carlsson et al., 2018). PAS deployed in remote regions (pop. <10 000 in a 20-km radius) tended to have levels of TBECH below the LOD or LOQ. The levels above LOD measured in non-urban locations in this study are among the lowest ever reported, comparable to what has been reported for Tibet and Antarctica (Ma et al., 2017; Zhao et al., 2020). However, previous measurements of TBECH in air from non-urban locations are rare. Overall, the alignment of the air concentration data with those reported previously supports the validity of the results of this study.

BDE-47, despite its international ban under the Stockholm Convention, can still be detected in the environment due to its persistence. Its presence in the atmosphere, along with other BDEs, has been documented over the years in Canada, such as in Ottawa, ON (Wilford et al., 2004), Alert, NU (Wong et al., 2021; Xiao et al., 2012), Yukon Territory (Yu et al., 2015), and the Great Lakes Basin (Shunthirasingham et al., 2018). In this study, BDE-47 was also detected in the air in all sampling regions, with comparable levels to TBECH. On Saturna Island, BDE-47 gas phase concentrations have decreased by one order of magnitude relative to almost two decades prior (Noël et al., 2009). Levels in the atmospheric particle phase and in precipitation in the area have similarly been decreasing.

3.1.2 Spatial variability of air concentrations in Canadian coastal regions

The spatial patterns in the air concentrations of α - and β -TBECH in the coastal regions of BC and QC as obtained from the PAS networks (Figure 1) show elevated levels in populated and urban areas. Specifically, in QC, higher levels are observed along the St. Lawrence River corridor between Montreal and Quebec City contrasting with lower levels on the shores of the St. Lawrence Estuary. In BC, higher levels are apparent in the lower mainland and in Victoria. The overall higher levels observed in the PASs from BC

when compared to those from QC are likely the result of more urbanized sampling locations in the former. Earlier studies also indicate that urban areas have higher TBECH air concentrations than remote regions (Table S13).

The α -/ β -TBECH ratio at sites where both isomers were present above their LODs (Figure S3) is remarkably consistent in space on either coast, i.e., there is no indication that the ratio varies in space, e.g., by being correlated with the absolute concentration level. The ratio was typically close to or above one at sites with detectable amounts of both isomers in the air. An exception (α -/ β -TBECH = 0.29) was at a site located 10 kilometres away from Quebec City, QC (S26). However, because the air concentrations of both isomers measured at this site were below their LOQs, this value should be interpreted with caution.

Not only are the volumetric air concentrations of BDE-47 on the same order of magnitude as TBECH, but they also share a similar spatial distribution in the atmosphere (Figure 1). This is also apparent from significant correlations between the concentration of both isomers of TBECH and those of BDE-47 in the PAS (Figure S4, Table S14, $R^2 > 0.24$, $p < 0.0001$), which seem to be strongly influenced by the urban sites with elevated BFR concentrations. One difference is the notable presence of BDE-47 at one site in Alma, QC (S48) during the first deployment period, despite BDE-47 at other sites in Alma (S49-53) and in the wider Saguenay region (S54-56) being below the LOQ. PASs deployed at the same site (S48_2) and a site in the vicinity (S54_2) a year later had BDE-47 levels below the LOQ, suggesting that the first data point at S48 was an outlier and not an indication of a local point source.

In the BC PAS network, air concentrations are linearly correlated with population within a 20-km radius around a PAS deployment site (NASA, 2015) (Figure S5, Table S15), more so for α - and β -TBECH ($R^2 = 0.27$ and 0.23 , respectively) than for BDE-47 ($R^2 = 0.09$). The relationships were generally stronger when explored separately with concentration data obtained at different average deployment temperature ($<10^\circ\text{C}$, $10\text{--}15^\circ\text{C}$, $>15^\circ\text{C}$; Figure S5). Weaker or absent relationships at the warmest temperature ($>15^\circ\text{C}$) are likely caused by the relatively small number of summer deployments. Increasing slopes of these relationships at warmer temperatures indicate a higher seasonal concentration amplitude at sites in populated areas than in remote regions. This is also consistent with the expectation of a stronger temperature dependence of the atmospheric concentrations of semi-volatile chemicals in source areas than at sites without local sources (Wania et al., 1998). To further demonstrate this relationship with both temperature and population, multiple linear regression was used on the log-transformed partial pressure of TBECH against population and the inverse temperature, which resulted in higher correlations (Adjusted

$R^2 = 0.56$ and 0.42 for α - and β -TBECH, respectively). The seasonal variability in the air concentrations of TBECH and BDE-47 is discussed in more depth when discussing the AAS results in section 3.1.3.

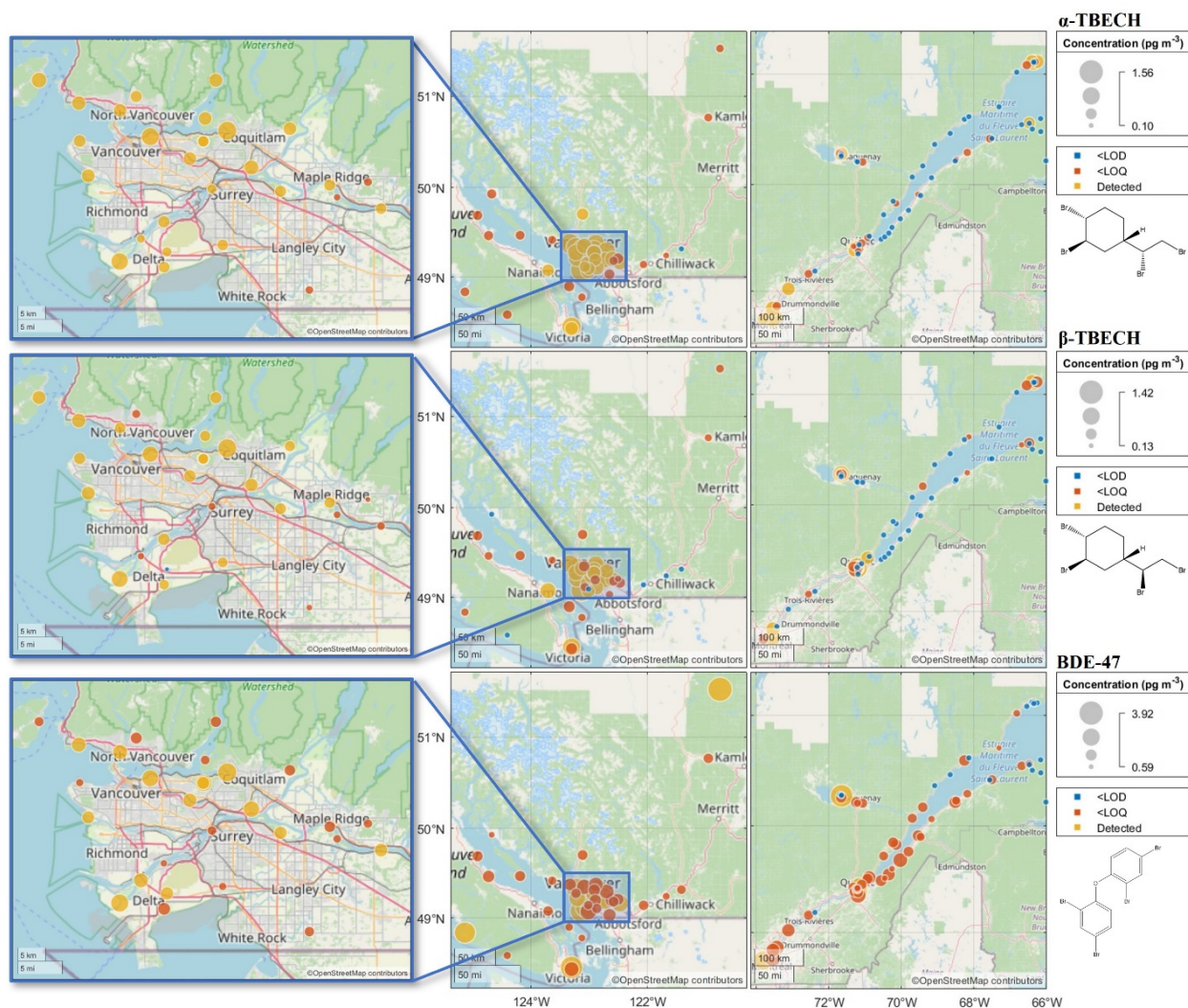


Fig. 1 The spatial distribution of the air concentrations of α -TBECH (top), β -TBECH (middle), and BDE-47 (bottom) in British Columbia and Quebec. Close-up maps (left) provide a detailed view of the Vancouver metropolitan area. Average air concentrations are displayed for sites with replicate deployments; therefore, the concentrations indicated on the figure may not align with concentrations listed in Table 2 and Table S1. Air concentrations below the LOD are marked in blue and display the value of the LOD. Air concentrations above the LOD and below the LOQ are marked in dark orange. Air concentrations above LOQ are marked in yellow. Concentration values are listed in Table S1.

3.1.3 Seasonal variability of air concentrations in urban and remote regions of Canada

Seasonal variability in Toronto

The seasonal trends of AAS-derived air concentrations of TBECH and BDE-47 in Toronto, ON (Table S2, Figure 2A and 2B) indicate a strong relationship with average air temperature (Figure 2C), being higher in the summer (April to August) and lower in winter (September to March). Accordingly, log-transformed partial pressures $\ln(p/\text{Pa})$ of α - and β -TBECH and BDE-47 were significantly correlated with inverse absolute temperature (Figure S6, Table S16, $R^2=0.61$, 0.55 , and 0.81 , respectively, $p<0.0001$). Such a temperature dependence of the atmospheric concentration of semi-volatile organic compounds is often interpreted as temperature driven air-surface exchange (Wania et al., 1998) or temperature-dependent rates of emission.

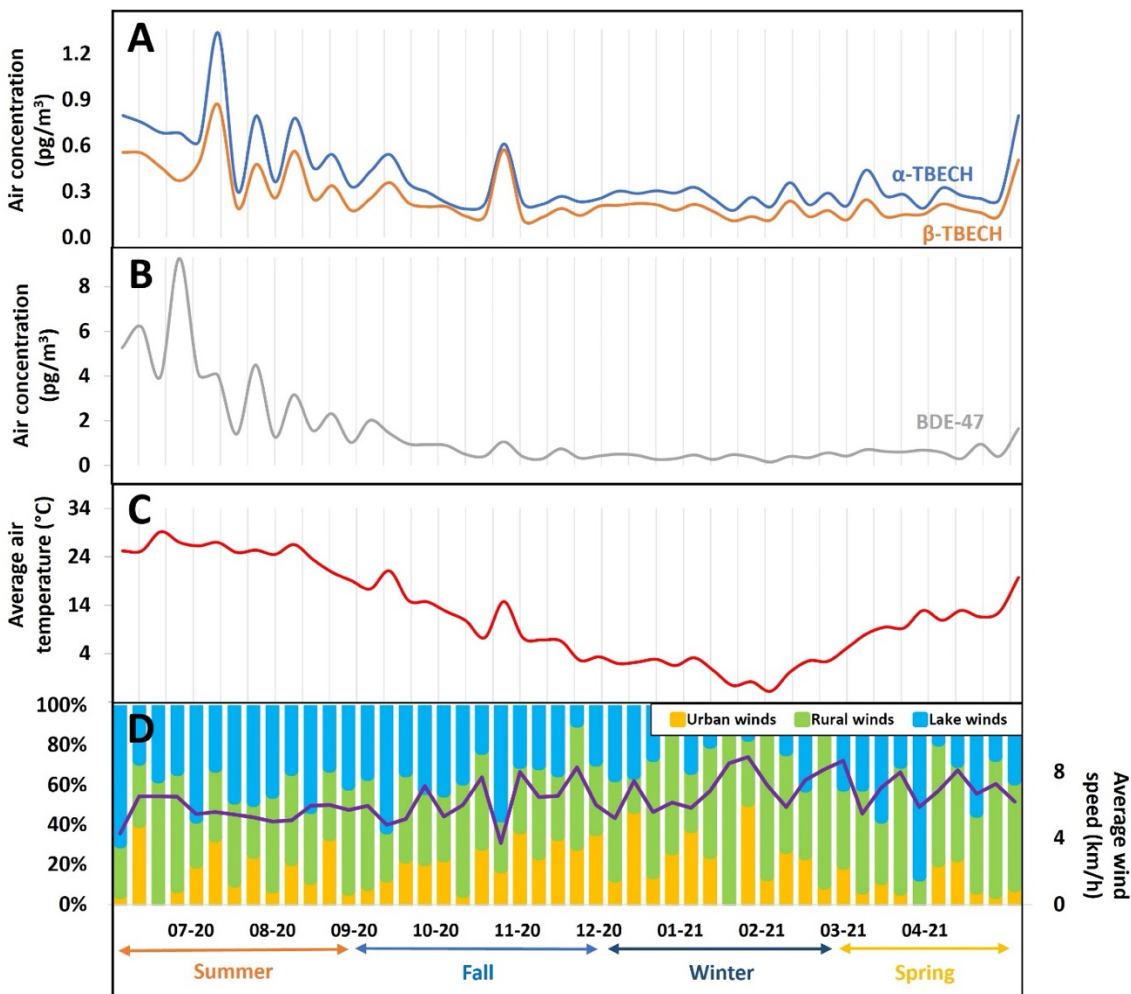


Fig. 2 The air concentration of α -TBECH, β -TBECH, and BDE-47 and meteorological parameters in Toronto, Ontario during 48 weekly active air sampling periods between June 2020 and May 2021.

With the sampling site located in an Eastern suburb of a large urban conglomeration, wind also influenced the air concentrations of TBECH and BDE-47. Higher levels were recorded when weak winds were blowing from the urban core of Toronto, approximately 20 km to the SW of the sampling site. Text S7 and Figure S7 provide detail on how an urban wind fraction was derived. The average wind speed and the fraction of wind originating over urban areas, rural regions and Lake Ontario are shown in Fig. 2D. Multivariate regressions of the $\ln(p/\text{Pa})$ with both reciprocal temperature and the urban wind fraction are highly significant for all three BFRs and stronger than univariate regressions with reciprocal temperature only (Table S17).

Seasonal variability in Saturna Island and in Tadoussac

The AAS-derived air concentrations of TBECH and BDE-47 on Saturna Island were very low (Table S2). Whereas BDE-47 showed a clear seasonal pattern with higher levels in summer than in winter, any seasonal pattern of the TBECH isomers was obscured by levels below the LOD in air samples taken in December, June and July (Figure S8). Accordingly, whereas the $\ln(p/\text{Pa})$ of BDE-47 was significantly correlated with reciprocal temperature ($R^2=0.44$ and $p=0.027$), for both TBECH isomers those relationships were generally weak and insignificant (Table S16). Weak or absent $\ln(p/\text{Pa})$ versus $1/T$ relationships are typical for remote sites without local sources, where the concentration of a compound is controlled by advection from elsewhere (Wania et al., 1998).

In contrast to Saturna Island, AAS-derived air concentrations of TBECH and BDE-47 in Tadoussac (Table S2) showed a clear seasonal trend with higher levels in summer and levels often below the LOD in winter (Figure S9). $\ln(p/\text{Pa})$ versus $1/T$ regressions (Figure S6) were significant but only explained a relatively small fraction of the overall variability ($R^2 > 0.30$; Table S16). One factor that may have contributed to the differences in the seasonal patterns of TBECH at the two coastal sites are the much larger seasonal temperature range in QC (-12 to +18 °C) than in BC (+1 to +18 °C).

We also sought to relate the temporal variabilities in the measured air concentrations with the history and origin of the sampled air masses using the Lagrangian atmospheric dispersion model FLEXPART (Pisso et al., 2019). TBECH levels below the LODs in June and July on Saturna Island despite the relatively warm temperatures may be related to air masses arriving at the sampling site directly from the Pacific Ocean, i.e., without encountering any potential urban source areas. Overall, TBECH levels on Saturna Island arise from competing influences of air mass origin and temperature. More detail is provided in Text S8.

3.2 Concentrations in passive water samples

The water concentrations of the BFRs measured with PWSs in the coastal regions of BC and QC are summarized in Table 2 with all data provided in Table S9. Whereas the TBECH isomers were below the LODs in all water samples from QC, in BC, α - and β -TBECH ranged between <LOD to 1.75 pg/L and <LOD to 1.15 pg/L, respectively, and were typically above the LODs at sites close to urban centers (Victoria, Vancouver) (Figure S10). BDE-47 was detected at all sites of this study, with higher levels close to Victoria (Figure S12). BDE-47 water concentrations were also generally slightly higher compared to those of TBECH, albeit on the same order of magnitude.

We compared the results from the PWS network in this study with water concentrations reported by the Federal Whales Initiative (FWI) of Canada (ECCC, 2022). Sampling campaigns conducted by the FWI occurred in the Fraser River, BC, including its main tributaries (Thompson River and Harrison River) between 2019 to 2021. The median water grab sampling concentrations of TBECH (sum of all isomers) and BDE-47 reported by the FWI were 22.9 pg/L (presumably incorrectly labelled as ng/L in the database) and 32 pg/L, respectively, which are one to two orders of magnitude higher than the PWS measurements. However, the median calculated for TBECH only reflects the three out of 122 samples analyzed in total with concentrations above the LOD of 1.22 pg/L. This may be attributed to the grab sampling technique used and the FWI sampling at inland freshwater sites, whereas the PWSs in this study were deployed in sea water, which is expected to be more diluted. BDE-47 concentrations measured in the water of the Juan de Fuca Strait, BC (Sun et al., 2023) were at comparable levels (0.6-2.0 pg/L) to the ones in this study, giving credence to this theory.

3.3 Concentrations in precipitation samples

TBECH and BDE-47 could be quantified in almost all precipitation samples from Saturna Island and Tadoussac (Table S3), with levels generally being higher on the west coast. The concentrations of TBECH varied strongly between different months, without displaying a clear seasonal trend (Figure S13). Both isomers exhibited similar fluctuations. The BDE-47 concentrations in precipitation were generally lower and did not fluctuate as strongly as TBECH.

3.4 Enantiomeric fractions of α -TBECH

The results of the chiral analysis are presented using enantiomeric fractions (EFs), where the chromatographic elution order of the enantiomers was used to calculate $EF = E1/(E1+E2)$. A racemate with equal amounts of the (+) and (-) enantiomers has an EF of 0.50. EFs that are significantly above or below

0.5 indicate the occurrence of enantioselective processes, typically biological pathways relying on enzymes or enantioselective membranes. The α -TBECH standard had an EF = 0.502 ± 0.001 . The EFs of α -TBECH in the PAS extracts had values that were significantly above and below this value, ranging from 0.32 at L2 to 0.66 at L6 (Table S18). While PAS extracts from non-urban sites rarely had sufficient amounts of α -TBECH for reliable chiral analysis, samples from a few coastal sites on the St. Lawrence Estuary and in the Saguenay area in QC and on Vancouver Island in BC had EFs below 0.50 (Figure 3). Conversely, samples from populated urban sites in Quebec City and Vancouver generally had EF greater than 0.50. Several sites in the Vancouver area and in Victoria with EF < 0.50 are located on the shore of Burrard Inlet/Vancouver Harbour and Oak Bay, respectively.

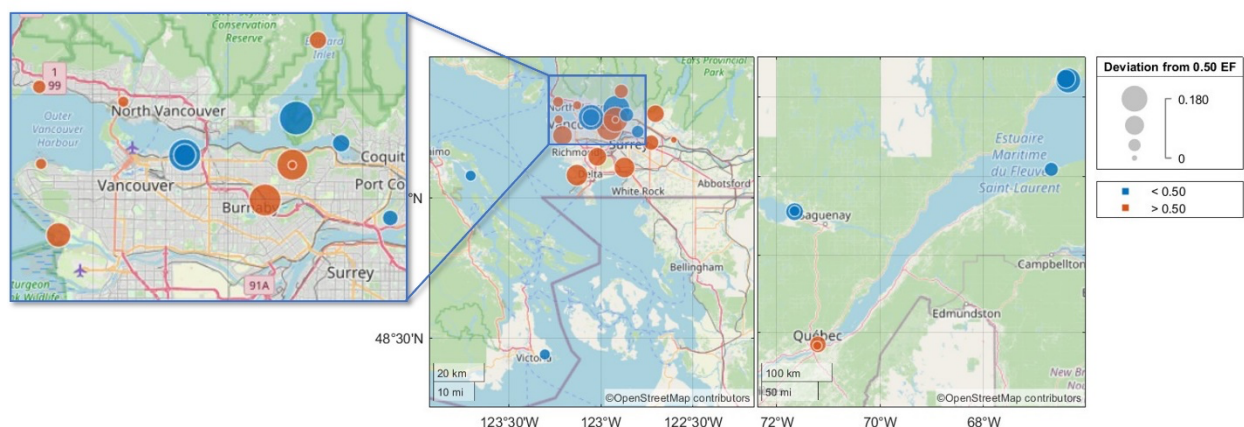


Fig. 3 The spatial distribution of the enantiomeric fraction (EF) of α -TBECH in selected BC and QC PAS. The absolute deviation from 0.50 (i.e., racemic mixture) of each site is plotted on the map, with values further from 0.00 indicating higher enantiomeric excess of one enantiomer. Sites with EF < 0.50 and EF > 0.50 are marked in blue and red, respectively.

Consistent with the PAS from urban deployments in BC and QC generally having EFs > 0.5, the EFs in the AAS from Toronto were also mostly above 0.502 ± 0.001 (only one out of 36 samples had an EF < 0.502) (Table S19). While there was no clear seasonal trend in the EF, α -TBECH tended to be close to racemic in summertime air (Figure S14, Table S20; $R^2=0.14$, $p=0.023$). Conversely, the EFs of α -TBECH in the PWS extracts (Table S21) were below 0.5, agreeing with the EF spatial trends observed in the PAS network.

Despite its urban origin, the TBECH in Canada has clearly experienced enantioselective processing, i.e., has evaporated from reservoirs where it has undergone microbial transformations. This is in agreement with the observed enantiomeric excess for α -TBECH in soil experiments, with increasing excess seen after prolonged degradation (Wong et al., 2012). The consistent EF < 0.5 observed in water and marine air samples also suggests that at least some of the TBECH in the atmosphere evaporated from seawater.

Moreover, the microbial processes occurring in urban soils and in marine waters seem to favour opposite enantiomers, leading to the divergent enantiomeric enrichment of TBECH.

4. Discussion

4.1 Atmospheric deposition of TBECH

The log K_{OA} values less than 9 (Table 1) imply that TBECH will not sorb appreciably to atmospheric particles. This was confirmed by the failure to detect either isomer in the GFFs of the AAS in Saturna and Tadoussac. Atmospheric deposition thus must occur by diffusive gas exchange or by precipitation scavenging from the gas phase. We paired the analytical results in different types of samples to study these deposition processes.

4.1.1 Diffusive air-water gas exchange

By having measured TBECH and BDE-47 in both air and water, we can investigate the water-air equilibrium status and the potential direction of diffusive air-water gas exchange in the Salish Sea. We estimated water-air fugacity ratios f_w/f_a from the measured concentrations as described in Text S9. The f_w/f_a ratios for both TBECH isomers and BDE-47 were below unity throughout BC, indicating net deposition of the BFRs from the atmosphere to the Salish Sea. This is also the case for Vancouver and Victoria Harbour (Figure S15, Figure S16). While this analysis could not be done in QC for TBECH, as it could not be detected in water, the f_w/f_a ratios for BDE-47 in QC were found to also be below unity (Figure S16). We caution that these air-water exchange calculations have considerable uncertainty, which stems from the uncertainty (i) of volumetric air and water concentrations derived from passive sampling techniques, (ii) in the K_{AW} , which is apparent from differences in the predictions of different methods (Table 1), and (iii) arising from combining air and water data obtained during different time periods. While periods of deployment overlapped in this study, PWS were deployed for approx. one month (Table S9), whereas PAS deployment periods were considerably longer (Table S1).

4.1.2 Scavenging ratios

The monthly measurements of BFRs in air and precipitation from Saturna Island and Tadoussac were used to estimate scavenging ratios, i.e., the concentration of TBECH and BDE-47 in precipitation divided by their concentration in air (Text S9). The scavenging ratios of the TBECH and BDE-47 ranged between 10^5 to 10^7 , and 10^4 to 10^5 , respectively (Figure S17). Exchange of vapours between the air and water droplets in the atmosphere is assumed to occur fast enough to achieve almost instant equilibrium. If equilibrium between

the precipitation droplets and atmospheric gas phase was established, the scavenging ratio should equal the water-air partition ratio, K_{WA} ($=1/K_{AW}$). The measured scavenging ratios for TBECH in this study were one to three orders of magnitude higher than the predicted K_{WA} values (Table 1). Accordingly, rainwater-air fugacity ratios of the BFRs in Saturna Island and Tadoussac (Figure S18) were one to three orders of magnitude greater than the expected equilibrium value, i.e., one.

Several reasons may contribute to this deviation from equilibrium. We have combined air concentration measurements for a 24-hour period with precipitation samples collected over the course of an entire month. The AAS quantification is uncertain, due to the very low levels in the AAS extracts, as is the K_{AW} and the temperature. Other potential reasons include: i) differences in air masses at different altitudes, where the warm continental air containing higher TBECH levels at the cloud level is scavenged by precipitation and has overridden the cooler clean ocean air at lower altitudes that was sampled by AAS, ii) adsorption that occurs at the water-air interface (Hoff et al., 1993), or iii) the BFRs experience sorption to dissolved organic matter and other sorption phases (Poster and Baker, 1996), all which could lead to higher scavenging ratios. However, information on interface adsorption coefficients of the BFRs and other sorption phases at Saturna Island and Tadoussac is limited.

The month-to-month variability of the precipitation concentrations were also too large to reveal a clear seasonal pattern. This suggest that variability of TBECH levels in precipitation is controlled by factors that differ from those that control seasonal variability in air concentrations (e.g., temperature and air mass origin). Potential candidates for those factors are related to the nature of the precipitation events (e.g., frontal vs. convective storms, snow vs. rain, and precipitation rate). However, another phenomenon could also occur: Higher temperatures in summer favour higher air concentrations but lower the precipitation scavenging efficiencies of vapours, due to the temperature dependence of K_{WA} . This might explain why concentrations in precipitation do not peak in summer even if concentrations in air do.

Seasonal differences in scavenging ratios for some organic contaminants have been observed previously, with higher values measured during colder seasons (Wania and Haugen, 1999). This is likely because K_{WA} increases as the temperature lowers, resulting in more efficient scavenging. Another hypothesized reason is that snow at equivalent water content, having greater surface area, can act as a better scavenging medium than rain (Lei and Wania, 2004). The logarithm of the inverse scavenging ratio, $-\ln(SR)$ (i.e., $\ln(1/SR)$), was regressed with the reciprocal of the average air temperature. Whereas the scavenging ratios of TBECH did not significantly correlate with temperature (Table S22), the scavenging of BDE-47 at both sites increased with decreasing temperature (Figure S19).

4.2 Do the two TBECH isomer show divergent atmospheric fate?

In this study, the relative abundance of α - and β -TBECH was very consistent, with mean α -/ β -TBECH ratio generally ranging from 1.1 to 1.6, i.e., indicating a slightly higher abundance of the α -isomer relative to the β -isomer. In particular, this ratio was very similar in different parts of the country, with median α -/ β -TBECH in active air samples with concentrations of both isomers above the LOD being 1.56 (range 1.07 to 2.01) in Toronto, 1.72 (range 1.44 to 3.28) in Tadoussac, and 1.57 (range 1.08 to 2.28) on Saturna Island. Similarly, the median α -/ β -TBECH in PAS was the same in QC (1.12, range 0.29 to 1.99) and BC (1.16, range 0.51 to 3.20). This slightly higher abundance of the α -isomer relative to the β -isomer is consistent with earlier reports of TBECH elsewhere in the atmosphere (Table S13), as well as to the reported abundances in technical mixtures (Arsenault et al., 2008; Ruan et al., 2018).

The relative abundance of the two isomers is also generally very similar in different environmental media. The mean α -/ β -TBECH ratio in AAS (QC mean = 1.95; BC mean = 1.62; ON mean = 1.56) and PAS (QC mean = 1.03; BC mean = 1.21) bracket the values recorded in the PWS (BC mean = 1.52) and precipitation (QC mean = 1.21; BC mean = 1.22) (Figure 4). Moreover, isomer abundance was very similar in different samples of the same type. The two isomers exhibited nearly identical spatial patterns in air (Figure S3) and water (Figure S11). The seasonal patterns in air (Figure 2, Figure S8, Figure S9) and in precipitation (Figure S13) were also highly consistent for α - and β -TBECH. Not surprisingly, α - and β -TBECH had similar water-air equilibrium status in the Salish Sea (Figure S15) and essentially identical scavenging ratios (Figure S16).

Information on the atmospheric degradation of TBECH has been extremely limited, with no experimental results in the literature to date. Using density functionals, Wang et al. (2021) predicted rate constants for the stereospecific hydroxyl radical-initiated transformation of 7.1×10^{-11} and $1.2 \times 10^{-10} \text{ cm}^3/\text{s}$ at 293 K for α - and β -TBECH, respectively, which, when applying $9.7 \times 10^5 \text{ molecules/cm}^3$ as the concentration of OH radicals in the atmosphere, corresponds to atmospheric lifetimes of 4.04 and 2.44 hours. Such relatively short gas-phase lifetimes are difficult to reconcile with the relatively wide dispersal of TBECH recorded in the current study. Neither do our measurements support the idea that the atmospheric lifetime of the β -isomer is considerably short than that of α -TBECH, as this should have been apparent in an increasing relative abundance of α -TBECH with increasing distance from sources.

Rate constants predicted with COSMOtherm and the Atmospheric Oxidation Program for Microsoft Windows (AOPWIN) via EPI Suite (Table 1) are on the same order of magnitude and correspond to much longer atmospheric lifetimes (6.2 and 6.4 days for α - and β -TBECH, respectively, using COSMOtherm; 2.5

days for both isomers using AOPWIN) than those predicted by Wang et al. (2021). These longer lifetimes and the similar rates of reaction of the two main isomers are more consistent with the observed atmospheric dispersion of TBECH.

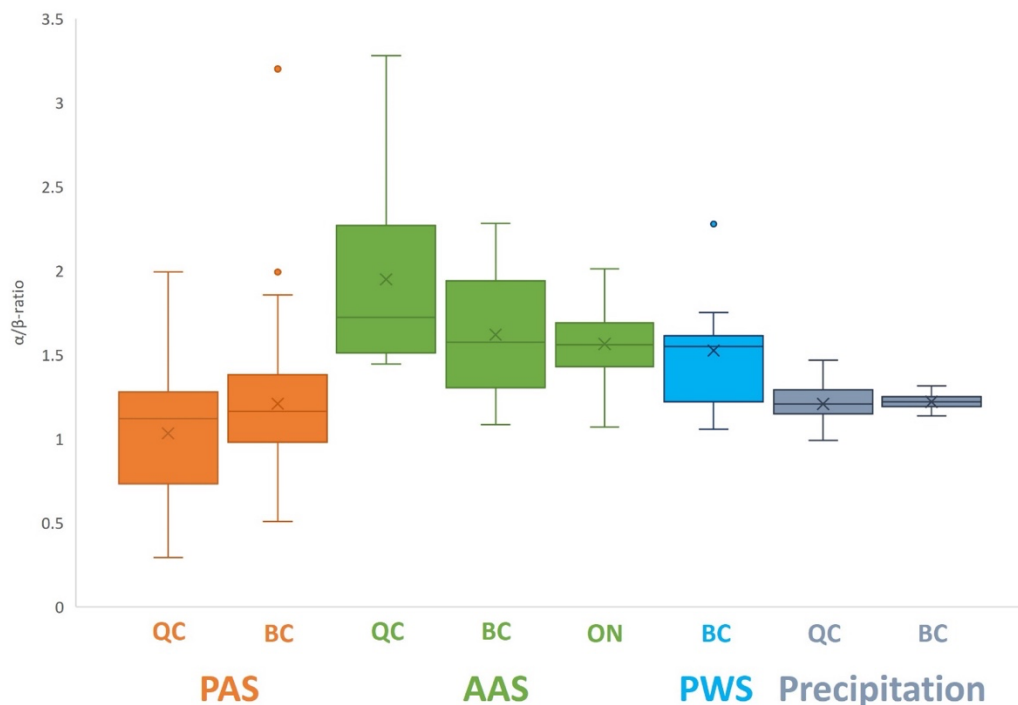


Fig. 4 Comparison of the α -/ β -TBECH ratio calculated in the sampling regions of this study, grouped in different environmental media/sampling methods. The mean α -/ β -TBECH ratio is indicated with an “x” for each method. For statistical analysis, outliers ($\alpha/\beta > 2.0$) were included but are explicitly marked on the plot as dots. Only measurements with both isomers above the LOD were used in this plot.

Taken together, this consistency in TBECH composition suggests that α - and β -TBECH exhibit similar atmospheric behaviours. This is also consistent with the very minor differences in partitioning behaviour predicted for the two congeners by COSMOtherm (Table 1). The slightly lower COSMOtherm-predicted air-water and slightly higher octanol-air partition ratios of the β -isomer compared to the α -isomer are not apparent in divergent atmospheric behaviour.

4.3 Sources of TBECH to the Canadian atmosphere

While literature on TBECH in the atmosphere has been limited, the few existing studies all point to TBECH levels generally being higher in populated urban areas. Using the spatial concentration patterns from this study, the first to compare urban and remote concentrations of TBECH within a single study, we were able

to confirm that TBECH strongly correlates with population. Moreover, the temporal trends of TBECH indicate that the air concentrations increase during the warmer season with fixed isomeric composition, particularly in the urban centres of Canada. Its year-round presence in remote regions in this study also suggests that TBECH has the potential for long range transport (LRT).

The inventory update phase 3 survey in 2017 under Canada's Chemical Management Plan (CMP) resulted in no reports of manufacturing or importing TBECH into the country by domestic companies, eliminating the possibility of point sources located in Canada for this flame retardant, such as factories that produce or import commercial TBECH. Similarly, the United States Environmental Protection Agency's (US EPA) Toxic Substances Control Act (TSCA) Chemical Substance Inventory contains no records of the production or importation of TBECH for commercial purposes in the US (USEPA, 2023), indicating that there are also no point sources of TBECH located in the US to contribute to the TBECH levels observed in Canada via atmospheric transport.

However, several recent international patents have included commercial TBECH as one of the flame retardants used mostly in electronics (Geng et al., 2018; Ke and Lv, 2020), pointing to the possibility that TBECH enters Canada almost exclusively as part of imported products. It is likely that most, if not all the TBECH detected in this study originate from the gradual release from these imported products. Populated urban areas, with typically greater overall usage of products containing flame retardants, e.g., electronics and plastics, have consistently shown higher TBECH levels with more pronounced temperature dependence compared to remote regions, and therefore suggest greater leakage. This is also consistent with previous studies reporting higher TBECH levels in indoor air, compared to outdoor (Table S13).

Chiral compounds are typically commercially produced as a racemate, including technical mixtures of TBECH (Ruan et al., 2018). Abiotic processes occurring in the environment, such as hydrolysis, oxidation, and volatilization, are unable to distinguish between enantiomers, and therefore, the EF of the compound will remain unchanged through these forms of physical processes. Microbial degradation, however, can result in the preferential consumption of one enantiomer over another, or in other words, deviations in the EF from 0.5. The variations in the EF of a compound can therefore be used to observe the enantiomeric transformations of a molecule in the environment. Therefore, the EF results of this study also indicate that secondary emissions of TBECH may occur in Canada. Once TBECH is deposited, a portion of it may undergo enantioselective processes in the environment, e.g., uptake, translocation, and metabolism by microbes. TBECH that re-volatilizes from these reservoirs has an excess in one enantiomer, with different enantiomer preferences seen in different environments (urban soils vs. marine waters).

5. Conclusion

Environmental assessments of chemicals are currently prioritized by the Government of Canada based on their persistence, bioaccumulation potential, and the quantity of domestic industrial manufacture, import, and/or export of a chemical. With neither official records of importation nor manufacturing existing in Canada, TBECH is, for environmental assessment purposes, not considered to be present in Canada. Therefore, despite being classified as persistent and bioaccumulative, it has been deemed a nonpriority for evaluation by Environment and Climate Change Canada (ECCC) and other governmental programs. However, the results of this study reveal that TBECH is ubiquitous in the Canadian atmosphere and waters at comparable levels with a legacy flame retardant, BDE-47, with elevated levels in populated areas. This, along with the strong seasonal variability of TBECH observed in urban areas, suggest that TBECH is emitted primarily from imported products. At least some of the TBECH in the atmosphere has been subject to microbial processing, i.e., entered the atmosphere after having been previously deposited to the surface (water/soil), resulting in enantiomeric enrichment.

With the current assessment requisites in place, TBECH and other chemicals of emerging concern (CECs) that are supposedly “nonexistent” in Canada would remain low priority for environmental assessment. This is particularly concerning for compounds that can enter in the country as part of imported products, potentially evading documentation. Such evasion has already been observed in Canada with short-chained chlorinated paraffins, which have been detected in imported products despite a ban on manufacture, usage, and import in 2013 (Kutarna et al., 2023). This raises the question whether the current assessment criteria are sufficient to address the relevant CECs in Canada. The increasing development and production of novel chemicals aimed to replace legacy POPs in their functions will only further highlight the limitations of the assessment requisites in place. We emphasize, with the results of this study, the importance of long-term environmental monitoring for EBFs and other CECs as part of working towards proper screening and risk assessment.

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7. Data availability

All data generated in this study are provided in the supplement.

8. Author Contribution

FZ, YL, and JO prepared and extracted the passive air samplers (PASs) and the Toronto active air samples (AAS). FZ and YL also took the Toronto AAS. YDL prepared standards and performed the instrumental analysis on all samples. CS prepared and obtained samples from Saturna Island and Tadoussac as well as the passive water samplers (PWSs) and performed the chiral analysis. KL and FAPCG deployed/retrieved PASs and PWSs in BC. ABC, ADC, ZL, NA, HH, FZ and FW deployed/retrieved PASs and PWSs in Quebec. provided guidance on sampling and sample analyses. JO compiled and interpreted data, with input from FW. JO and FW wrote the manuscript with input by the other co-authors. HH coordinated the project.

9. Competing Interests

The authors have no competing interests to declare.

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