1 **The atmospheric fate of 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH):**

2 **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

70   multimodal endocrine disruption which involves estrogenic (Asnake et al., 2014), anti-androgenic (Wong

71   et al., 2016), and thyroidal processes (Porter et al., 2014). This disrupting potential of TBECH is also seen

72   in the *in vivo* studies reporting changes in circulating hormones (Curran et al., 2017; Gemmill et al., 2011),

73   organ structure (Park et al., 2011), and reproduction (Marteinson et al., 2012a; Marteinson et al., 2012b)

74   after exposure to low concentrations of TBECH. More details on the reported toxicological effects of

75   TBECH from both *in vivo* and *in vitro* studies are discussed in Marteinson et al. (2021).

76   Presumably because no Canadian company reported the manufacture and importation of TBECH on a

77   commercial scale (ECCC, 2017), it has been deemed a non-priority for assessment under Canada's

78   Chemicals Management Plan (ECCC, 2019). As a result, TBECH remains unregulated at both national and

79   international levels, despite being judged to be persistent and bioaccumulative. There is evidence,

80   however, of its presence in the Canadian environment, as TBECH has been detected in different

81   environmental media, ranging from urban outdoor air in Toronto (Shoeib et al., 2014) to whale blubber

82   in the Arctic (Tomy et al., 2008). Only three studies have published on the enantiomeric composition of

83   TBECH in the environment (Ruan et al., 2018; Ruan et al., 2019), with one study on Canadian urban soils

84   (Wong et al., 2012). Therefore, concerted efforts to understand the sources, atmospheric behaviour, and

85   enantiomeric profile of TBECH have been limited, not only in Canada, but also worldwide.

86   With the objective to gain insight in the atmospheric fate of α- and β-TBECH in general and in Southern

87   Canada specifically, we sought to characterise the spatial and seasonal variability in their air

88   concentrations and to explore their potential for atmospheric deposition. We also compare the

89   atmospheric fate of TBECH with that of the PBDEs, in particular 2,2',4,4'-tetrabromodiphenyl ether (BDE-

90   47), one of the traditional BFRs that has been internationally banned under the UNEP-SC-POPs but can

91   still be detected in the environment. Spatial patterns were investigated with two passive air sampler (PAS)

92   networks in the coastal regions of Quebec (QC) and British Columbia (BC). Seasonal trends in air

93   concentrations were studied using active air samplers (AAS) at an urban site in Toronto and two remote

94   sites on either coast. The input to aquatic systems was studied by measuring year-round wet deposition

95   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.

126 2.1.3 Passive water sampling network

127 Passive water samplers consisting of low-density polyethylene (LDPE) sheets in a metal mesh cage were

128 deployed in 20 unique locations in BC and QC during the late spring and summer of 2021 (Table S9). Figure

129 S2 provides maps with the sampling sites. Before deployment, the LPDE sheets were infused with several

130 performance reference compounds (PRCs) to determine sampling rates. Details are provided in Text S2.

131 2.2 Sample analysis

132 The gas phase sorbent from the AAS at Saturna Island and Tadoussac was Soxhlet extracted. All other air

133 samples underwent pressurised liquid extraction using an accelerated solvent extractor. The precipitation

134 samples were filtered through 0.7 μm GFFs and the filtered samples were then subjected to liquid-liquid

135 extraction. The LDPE sheets were simply soaked in solvent overnight. Fourteen ^{13}C-labelled surrogates

136 were spiked into all samples prior to extraction. All extracts were reduced in volume and dried with

137 Na_2SO_4. Injection standards (^{13}C-PCB-105 and 180) were added to the final extracts. Details on the

138 extraction solvents, conditions, and the standards are provided in Text S3.

139 All samples were analyzed for a suite of 28 BFRs, including 15 PBDE congeners (BDE-17, 28, 47, 49, 66, 71,

140 85, 99, 100, 138, 153, 154, 183, 190 and 209), α-TBECH, β-TBECH, allyl 2,4,6-tribromophenyl ether (ATE),

141 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), pentabromobenzene (PBBz), hexabromobenzene

142 (HBBz), pentabromotoluene (PBT), pentabromoethyl benzene (PBEB), 2,3-dibromopropyl-2,4,6-

143 tribromophenyl ether (DBTE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB), 1,2-bis(2,4,6-

144 tribromophenoxy)ethane (BTBPE), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEHTBP), and

145 decabromodiphenyl ethane (DBDPE). Four additional halogenated flame retardants (Dec-602, Dec-604,

146 *syn*-DP, *anti*-DP) were also analyzed. Details of the instrumental analysis are provided in the Text S4. This

147 is also where information on the QA/QC procedures can be found, which includes many procedural and

148 field blanks. Limit of Detection (LOD) and Limit of Quantitation (LOQ) for different types of samples are

149 provided in Table S12.

150 Both α- and β-TBECH are chiral molecules but can be expected to enter the environment as a racemate,

151 i.e., with their two enantiomers being equally abundant (mean enantiomeric fraction $EF_{standards}$ = 0.502 ±

152 0.001). The unequal abundance of two enantiomers in environmental samples has been used to identify

153 the occurrence of enantioselective processing, such as microbial transformation reactions. The

154 enantiomeric composition of α- and β-TBECH was determined in samples with TBECH concentrations >

155 LOQ from the PAS network in BC and QC, from the AAS in Toronto, and in a few PWS. The amounts of β-

156 TBECH in the extract were generally too low for reliable chiral analysis, therefore, only results on the

157 enantiomeric analysis of α-TBECH are presented. A description of the analytical method for enantiomeric

158 analysis is provided in Text S4.

159 ## 2.3 Air and water concentration calculations

160 Volumetric air concentrations were derived from the amounts quantified in the PAS sorbent using

161 sampling rates reported by Li et al. (2023). Volumetric water concentrations were calculated from the

162 amount quantified in the LDPE sheets using the dissipation of PRCs and the approach by Booij and Smedes

163 (2010). Details are again in Text S5. For statistical purposes, the measurements below the LOD are

164 represented by the value of the compound specific LOD (Table S12).

165 ## 2.4 Partitioning properties calculations using COSMO-RS and other prediction tools

166 Equilibrium partition ratios between octanol and water (K_{ow}), octanol and air (K_{oa}), and air and water (K_{aw})

167 of TBECH were estimated using quantitative structure-activity relationship (QSAR) models integrated in

168 several chemical property prediction tools (EASE-Suite, EPI Suite, OPERA). Because these QSARs cannot

169 distinguish between the properties of α- and β-TBECH, we also applied COSMOtherm, which is based on

170 quantum chemistry and statistical thermodynamics. Details of these approaches have been described

171 previously (Baskaran et al., 2021). More details on COSMOtherm are also given in Text S6. In general, the

172 predicted partition ratios of TBECH from the different models are in good agreement, i.e., are typically

173 within 0.30 log units of each other (Table 1). COSMOtherm tends to give slightly lower log K_{OW} and log K_{AW}

174 values, suggesting a higher solvation in the aqueous phase than the QSARs. COSMOtherm-predicted

175 properties for the two isomers are also very similar, with α-TBECH being slightly more volatile than β-

176 TBECH.

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

		Log K_{ow}		Log K_{aw}		Log K_{oa}		$k \times 10^{-12}$ (cm³/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	-TBECH				-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

199 To place these concentrations into context, Table S13 summarises all atmospheric concentrations of

200 TBECH previously reported in the literature. A review of the occurrences of TBECH in other environmental

201 media (e.g., soil, water, sediment) can be found in Marteinson et al. (2021). The concentrations of TBECH

202 recorded here are at the lower end of the range of levels detected in urban outdoor air elsewhere. In

203 particular, levels in Canadian urban locations are similar to those reported for outdoor air in Stockholm,

204 Sweden (Newton et al., 2015; Wong et al., 2018), but somewhat lower than those measured in

205 Birmingham, UK (Drage et al., 2016), Brno, Czech Republic (Bohlin et al., 2014; Melymuk et al., 2016) and

206 previous measurements taken in Toronto (Shoeib et al., 2014). Much higher values had been reported for

207 indoor air (Cequier et al., 2014; Genisoglu et al., 2019; Melymuk et al., 2016; Newton et al., 2015; Newton

208 et al., 2016; Tao et al., 2016; Wong et al., 2018), an electronic waste facility in China (Hong et al., 2018)

209 and - somewhat incongruously - in Longyearbyen, Svalbard (Carlsson et al., 2018). PAS deployed in remote

210 regions (pop. <10 000 in a 20-km radius) tended to have levels of TBECH below the LOD or LOQ. The levels

211 above LOD measured in non-urban locations in this study are among the lowest ever reported,

212 comparable to what has been reported for Tibet and Antarctica (Ma et al., 2017; Zhao et al., 2020).

213 However, previous measurements of TBECH in air from non-urban locations are rare. Overall, the

214 alignment of the air concentration data with those reported previously supports the validity of the results

215 of this study.

216 BDE-47, despite its international ban under the Stockholm Convention, can still be detected in the

217 environment due to its persistence. Its presence in the atmosphere, along with other BDEs, has been

218 documented over the years in Canada, such as in Ottawa, ON (Wilford et al., 2004), Alert, NU (Wong et

219 al., 2021; Xiao et al., 2012), Yukon Territory (Yu et al., 2015), and the Great Lakes Basin (Shunthirasingham

220 et al., 2018). In this study, BDE-47 was also detected in the air in all sampling regions, with comparable

221 levels to TBECH. On Saturna Island, BDE-47 gas phase concentrations have decreased by one order of

222 magnitude relative to almost two decades prior (Noël et al., 2009). Levels in the atmospheric particle

223 phase and in precipitation in the area have similarly been decreasing.

224 3.1.2 Spatial variability of air concentrations in Canadian coastal regions

225 The spatial patterns in the air concentrations of α- and β-TBECH in the coastal regions of BC and QC as

226 obtained from the PAS networks (Figure 1) show elevated levels in populated and urban areas. Specifically,

227 in QC, higher levels are observed along the St. Lawrence River corridor between Montreal and Quebec

228 City contrasting with lower levels on the shores of the St. Lawrence Estuary. In BC, higher levels are

229 apparent in the lower mainland and in Victoria. The overall higher levels observed in the PASs from BC

230   when compared to those from QC are likely the result of more urbanized sampling locations in the former.

231   Earlier studies also indicate that urban areas have higher TBECH air concentrations than remote regions

232   (Table S13).

233   The α-/β-TBECH ratio at sites where both isomers were present above their LODs (Figure S3) is remarkably

234   consistent in space on either coast, i.e., there is no indication that the ratio varies in space, e.g., by being

235   correlated with the absolute concentration level. The ratio was typically close to or above one at sites

236   with detectable amounts of both isomers in the air. An exception (α-/β-TBECH = 0.29) was at a site located

237   10 kilometres away from Quebec City, QC (S26). However, because the air concentrations of both isomers

238   measured at this site were below their LOQs, this value should be interpreted with caution.

239   Not only are the volumetric air concentrations of BDE-47 on the same order of magnitude as TBECH, but

240   they also share a similar spatial distribution in the atmosphere (Figure 1). This is also apparent from

241   significant correlations between the concentration of both isomers of TBECH and those of BDE-47 in the

242   PAS (Figure S4, Table S14, $R^2 > 0.24$, $p < 0.0001$), which seem to be strongly influenced by the urban sites

243   with elevated BFR concentrations. One difference is the notable presence of BDE-47 at one site in Alma,

244   QC (S48) during the first deployment period, despite BDE-47 at other sites in Alma (S49-53) and in the

245   wider Saguenay region (S54-56) being below the LOQ. PASs deployed at the same site (S48_2) and a site

246   in the vicinity (S54_2) a year later had BDE-47 levels below the LOQ, suggesting that the first data point at

247   S48 was an outlier and not an indication of a local point source.

248   In the BC PAS network, air concentrations are linearly correlated with population within a 20-km radius

249   around a PAS deployment site (NASA, 2015) (Figure S5, Table S15), more so for α- and β-TBECH ($R^2 = 0.27$

250   and 0.23, respectively) than for BDE-47 ($R^2 = 0.09$). The relationships were generally stronger when

251   explored separately with concentration data obtained at different average deployment temperature

252   (<10°C, 10-15°C, >15°C; Figure S5). Weaker or absent relationships at the warmest temperature (>15°C)

253   are likely caused by the relatively small number of summer deployments. Increasing slopes of these

254   relationships at warmer temperatures indicate a higher seasonal concentration amplitude at sites in

255   populated areas than in remote regions. This is also consistent with the expectation of a stronger

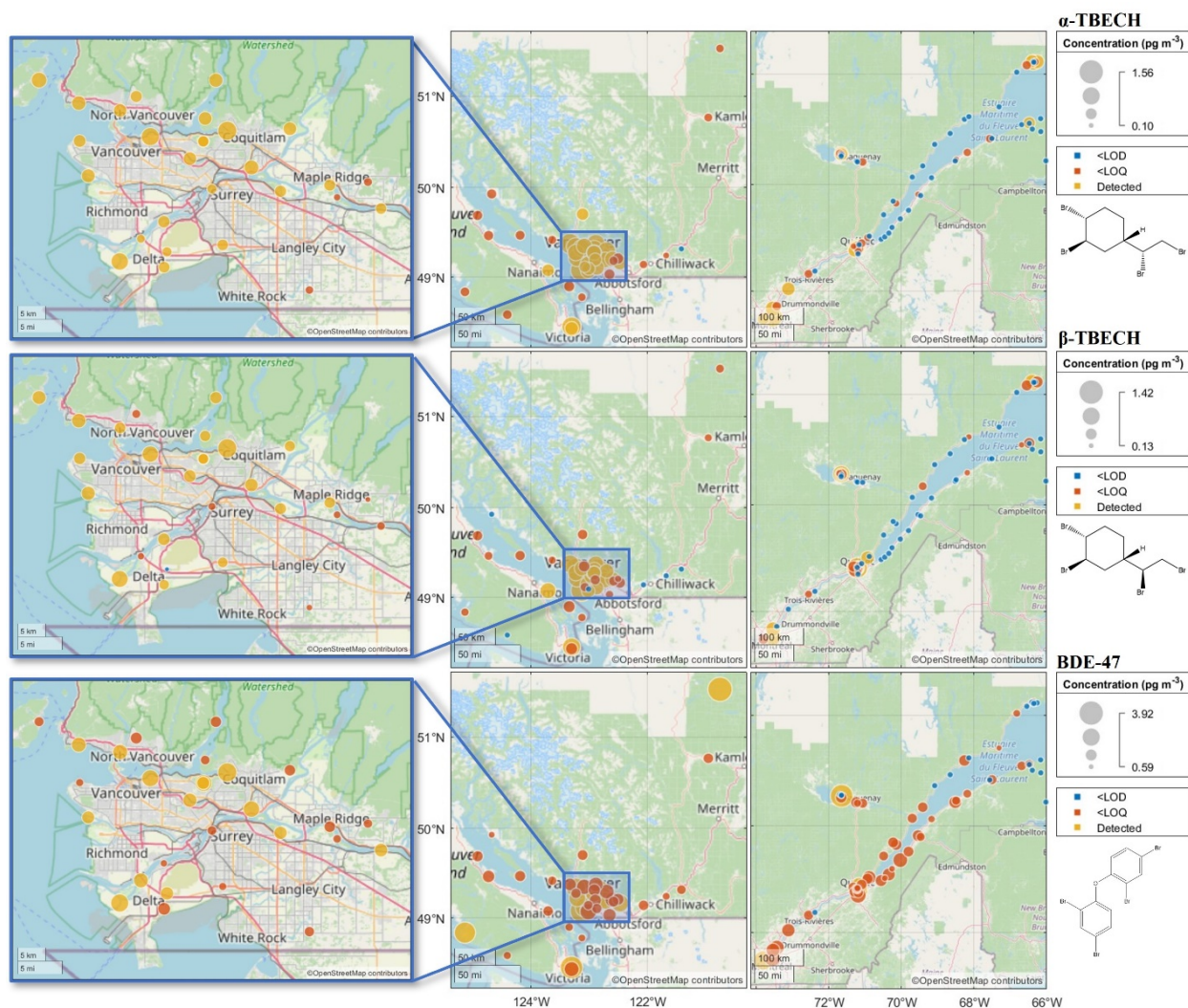
256   temperature dependence of the atmospheric concentrations of semi-volatile chemicals in source areas

257   than at sites without local sources (Wania et al., 1998). To further demonstrate this relationship with both

258   temperature and population, multiple linear regression was used on the log-transformed partial pressure

259   of TBECH against population and the inverse temperature, which resulted in higher correlations (Adjusted

260 R^2 = 0.56 and 0.42 for α- and β-TBECH, respectively). The seasonal variability in the air concentrations of

261 TBECH and BDE-47 is discussed in more depth when discussing the AAS results in section 3.1.3.

262
263 Fig. 1 The spatial distribution of the air concentrations of α-TBECH (top), β-TBECH (middle), and BDE-47
264   (bottom) in British Columbia and Quebec. Close-up maps (left) provide a detailed view of the
265   Vancouver metropolitan area. Average air concentrations are displayed for sites with replicate
266   deployments; therefore, the concentrations indicated on the figure may not align with
267   concentrations listed in Table 2 and Table S1. Air concentrations below the LOD are marked in
268   blue and display the value of the LOD. Air concentrations above the LOD and below the LOQ are
269   marked in dark orange. Air concentrations above LOQ are marked in yellow. Concentration values
270   are listed in Table S1.

271   3.1.3 Seasonal variability of air concentrations in urban and remote regions of Canada

272   *Seasonal variability in Toronto*

273   The seasonal trends of AAS-derived air concentrations of TBECH and BDE-47 in Toronto, ON (Table S2,

274   Figure 2A and 2B) indicate a strong relationship with average air temperature (Figure 2C), being higher in

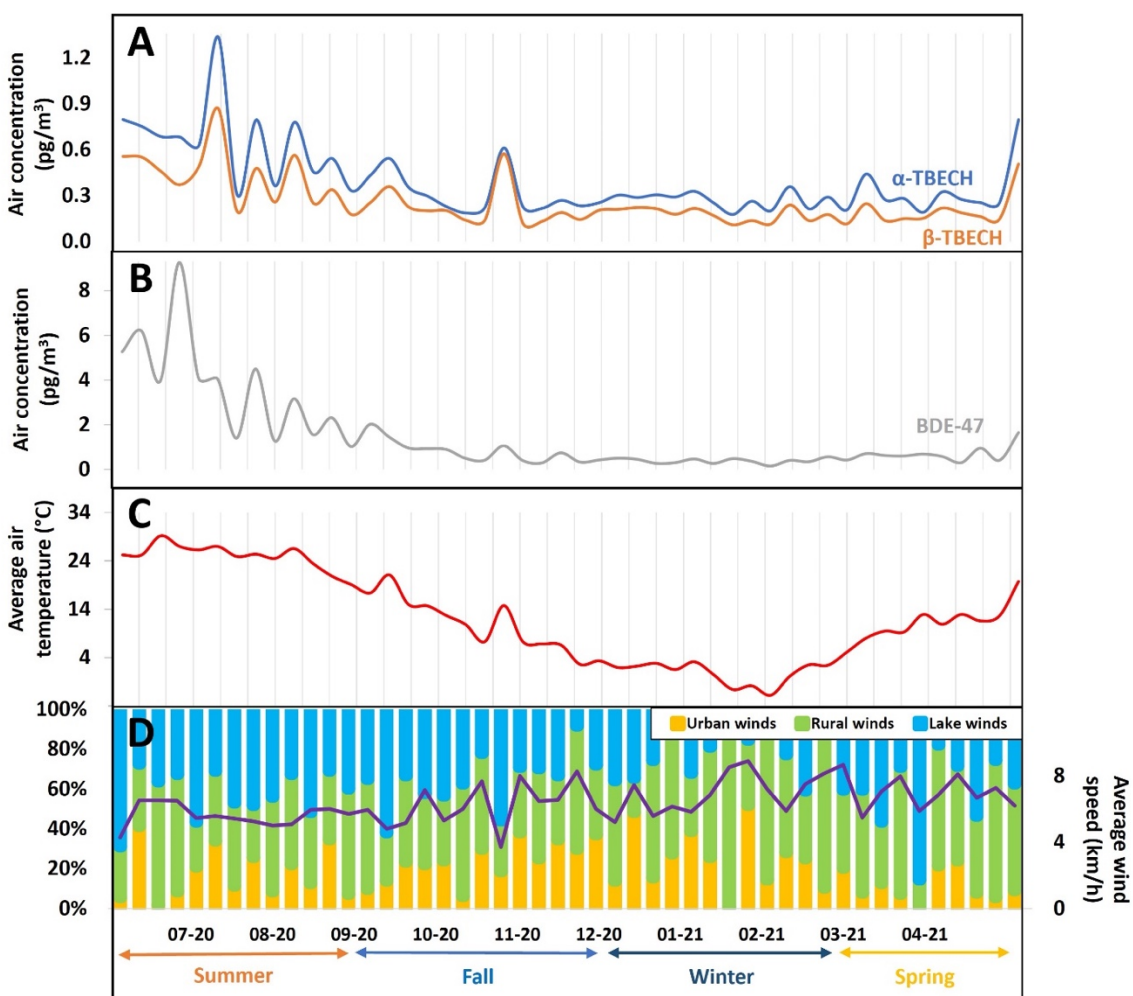
275   the summer (April to August) and lower in winter (September to March). Accordingly, log-transformed

276   partial pressures $\ln(p/Pa)$ of α- and β-TBECH and BDE-47 were significantly correlated with inverse

277   absolute temperature (Figure S6, Table S16, R^2=0.61, 0.55, and 0.81, respectively, p<0.0001). Such a

278   temperature dependence of the atmospheric concentration of semi-volatile organic compounds is often

279   interpreted as temperature driven air-surface exchange (Wania et al., 1998) or temperature-dependent

280   rates of emission.

281

282   Fig. 2   The air concentration of α-TBECH, β-TBECH, and BDE-47 and meteorological parameters in
283   Toronto, Ontario during 48 weekly active air sampling periods between June 2020 and May
284   2021.

285   With the sampling site located in an Eastern suburb of a large urban conglomeration, wind also influenced

286   the air concentrations of TBECH and BDE-47. Higher levels were recorded when weak winds were blowing

287   from the urban core of Toronto, approximately 20 km to the SW of the sampling site. Text S7 and Figure

288   S7 provide detail on how an urban wind fraction was derived. The average wind speed and the fraction of

289   wind originating over urban areas, rural regions and Lake Ontario are shown in Fig. 2D. Multivariate

290   regressions of the ln(p/Pa) with both reciprocal temperature and the urban wind fraction are highly

291   significant for all three BFRs and stronger than univariate regressions with reciprocal temperature only

292   (Table S17).

293   *Seasonal variability in Saturna Island and in Tadoussac*

294   The AAS-derived air concentrations of TBECH and BDE-47 on Saturna Island were very low (Table S2).

295   Whereas BDE-47 showed a clear seasonal pattern with higher levels in summer than in winter, any

296   seasonal pattern of the TBECH isomers was obscured by levels below the LOD in air samples taken in

297   December, June and July (Figure S8). Accordingly, whereas the ln(p/Pa) of BDE-47 was significantly

298   correlated with reciprocal temperature (R^2=0.44 and *p*=0.027), for both TBECH isomers those

299   relationships were generally weak and insignificant (Table S16). Weak or absent ln(p/Pa) versus 1/T

300   relationships are typical for remote sites without local sources, where the concentration of a compound

301   is controlled by advection from elsewhere (Wania et al., 1998).

302   In contrast to Saturna Island, AAS-derived air concentrations of TBECH and BDE-47 in Tadoussac (Table

303   S2) showed a clear seasonal trend with higher levels in summer and levels often below the LOD in winter

304   (Figure S9). Ln(p/Pa) versus 1/T regressions (Figure S6) were significant but only explained a relatively

305   small fraction of the overall variability ($R^2 > 0.30$; Table S16). One factor that may have contributed to the

306   differences in the seasonal patterns of TBECH at the two coastal sites are the much larger seasonal

307   temperature range in QC (-12 to +18 °C) than in BC (+1 to +18 °C).

308   We also sought to relate the temporal variabilities in the measured air concentrations with the history

309   and origin of the sampled air masses using the Lagrangian atmospheric dispersion model FLEXPART (Pisso

310   et al., 2019). TBECH levels below the LODs in June and July on Saturna Island despite the relatively warm

311   temperatures may be related to air masses arriving at the sampling site directly from the Pacific Ocean,

312   i.e., without encountering any potential urban source areas. Overall, TBECH levels on Saturna Island arise

313   from competing influences of air mass origin and temperature. More detail in provided in Text S8.

314 3.2 Concentrations in passive water samples

315 The water concentrations of the BFRs measured with PWSs in the coastal regions of BC and QC are

316 summarized in Table 2 with all data provided in Table S9. Whereas the TBECH isomers were below the

317 LODs in all water samples from QC, in BC, α- and β-TBECH ranged between <LOD to 1.75 pg/L and <LOD

318 to 1.15 pg/L, respectively, and were typically above the LODs at sites close to urban centers (Victoria,

319 Vancouver) (Figure S10). BDE-47 was detected at all sites of this study, with higher levels close to Victoria

320 (Figure S12). BDE-47 water concentrations were also generally slightly higher compared to those of

321 TBECH, albeit on the same order of magnitude.

322 We compared the results from the PWS network in this study with water concentrations reported by the

323 Federal Whales Initiative (FWI) of Canada (ECCC, 2022). Sampling campaigns conducted by the FWI

324 occurred in the Fraser River, BC, including its main tributaries (Thompson River and Harrison River)

325 between 2019 to 2021. The median water grab sampling concentrations of TBECH (sum of all isomers)

326 and BDE-47 reported by the FWI were 22.9 pg/L (presumably incorrectly labelled as ng/L in the database)

327 and 32 pg/L, respectively, which are one to two orders of magnitude higher than the PWS measurements.

328 However, the median calculated for TBECH only reflects the three out of 122 samples analyzed in total

329 with concentrations above the LOD of 1.22 pg/L. This may be attributed to the grab sampling technique

330 used and the FWI sampling at inland freshwater sites, whereas the PWSs in this study were deployed in

331 sea water, which is expected to be more diluted. BDE-47 concentrations measured in the water of the

332 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,

333 giving credence to this theory.

334 3.3 Concentrations in precipitation samples

335 TBECH and BDE-47 could be quantified in almost all precipitation samples from Saturna Island and

336 Tadoussac (Table S3), with levels generally being higher on the west coast. The concentrations of TBECH

337 varied strongly between different months, without displaying a clear seasonal trend (Figure S13). Both

338 isomers exhibited similar fluctuations. The BDE-47 concentrations in precipitation were generally lower

339 and did not fluctuate as strongly as TBECH.

340 3.4 Enantiomeric fractions of α-TBECH

341 The results of the chiral analysis are presented using enantiomeric fractions (EFs), where the

342 chromatographic elution order of the enantiomers was used to calculate EF=E1/(E1+E2). A racemate with

343 equal amounts of the (+) and (-) enantiomers has an EF of 0.50. EFs that are significantly above or below

344 0.5 indicate the occurrence of enantioselective processes, typically biological pathways relying on
345 enzymes or enantioselective membranes. The α-TBECH standard had an EF = 0.502± 0.001. The EFs of α-
346 TBECH in the PAS extracts had values that were significantly above and below this value, ranging from
347 0.32 at L2 to 0.66 at L6 (Table S18). While PAS extracts from non-urban sites rarely had sufficient amounts
348 of α-TBECH for reliable chiral analysis, samples from a few coastal sites on the St. Lawrence Estuary and
349 in the Saguenay area in QC and on Vancouver Island in BC had EFs below 0.50 (Figure 3). Conversely,
350 samples from populated urban sites in Quebec City and Vancouver generally had EF greater than 0.50.
351 Several sites in the Vancouver area and in Victoria with EF < 0.50 are located on the shore of Burrard
352 Inlet/Vancouver Harbour and Oak Bay, respectively.

353

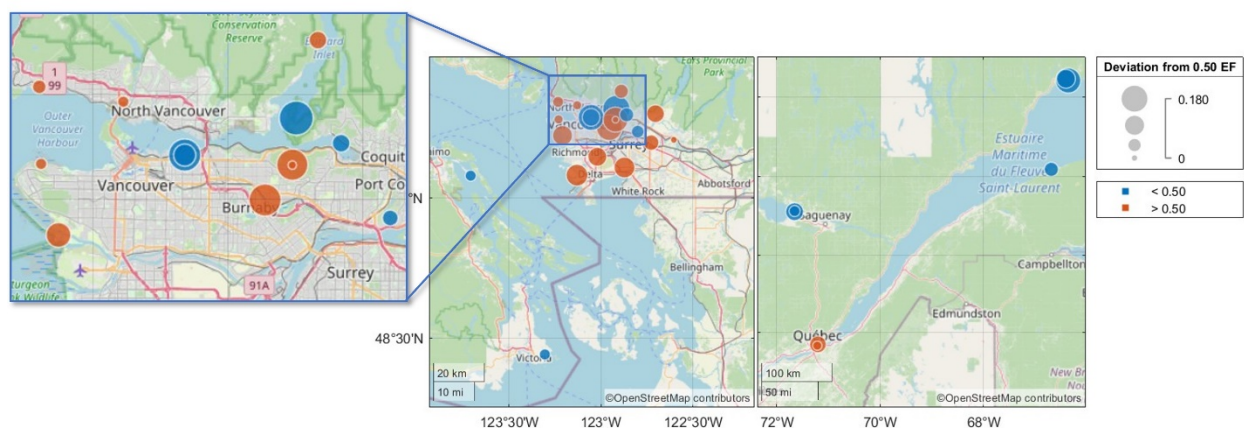



Fig. 3 The spatial distribution of the enantiomeric fraction (EF) of α-TBECH in selected BC and QC PAS.
354 The absolute deviation from 0.50 (i.e., racemic mixture) of each site is plotted on the map, with
355 values further from 0.00 indicating higher enantiomeric excess of one enantiomer. Sites with EF
356 < 0.50 and EF > 0.50 are marked in blue and red, respectively.
357

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

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

368   Moreover, the microbial processes occurring in urban soils and in marine waters seem to favour opposite

369   enantiomers, leading to the divergent enantiomeric enrichment of TBECH.

4. Discussion

4.1 Atmospheric deposition of TBECH

372   The log K_{OA} values less than 9 (Table 1) imply that TBECH will not sorb appreciably to atmospheric particles.

373   This was confirmed by the failure to detect either isomer in the GFFs of the AAS in Saturna and Tadoussac.

374   Atmospheric deposition thus must occur by diffusive gas exchange or by precipitation scavenging from

375   the gas phase. We paired the analytical results in different types of samples to study these deposition

376   processes.

4.1.1 Diffusive air-water gas exchange

378   By having measured TBECH and BDE-47 in both air and water, we can investigate the water-air equilibrium

379   status and the potential direction of diffusive air-water gas exchange in the Salish Sea. We estimated

380   water-air fugacity ratios f_W/f_A from the measured concentrations as described in Text S9. The f_W/f_A ratios

381   for both TBECH isomers and BDE-47 were below unity throughout BC, indicating net deposition of the

382   BFRs from the atmosphere to the Salish Sea. This is also the case for Vancouver and Victoria Harbour

383   (Figure S15, Figure S16). While this analysis could not be done in QC for TBECH, as it could not be detected

384   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

385   these air-water exchange calculations have considerable uncertainty, which stems from the uncertainty

386   (i) of volumetric air and water concentrations derived from passive sampling techniques, (ii) in the K_{AW},

387   which is apparent from differences in the predictions of different methods (Table 1), and (iii) arising from

388   combining air and water data obtained during different time periods. While periods of deployment

389   overlapped in this study, PWS were deployed for approx. one month (Table S9), whereas PAS deployment

390   periods were considerably longer (Table S1).

4.1.2 Scavenging ratios

392   The monthly measurements of BFRs in air and precipitation from Saturna Island and Tadoussac were used

393   to estimate scavenging ratios, i.e., the concentration of TBECH and BDE-47 in precipitation divided by their

394   concentration in air (Text S9). The scavenging ratios of the TBECH and BDE-47 ranged between 10^5 to 10^7,

395   and 10^4 to 10^5, respectively (Figure S17). Exchange of vapours between the air and water droplets in the

396   atmosphere is assumed to occur fast enough to achieve almost instant equilibrium. If equilibrium between

397 the precipitation droplets and atmospheric gas phase was established, the scavenging ratio should equal

398 the water-air partition ratio, K_{WA} (=1/K_{AW}). The measured scavenging ratios for TBECH in this study were

399 one to three orders of magnitude higher than the predicted K_{WA} values (Table 1). Accordingly, rainwater-

400 air fugacity ratios of the BFRs in Saturna Island and Tadoussac (Figure S18) were one to three orders of

401 magnitude greater than the expected equilibrium value, i.e., one.

402 Several reasons may contribute to this deviation from equilibrium. We have combined air concentration

403 measurements for a 24-hour period with precipitation samples collected over the course of an entire

404 month. The AAS quantification is uncertain, due to the very low levels in the AAS extracts, as is the K_{AW}

405 and the temperature. Other potential reasons include: i) differences in air masses at different altitudes,

406 where the warm continental air containing higher TBECH levels at the cloud level is scavenged by

407 precipitation and has overridden the cooler clean ocean air at lower altitudes that was sampled by AAS,

408 ii) adsorption that occurs at the water-air interface (Hoff et al., 1993), or iii) the BFRs experience sorption

409 to dissolved organic matter and other sorption phases (Poster and Baker, 1996), all which could lead to

410 higher scavenging ratios. However, information on interface adsorption coefficients of the BFRs and other

411 sorption phases at Saturna Island and Tadoussac is limited.

412 The month-to-month variability of the precipitation concentrations were also too large to reveal a clear

413 seasonal pattern. This suggest that variability of TBECH levels in precipitation is controlled by factors that

414 differ from those that control seasonal variability in air concentrations (e.g., temperature and air mass

415 origin). Potential candidates for those factors are related to the nature of the precipitation events (e.g.,

416 frontal vs. convective storms, snow vs. rain, and precipitation rate). However, another phenomenon could

417 also occur: Higher temperatures in summer favour higher air concentrations but lower the precipitation

418 scavenging efficiencies of vapours, due to the temperature dependence of K_{WA}. This might explain why

419 concentrations in precipitation do not peak in summer even if concentrations in air do.

420 Seasonal differences in scavenging ratios for some organic contaminants have been observed previously,

421 with higher values measured during colder seasons (Wania and Haugen, 1999). This is likely because K_{WA}

422 increases as the temperature lowers, resulting in more efficient scavenging. Another hypothesized reason

423 is that snow at equivalent water content, having greater surface area, can act as a better scavenging

424 medium than rain (Lei and Wania, 2004). The logarithm of the inverse scavenging ratio, -ln(SR) (i.e.,

425 ln(1/SR)), was regressed with the reciprocal of the average air temperature. Whereas the scavenging

426 ratios of TBECH did not significantly correlate with temperature (Table S22), the scavenging of BDE-47 at

427 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).

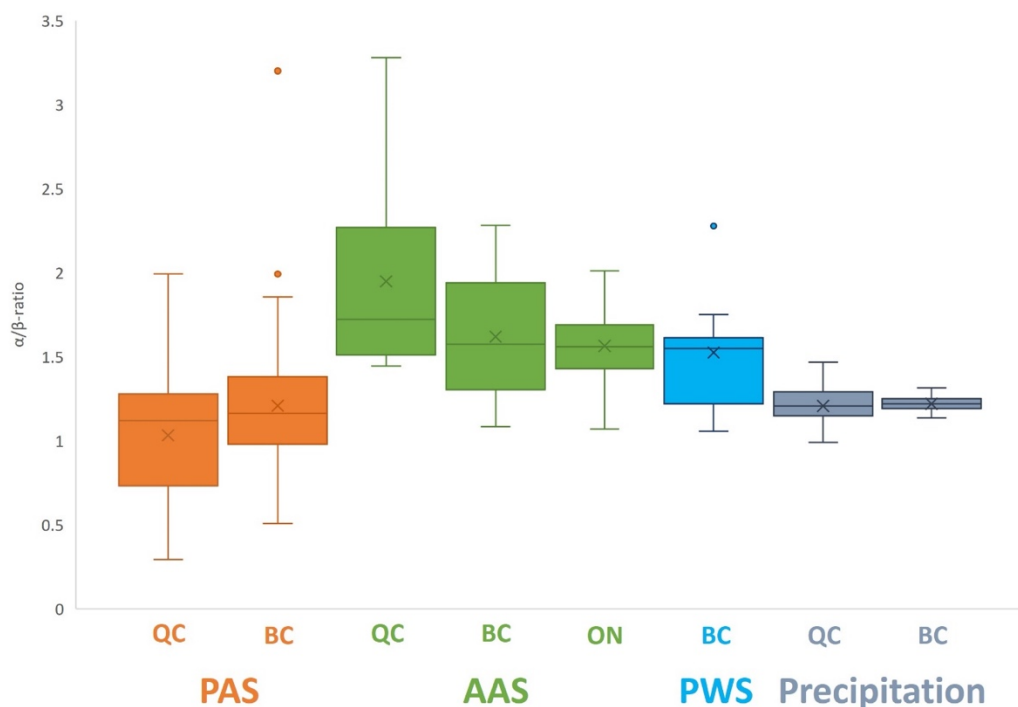
The relative abundance of the two isomers is also generally very similar in different environmental media. The mean α-/β-TBECH ratio in AAS (QC mean = 1.95; BC mean = 1.62; ON mean = 1.56) and PAS (QC mean = 1.03; BC mean =1.21) bracket the values recorded in the PWS (BC mean = 1.52) and precipitation (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 1.2×10^{-10} cm^3/s at 293 K for α- and β-TBECH, respectively, which, when applying 9.7×10^5 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 b-isomer is considerably short than that of a-TBECH, as this should have been apparent in an increasing relative abundance of a-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

458   days for both isomers using AOPWIN) than those predicted by Wang et al. (2021). These longer lifetimes

459   and the similar rates of reaction of the two main isomers are more consistent with the observed

460   atmospheric dispersion of TBECH.

461

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

467   Taken together, this consistency in TBECH composition suggests that α- and β-TBECH exhibit similar

468   atmospheric behaviours. This is also consistent with the very minor differences in partitioning behaviour

469   predicted for the two congeners by COSMOtherm (Table 1). The slightly lower COSMOtherm-predicted

470   air-water and slightly higher octanol-air partition ratios of the β-isomer compared to the α-isomer are not

471   apparent in divergent atmospheric behaviour.

472   4.3 Sources of TBECH to the Canadian atmosphere

473   While literature on TBECH in the atmosphere has been limited, the few existing studies all point to TBECH

474   levels generally being higher in populated urban areas. Using the spatial concentration patterns from this

475   study, the first to compare urban and remote concentrations of TBECH within a single study, we were able

476   to confirm that TBECH strongly correlates with population. Moreover, the temporal trends of TBECH

477   indicate that the air concentrations increase during the warmer season with fixed isomeric composition,

478   particularly in the urban centres of Canada. Its year-round presence in remote regions in this study also

479   suggests that TBECH has the potential for long range transport (LRT).

480   The inventory update phase 3 survey in 2017 under Canada's Chemical Management Plan (CMP) resulted

481   in no reports of manufacturing or importing TBECH into the country by domestic companies, eliminating

482   the possibility of point sources located in Canada for this flame retardant, such as factories that produce

483   or import commercial TBECH. Similarly, the United States Environmental Protection Agency's (US EPA)

484   Toxic Substances Control Act (TSCA) Chemical Substance Inventory contains no records of the production

485   or importation of TBECH for commercial purposes in the US (USEPA, 2023), indicating that there are also

486   no point sources of TBECH located in the US to contribute to the TBECH levels observed in Canada *via*

487   atmospheric transport.

488   However, several recent international patents have included commercial TBECH as one of the flame

489   retardants used mostly in electronics (Geng et al., 2018; Ke and Lv, 2020), pointing to the possibility that

490   TBECH enters Canada almost exclusively as part of imported products. It is likely that most, if not all the

491   TBECH detected in this study originate from the gradual release from these imported products. Populated

492   urban areas, with typically greater overall usage of products containing flame retardants, e.g., electronics

493   and plastics, have consistently shown higher TBECH levels with more pronounced temperature

494   dependence compared to remote regions, and therefore suggest greater leakage. This is also consistent

495   with previous studies reporting higher TBECH levels in indoor air, compared to outdoor (Table S13).

496   Chiral compounds are typically commercially produced as a racemate, including technical mixtures of

497   TBECH (Ruan et al., 2018). Abiotic processes occurring in the environment, such as hydrolysis, oxidation,

498   and volatilization, are unable to distinguish between enantiomers, and therefore, the EF of the compound

499   will remain unchanged through these forms of physical processes. Microbial degradation, however, can

500   result in the preferential consumption of one enantiomer over another, or in other words, deviations in

501   the EF from 0.5. The variations in the EF of a compound can therefore be used to observe the enantiomeric

502   transformations of a molecule in the environment. Therefore, the EF results of this study also indicate

503   that secondary emissions of TBECH may occur in Canada. Once TBECH is deposited, a portion of it may

504   undergo enantioselective processes in the environment, e.g., uptake, translocation, and metabolism by

505   microbes. TBECH that re-volatilizes from these reservoirs has an excess in one enantiomer, with different

506   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 EBFRs and other CECs as part of working towards proper screening and risk assessment.

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538 License (https://www.openstreetmap.org/copyright).

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7. Data availability

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

8. Author Contribution

544 FZ, YL, and JO prepared and extracted the passive air samplers (PASs) and the Toronto active air samples

545 (AAS). FZ and YL also took the Toronto AAS. YDL prepared standards and performed the instrumental

546 analysis on all samples. CS prepared and obtained samples from Saturna Island and Tadoussac as well as

547 the passive water samplers (PWSs) and performed the chiral analysis. KL and FAPCG deployed/retrieved

548 PASs and PWSs in BC. ABC, ADC, ZL, NA, HH, FZ and FW deployed/retrieved PASs and PWSs in Quebec.

549 provided guidance on sampling and sample analyses. JO compiled and interpreted data, with input from

550 FW. JO and FW wrote the manuscript with input by the other co-authors. HH coordinated the project.

9. Competing Interests

552 The authors have no competing interests to declare.

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