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) cyclo–hexane (TBECH) 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

40

41 Starting from the 1970s, brominated flame retardants (BFRs) have been used extensively in commercial

42 products to reduce ignition and increase their resistance to fire. To date, at least 75 different kinds of BFRs

43 have been commercially produced, with polybrominated diphenyl ethers (PBDEs) being historically the

44 most used class (Alaee et al., 2003). However, their toxicity, potential for bioaccumulation, and

45 persistence in the environment soon became apparent (Christensen et al., 2005; de Wit et al., 2006; Palm

46 et al., 2002; Ruan et al., 2019), and PBDEs, along with other traditional BFRs, were eventually classified as

47 persistent organic pollutants (POPs) (POPRC, 2009). As usage and production of these BFRs were restricted

48 internationally in 2009 under the United Nations Environment Programme Stockholm Convention on

49 POPs (UNEP-SC-POPs) (UNECE, 2018), emerging brominated flame retardants (EBFRs) entered into the

50 market (Betts, 2008), which are touted to be less persistent than their traditional BFR counterparts.

51 However, studies on their environmental behaviours have been limited.

52 1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH) is an EBFR that is widely used in plastics, fabric

53 adhesives, and building insulation materials (Alaee et al., 2003). TBECH exists as four diastereomers (α, β,

54 γ, and δ-TBECH). Furthermore, TBECH exhibits chirality and thus each diastereomer consists of a pair of

55 enantiomers. While commercial TBECH comprises mostly the α- and β-isomers, TBECH has been reported

56 to thermally isomerize to the γ and δ isomers when heated to 123 °C (Arsenault et al., 2008). Although

57 global production volumes or emissions of TBECH are difficult to establish, reports on its detection in the

58 environment have been increasing over the years, attributed to the rising demand for EBFRs (Bohlin et al.,

59 2014; Cequier et al., 2014; Drage et al., 2016; Genisoglu et al., 2019; Gentes et al., 2012; Newton et al.,

60 2015; Pasecnaja et al., 2021; Tao et al., 2017; Zacs et al., 2021). TBECH was first detected in sediment

61 samples collected in 1996 near a discharge pipe of the Frutarom plastics plant near Haifa, Israel (Santillo

62 et al., 1997). Since then, TBECH was found in various environmental media worldwide, such as biota and

63 water, with α- and β-TBECH being the dominant isomers. TBECH concentrations appear to be particularly

64 high in indoor settings, such as offices and residences (Melymuk et al., 2016; Newton et al., 2015; Wong

65 et al., 2018).

66 There is evidence that TBECH displays toxic effects at low concentrations both *in vitro* and *in vivo*. All

67 TBECH isomers have shown to be strong androgen agonists, where TBECH competitively binds to the

68 androgen receptor active site in varying degrees, first determined *in vitro* in human cell lines (Khalaf et

69 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.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

94   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

98   Networks of XAD-2 resin-based PASs (Wania et al., 2003) were installed in QC along the ca. 1000-km

99   stretch of the St. Lawrence River and Estuary between Montreal and the Gulf of St. Lawrence, as well as

100   in BC on the coast of the Central Salish Sea. PAS housings, containing two XAD-resin filled mesh cylinders

101   each, were deployed at a height of ca. 3 to 5 m above ground on trees or other structures at 118 unique

102   sites between 2019 and 2022. Because PASs were deployed at some sites more than once, there was a

103   total of 169 PASs. Maps of the networks are shown in Figure S1, while coordinates of the sampling sites,

104   dates of deployment and retrieval, and deployment duration are provided in Table S1 in the Supporting

105   Information. By revealing the spatial variability in the air concentration of TBECH and other BFRs across a

106   wide region, the networks can identify the location of emissions to the atmosphere. The networks

107   included sites in highly urbanized and industrialised area, but also rural and remote sites. Additional

108   details are provided in Text S1. After retrieval, the PASs were stored in metal shipping containers sealed

109   with Teflon tape coated stoppers at -20°C until analysis.

110   2.1.2 Active air sampling and precipitation collection

111   To quantify the seasonal variability in the air concentration of TBECH and other BFRs in an urban source

112   region, 48 consecutive week-long AASs were taken on the campus of the University of Toronto

113   Scarborough in the eastern suburbs of Toronto, Ontario between June 2020 and May 2021 (Li et al., 2023).

114   These measurements were complemented by 24-hour AAS taken once a month for one year at two

115   remote coastal sites far from large urban centres and therefore, less likely to be influenced by local

116   emission sources. These were on Saturna Island, BC (L43; ca. 42 km NNE of Victoria; pop. ~300; Dec. 2019

117   - Nov. 2020; n=11) and Tadoussac, QC (S57; ca. 190 km NE of Quebec City; pop. ~800; Dec. 2020 and Nov.

118   2021; n=12). Contaminants in the particle and gas phase were collected on a glass-fiber filter (GFF) and a

119   polyurethane foam (PUF)/XAD-2/PUF sandwich, respectively. The sampling periods are listed in Table S2.

120   At Saturna Island and Tadoussac, monthly-integrated wet deposition samples were taken during the same

121   twelve-month period as the AAS. Precipitation samples were collected for one month each in sample

122   bottles containing 0.2 L dichloromethane, which were connected to overflow bottles to capture any

123   overflowing precipitation from the sample bottles. The sampling periods are listed in Table S3.

124   2.1.3 Passive water sampling network

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

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

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

128   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 $EF_{standards}$ = 0.502 ± 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.

157 2.3 Air and water concentration calculations

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

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

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

161 (2010). Details are again in Text S5. For statistical purposes, the measurements below the LOD are

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

163 2.5 Partitioning properties calculations using COSMO-RS and other prediction tools

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

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

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

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

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

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

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

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

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

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

174 TBECH.

3. Results

176 3.1 Air concentrations

177 3.1.1 Absolute concentrations ranges, isomer composition, and comparison with previous

178 measurements

179 α- and β-TBECH and BDE-47 were the most consistently detected BFRs in air samples taken across Canada,

180 detected in 69%, 59%, and 80% of samples from the PAS network, respectively. Table 2 summarises the

181 results, whereas data for each individual sample are documented in Tables S1 and S2. To a lesser extent,

182 several other EBFRs and PBDE congeners were also detected in the samples of this study, with their

183 detection frequencies or concentrations summarized in Tables S4 to S8. Because of their much higher

184 detection frequencies, the remainder of the manuscript is focused on TBECH and BDE-47.

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

186 TBECH previously reported in the literature. The concentrations of TBECH recorded here are at the lower

187 end of the range of levels detected in urban outdoor air elsewhere. In particular, levels in Canadian urban

188 locations are similar to those reported for outdoor air in Stockholm, Sweden (Newton et al., 2015; Wong

189 et al., 2018), but somewhat lower than those measured in Birmingham, UK (Drage et al., 2016), Brno,

190 Czech Republic (Bohlin et al., 2014; Melymuk et al., 2016) and previous measurements taken in Toronto

191 (Shoeib et al., 2014). Much higher values had been reported for indoor air (Cequier et al., 2014; Genisoglu

192 et al., 2019; Melymuk et al., 2016; Newton et al., 2015; Newton et al., 2016; Tao et al., 2016; Wong et al.,

193 2018), an electronic waste facility in China (Hong et al., 2018) and - somewhat incongruously - in

194 Longyearbyen, Svalbard (Carlsson et al., 2018). PAS deployed in remote regions (pop. <10 000 in a 20-km

195 radius) tended to have levels of TBECH below the LOD or LOQ. The levels above LOD measured in non-

196 urban locations in this study are among the lowest ever reported, comparable to what has been reported

197 for Tibet and Antarctica (Ma et al., 2017; Zhao et al., 2020). However, previous measurements of TBECH

198 in air from non-urban locations are rare. Overall, the alignment of the air concentration data with those

199 reported previously supports the validity of the results of this study.

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

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

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

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

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

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

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

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

208 3.1.2 Spatial variability of air concentrations in Canadian coastal regions

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

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

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

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

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

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

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

216   (Table S13).

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

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

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

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

221   10 kilometres away from Quebec City, QC (S26). However, because the air concentrations of both isomers

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

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

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

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

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

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

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

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

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

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

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

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

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

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

236   (<10°C, 10-15°C, >15°C; Figure S5). Weaker or absent relationships at the warmest temperature (>15°C)

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

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

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

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

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

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

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

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

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

Table 1   Equilibrium partition ratios 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}	
		0°C	25°C	0°C	25°C	0°C	25°C
COSMOtherm	**α-TBECH**	4.49	4.45	-4.67	-3.82	8.93	8.36
	β-TBECH	4.39	4.35	-4.92	-4.07	9.08	8.51
EAS-E Suite	**TBECH**	5.70	5.43 ± 0.52	-4.41	-3.34 ± 0.36	10.14	8.80 ± 0.81
EPI Suite			5.24		-2.77		8.00
OPERA			5.24 ± 0.03		-3.72 ± 1.20		8.42 ± 0.13

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

254
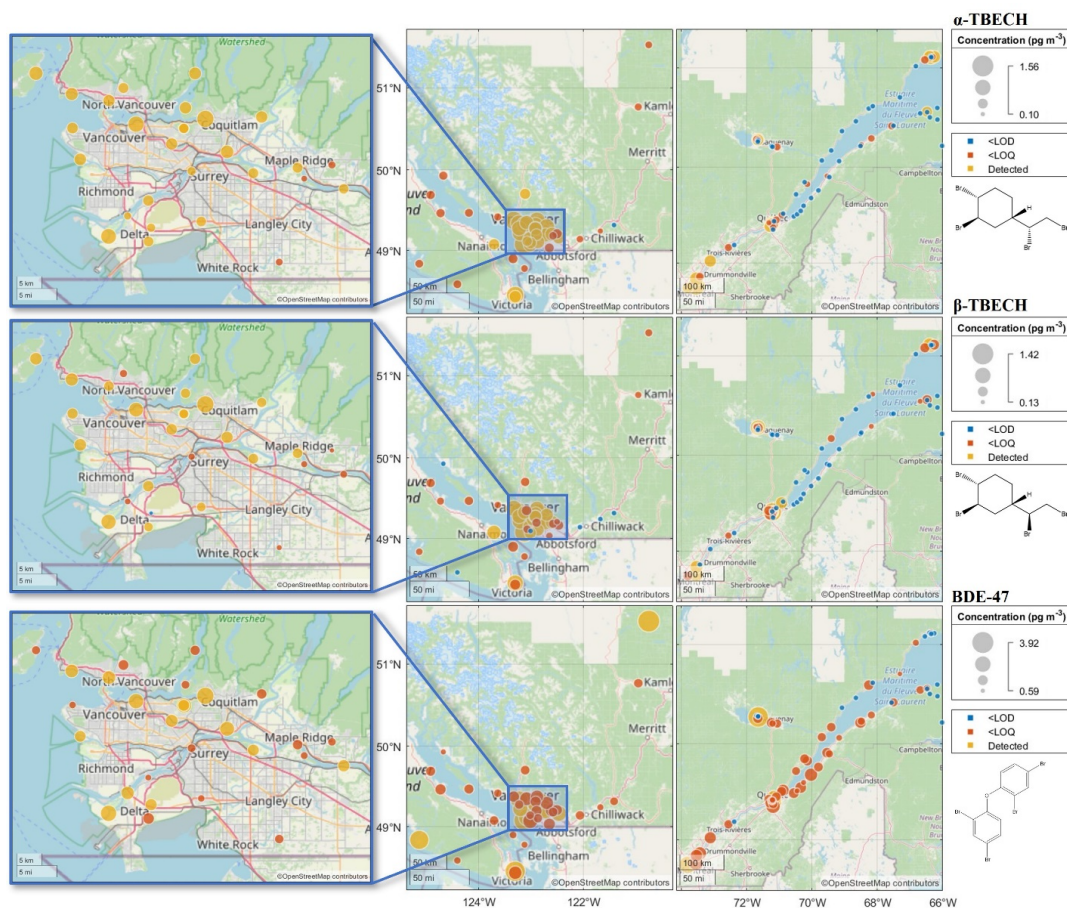
Fig. 1 The spatial distribution of the air concentrations of α-TBECH (top), β-TBECH (middle), and BDE-47 (bottom) in British Columbia and Quebec. Close-up maps (left) provide a detailed view of the Vancouver metropolitan area. Average air concentrations are displayed for sites with replicate deployments; 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.

263 3.1.3 Seasonal variability of air concentrations in urban and remote regions of Canada

264 *Seasonal variability in Toronto*

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

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

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

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

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

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

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

272   rates of emission.
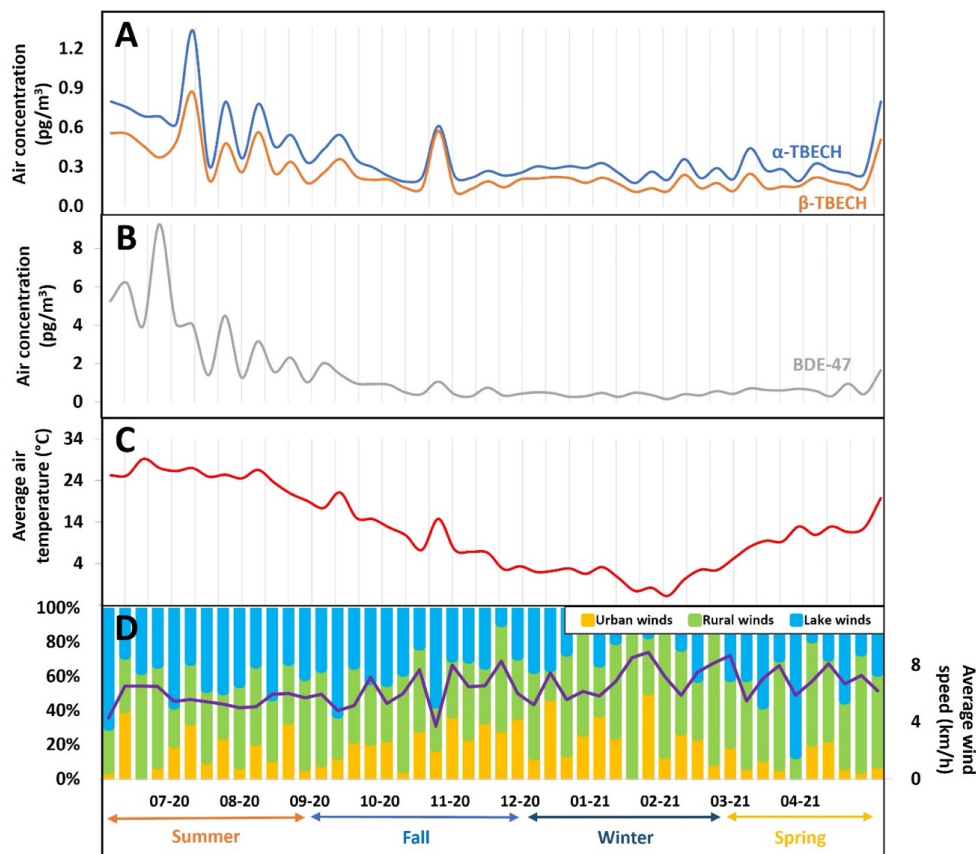
273

274   Fig. 2   The air concentration of α-TBECH, β-TBECH, and BDE-47 and meteorological parameters in
275   Toronto, Ontario during 48 weekly active air sampling periods between June 2020 and May
276   2021.

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

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

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

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

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

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

12

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

284 (Table S17).

285 *Seasonal variability in Saturna Island and in Tadoussac*

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

306 3.2 Concentrations in passive water samples

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

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

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

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

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

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

313   TBECH, albeit on the same order of magnitude.

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

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

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

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

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

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

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

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

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

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

324   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,

325   giving credence to this theory.

326   3.3 Concentrations in precipitation samples

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

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

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

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

331   and did not fluctuate as strongly as TBECH.

332   3.4 Enantiomeric fractions of α-TBECH

333   The results of the chiral analysis are presented using enantiomeric fractions (EFs). A racemate with equal

334   amounts of the (+) and (-) enantiomers has an EF of 0.50. EFs that are significantly above or below 0.5

335   indicate the occurrence of enantioselective processes, typically biological pathways relying on enzymes

336   or enantioselective membranes. The α-TBECH standard had an EF = 0.502± 0.001. The EFs of α-TBECH in

337   the PAS extracts had values that were significantly above and below this value, ranging from 0.32 at L2 to

338   0.66 at L6 (Table S18). While PAS extracts from non-urban sites rarely had sufficient amounts of α-TBECH

339   for reliable chiral analysis, samples from a few coastal sites on the St. Lawrence Estuary and in the

340   Saguenay area in QC and on Vancouver Island in BC had EFs below 0.50 (Figure 3). Conversely, samples

341   from populated urban sites in Quebec City and Vancouver generally had EF greater than 0.50. Several sites

342   in the Vancouver area and in Victoria with EF < 0.50 are located on the shore of Burrard Inlet/Vancouver

343   Harbour and Oak Bay, respectively.
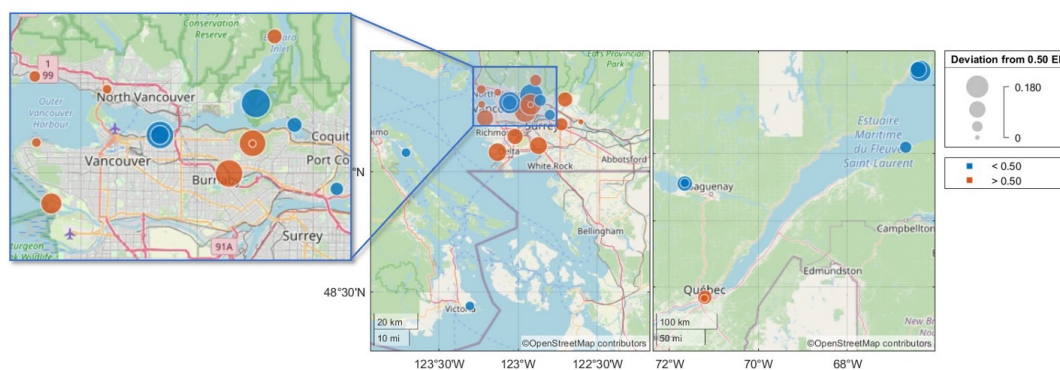
344

345   Fig. 3   The spatial distribution of the enantiomeric fraction (EF) of α-TBECH in selected BC and QC PAS.
346   The absolute deviation from 0.50 (i.e., racemic mixture) of each site is plotted on the map, with
347   values further from 0.00 indicating higher enantiomeric excess of one enantiomer. Sites with EF
348   < 0.50 and EF > 0.50 are marked in blue and red, respectively.

349   Consistent with the PAS from urban deployments in BC and QC generally having EFs > 0.5, the EFs in the

350   AAS from Toronto were also mostly above 0.502 ± 0.001 (only one out of 36 samples had an EF<0.502)

351   (Table S19). While there was no clear seasonal trend in the EF, α-TBECH tended to be close to racemic in

352   summertime air (Figure S14, Table S20; R^2=0.14, p=0.023). Conversely, the EFs of α-TBECH in the PWS

353   extracts (Table S21) were below 0.5, agreeing with the EF spatial trends observed in the PAS network.

354   Despite its urban origin, the TBECH in Canada has clearly experienced enantioselective processing, i.e.,

355   has evaporated from reservoirs where it has undergone microbial transformations. This is in agreement

356   with the observed enantiomeric excess for α-TBECH in soil experiments, with increasing excess seen after

357   prolonged degradation (Wong et al., 2012). The consistent EF < 0.5 observed in water and marine air

358   samples also suggests that at least some of the TBECH in the atmosphere evaporated from seawater.

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

360   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-

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

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

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

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

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

396   and the temperature. Other potential reasons include that adsorption occurs at the water-air interface

397   (Hoff et al., 1993), or that the BFRs experience sorption to dissolved organic matter and other sorption

398   phases (Poster & Baker, 1996), all which could lead to higher scavenging ratios. However, information on

399   interface adsorption coefficients of the BFRs and other sorption phases at Saturna Island and Tadoussac

400   is limited.

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

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

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

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

405   medium than rain (Lei & Wania, 2004; Paramonov et al., 2011). The logarithm of the inverse scavenging

406   ratio, -ln(SR) (i.e., ln(1/SR)), was regressed with the reciprocal of the average air temperature. Whereas

407   the scavenging ratios of TBECH did not significantly correlate with temperature (Table S22), the

408   scavenging of BDE-47 at both sites increased with decreasing temperature (Figure S19).

409   4.2 Do the two TBECH isomer show divergent atmospheric fate?

410   In this study, the relative abundance of α- and β-TBECH was very consistent, with mean α-/β-TBECH ratio

411   generally ranging from 1.1 to 1.6, i.e., indicating a slightly higher abundance of the α-isomer relative to

412   the β-isomer. In particular, this ratio was very similar in different parts of the country, with median α-/β-

413   TBECH in active air samples with concentrations of both isomers above the LOD being 1.56 (range 1.07 to

414   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.

415   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

416   0.51 to 3.20). This slightly higher abundance of the α-isomer relative to the β-isomer is consistent with

417   earlier reports of TBECH elsewhere in the atmosphere (Table S13).

418   The relative abundance of the two isomers is also generally very similar in different environmental media.

419   The mean α-/β-TBECH ratio in AAS (QC mean = 1.95; BC mean = 1.62; ON mean = 1.56) and PAS (QC mean

420   = 1.03; BC mean =1.21) bracket the values recorded in the PWS (BC mean = 1.52) and precipitation (QC

421 mean = 1.21; BC mean=1.22) (Figure 4). Moreover, isomer abundance was very similar in different samples

422 of the same type. The two isomers exhibited nearly identical spatial patterns in air (Figure S3) and water

423 (Figure S11). The seasonal patterns in air (Figure 2, Figure S8, Figure S9) and in precipitation (Figure S13)

424 were also highly consistent for α- and β-TBECH. Not surprisingly, α- and β-TBECH had similar water-air

425 equilibrium status in the Salish Sea (Figure S15) and essentially identical scavenging ratios (Figure S16).
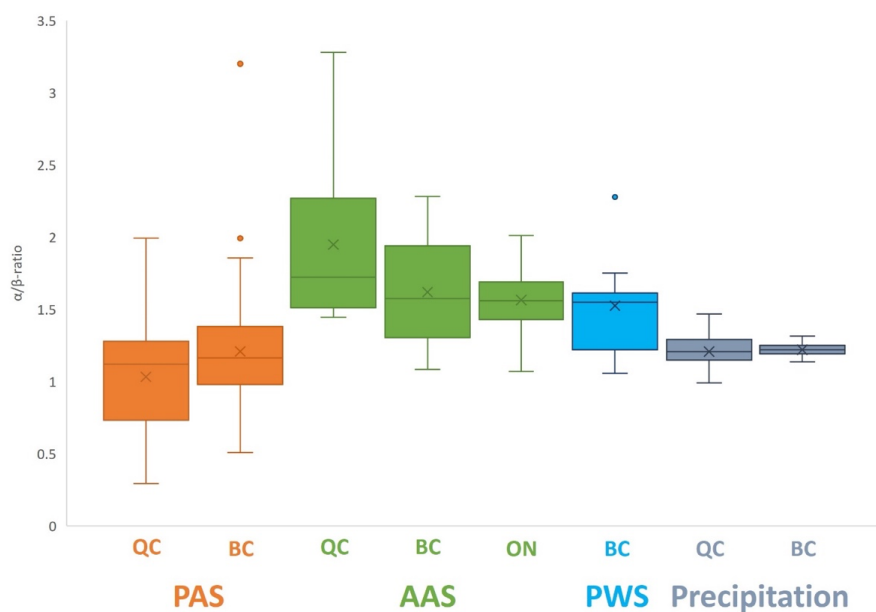
426

427 Fig. 4 Comparison of the α-/β-TBECH ratio calculated in the sampling regions of this study, grouped in

428   different environmental media/sampling methods. The mean α-/β-TBECH ratio is indicated with

429   an "x" for each method. For statistical analysis, outliers (α/β > 2.0) were included but are explicitly

430   marked on the plot as dots. Only measurements with both isomers above the LOD were used in

431   this plot.

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

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

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

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

436 apparent in divergent atmospheric behaviour.

4.3 Sources of TBECH to the Canadian atmosphere

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

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

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

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

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

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

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

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

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

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

448 or import commercial TBECH. However, several recent international patents have included commercial

449 TBECH as one of the flame retardants used mostly in electronics (Geng et al., 2018; Ke & Lv, 2020), pointing

450 to the possibility that TBECH enters Canada almost exclusively as part of imported products. It is likely

451 that most, if not all the TBECH detected in this study originate from the gradual release from these

452 imported products. Populated urban areas, with typically greater overall usage of products containing

453 flame retardants, e.g., electronics and plastics, have consistently shown higher TBECH levels with more

454 pronounced temperature dependence compared to remote regions, and therefore suggest greater

455 leakage. This is also consistent with previous studies reporting higher TBECH levels in indoor air, compared

456 to outdoor (Table S13).

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

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

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

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

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

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

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

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

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

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

467 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.

6. Acknowledgements

7. Data availability

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

8. Author Contribution

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

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

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

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

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

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

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

9. Competing Interests

511   The authors have no competing interests to declare.

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