

# Elevated Concentrations of 4-Bromobiphenyl and 1,3,5-Tribromobenzene Found in Deep Water of Lake Geneva Based on GC×GC-ENCI-TOFMS and GC×GC-μECD

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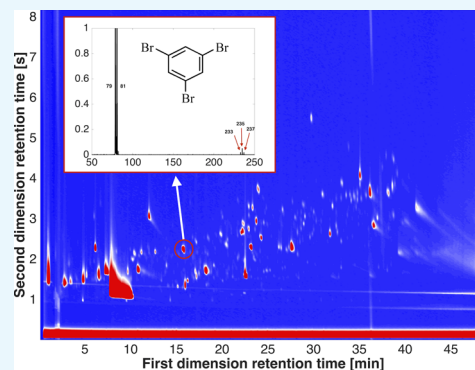
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## S Supporting Information

**ABSTRACT:** We quantified the concentrations of two little-studied brominated pollutants, 1,3,5-tribromobenzene (TBB) and 4-bromobiphenyl (4BBP), in the deep water column and sediments of Lake Geneva. We found aqueous concentrations of  $625 \pm 68 \text{ pg L}^{-1}$  for TBB and  $668 \pm 86 \text{ pg L}^{-1}$  for 4BBP over a depth range of 70–191.5 m (near-bottom depth), based on duplicate measurements taken at five depths during three separate 1 month sampling periods at our sampling site near Vidy Bay. These levels of TBB and 4BBP were 1 or 2 orders of magnitude higher than the quantified aqueous concentrations of the components of the pentabrominated biphenyl ether technical mixture, which is a flame retardant product that had a high production volume in Europe before 2001. We observed statistically significant vertical concentration trends for both TBB and 2,2',4,4',6-pentabromobiphenyl ether in the deep water column, which indicates that transport and/or degradation processes affect these compounds. These measurements were enabled by application of a comprehensive two-dimensional gas chromatograph coupled to an electron capture negative chemical ionization time-of-flight mass spectrometer (GC×GC-ENCI-TOFMS) and to a micro-electron capture detector (GC×GC-μECD). GC×GC-ENCI-TOFMS and GC×GC-μECD were found to be >10× more sensitive toward brominated pollutants than conventional GC×GC-EI-TOFMS (with an electron impact (EI) ionization source), the latter of which had insufficient sensitivity to detect these emerging brominated pollutants in the analyzed samples. GC×GC also enabled the estimation of several environmentally relevant partitioning properties of TBB and 4BBP, further confirming previous evidence that these pollutants are bioaccumulative and have long-range transport potential.



## INTRODUCTION

Many brominated organic pollutants have been found to persist in the environment,<sup>1–6</sup> bioaccumulate,<sup>2,3</sup> and pose a risk to human health and ecosystems through their toxicity.<sup>2,3,7</sup> Most of these compounds are brominated flame retardants (BFRs)<sup>3,8</sup> or industrial chemicals<sup>5,9</sup> having wide commercial use.<sup>4,5</sup> These brominated persistent and bioaccumulative pollutants (Br-PBPs) may occur in surface water systems as a result of inputs from urban wastewater and runoff, atmospheric deposition, and associated long-range transport.<sup>10–17</sup> For example, polybrominated biphenyls (PBBs) and/or polybrominated diphenyl ethers (PBDEs) have been found in the precipitation and lake water of the Great Lakes, in biota of the Baltic Sea and North Sea, in surface waters of the Arctic, and in lake sediments in Europe.<sup>10–18</sup> Many of the PBBs and PBDEs have been widely studied for their environmental fate and behavior.<sup>3,19</sup>

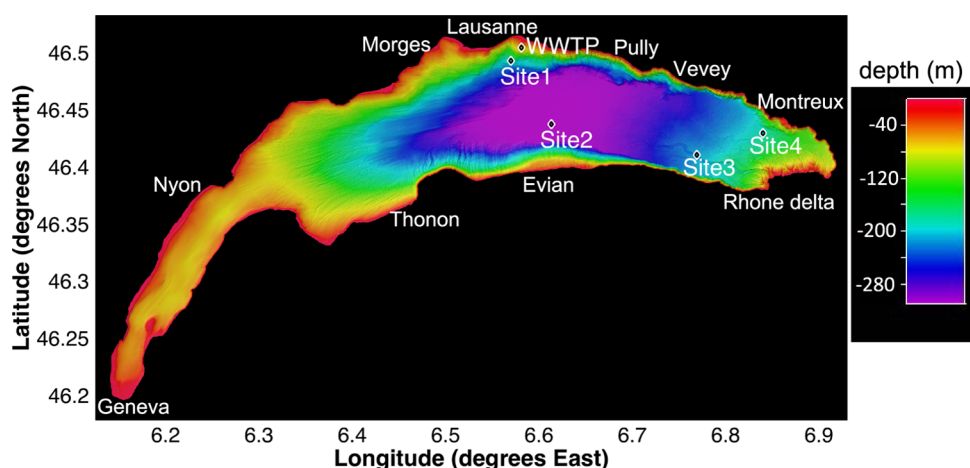
The production and sale of the most commonly used PBBs (e.g., Firemaster technical mixture) in the United States was stopped in 1974,<sup>7</sup> and production in Europe was discontinued after 2000.<sup>13</sup> Global restrictions have also been placed on the production and use of PBDEs, employed as flame retardants (e.g., the pentabrominated diphenyl ether (pentaBDE) technical mixture).<sup>20</sup>

However, other potential Br-PBPs are currently produced that have undergone little scrutiny for their environmental impact. These include so-called novel BFRs (NBFRs), which came to be used as replacements for the discontinued PBDEs and PBBs.<sup>21</sup> Howard and Muir recently identified 80 Br-PBPs

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**Figure 1.** Map depicting the four sediment sampling locations (Sites 1–4), the location where passive samplers were deployed in the water column (Site 1), and the outfall of Lausanne’s wastewater treatment plant (WWTP; 30 m depth). The locations of major communities bordering the lake are also labeled.

of diverse origins that have annual global production volumes of  $>1 \text{ t year}^{-1}$  and were considered as potentially bioaccumulative and persistent in the environment.<sup>4</sup> Among the 80 Br-PBPs, 65 were neither legacy pollutants nor well monitored.<sup>4</sup> Hereafter, we refer to these as emerging or novel Br-PBPs.

Despite their importance, Br-PBPs are difficult to measure in environmental samples due to the complexity of the analyzed matrices and trace concentration levels of these compounds.<sup>12–14,18,22–27</sup> Measurement of Br-PBPs by conventional gas chromatography–mass spectrometry (GC–MS) typically requires intensive cleanup and fractionation of the environmental sample, which alters the sample and may compromise the ability to detect and quantify some brominated pollutants.<sup>28</sup> By comparison, the chromatographic resolution provided by comprehensive two-dimensional gas chromatography (GC×GC) mitigates the problem of sample complexity and can avert the need for intensive sample cleanup steps. GC×GC has been shown to be an effective analytical tool for separation of Br-PBPs in complex samples.<sup>27–33</sup>

The choice of instrument detector is an important consideration for the identification and quantification of Br-PBPs. Mass spectrometry with electron capture negative chemical ionization (ENCI; also called ECNI or NCI) in single-ion mode (SIM) is a common detection strategy for analysis of Br-PBPs in environmental samples, due to the high sensitivity of ENCI toward halogenated chemicals.<sup>28,34–38</sup> However, this detection method can be affected by matrix<sup>36,39</sup> and provides less confident analyte identification than that by electron impact (EI) ionization with the full scan mode. Therefore, a high degree of chromatographic resolution is needed to ensure confident identification and quantification of Br-PBPs in complex samples when employing GC–ENCI-MS with SIM (e.g., as reviewed by Papachlitzou et al.<sup>28</sup>). EI ionization in the full scan mode provides a higher selectivity compared to that of ENCI with an SIM, while having a lower sensitivity for Br-PBPs.<sup>28,40</sup> Therefore, sample preparation and cleanup become crucial steps during the analysis of Br-PBPs in environmental samples when using GC–EI-MS in the full scan mode.

In two recent studies, we developed and validated a highly sensitive analytical method for the detection and quantification of trace-level halogenated hydrocarbons in environmental

samples, with limited cleanup.<sup>29,30</sup> This method employs a comprehensive two-dimensional gas chromatograph coupled to two detectors that are both highly sensitive for halogenated analytes: an electron capture negative chemical ionization time-of-flight mass spectrometer (GC×GC-ENCI-TOFMS) in the full scan mode and a micro-electron capture detector (GC×GC- $\mu$ ECD). By employing limited sample cleanup, we could conduct an analysis that broadly encompasses several families of nonpolar halogenated analytes. This approach previously enabled us to successfully detect and quantify picogram/liter levels of chlorinated hydrocarbons in aquatic samples.<sup>29</sup> In comparison, low-resolution GC×GC-TOFMS with a conventional EI ion source in full scan mode has a poorer sensitivity toward both chlorinated and brominated hydrocarbons.<sup>28,31,32</sup>

In the present study, we apply GC×GC-ENCI-TOFMS and GC×GC- $\mu$ ECD for the detection and quantification of a suite of Br-PBPs in samples from both the water column and sediments of Lake Geneva. These chemical analysis results are compared to those obtained by GC×GC-EI-TOFMS with a conventional EI source. The analyzed Br-PBPs include four emerging brominated pollutants that have received little attention: 1,3,5-tribromobenzene (TBB), 4-bromobiphenyl (4BBP), hexabromobenzene (HBB), and pentabromoethylbenzene (PBEB), as well as the five components of the legacy pentaBDE technical mixture (see [Selection of Target Analytes](#)). We report on the concentrations of these Br-PBPs in the deep water column and sediments at selected locations of Lake Geneva. Finally, we employ GC×GC to estimate several environmentally relevant partitioning properties for these emerging Br-PBPs.

## RESULTS AND DISCUSSION

**Comparison of GC×GC- $\mu$ ECD, GC×GC-ENCI-TOFMS, and GC×GC-EI-TOFMS for Analysis of Br-PBPs in Sediment Extracts.** Two sediment samples collected at Sites 1 and 2 (Figure 1) were used to compare analyses results by GC×GC- $\mu$ ECD, GC×GC-ENCI-TOFMS, and GC×GC-EI-TOFMS. These two sampling sites were both considered likely to have elevated levels of other persistent pollutants (i.e., chlorinated hydrocarbons and polycyclic aromatic hydrocarbons), on the basis of previous reports.<sup>41,42</sup>

**Table 1. GC×GC Retention Times and Monitored Unit  $m/z$  Values for Detection by ENCI-TOFMS and EI-TOFMS (Section S6 of the Supporting Information), and the Frequency of Positive Detection of the Target Br-PBPs in Sediment Samples by GC×GC- $\mu$ ECD, GC×GC-ENCI-TOFMS, and GC×GC-EI-TOFMS**

	acronym	compound	$t_{r,i}^d$ (min)	$t_p^e$ (s)	molecular weight ( $M_w$ )	mass spectra <sup>c</sup>						LOD <sub>1</sub> (pg mL <sup>-1</sup> ) <sup>a</sup>						frequency of positive detection <sup>b</sup>			
						$(m/z)_1$	$(m/z)_2$	$(m/z)_3$	$(m/z)_4$	GC×GC $\mu$ ECD	GC×GC ENCI-TOFMS	GC×GC EI-TOFMS	GC×GC $\mu$ ECD	GC×GC ENCI-TOFMS	GC×GC EI-TOFMS	GC×GC $\mu$ ECD	GC×GC ENCI-TOFMS	GC×GC EI-TOFMS	GC×GC $\mu$ ECD	GC×GC ENCI-TOFMS	GC×GC EI-TOFMS
less studied target analytes	TBB	1,3,5-tribromobenzene	14.47	2.78	314.7999	79	233	235		1.4	2.1	67.8	0/2	0/2	0/2	0/2	0/2	0/2			
	4BBP	4-bromobiphenyl	20.37	3.54	233.1039	79	233	235		1.4	2.2	48.2	2/2	2/2	2/2	2/2	2/2	0/2			
in use NBFs	PBEB	2,3,4,5,6-pentabromoethylbenzene	32.53	4.55	500.6453	79 <sup>68</sup>	500 <sup>8</sup>	502 <sup>8</sup>		1.3	1.9	57.4	2/2	2/2	2/2	2/2	0/2	0/2			
	HBB	hexabromobenzene	36.93	5.42	551.4882	79	233	235	315	1.1	1.7	66.6	0/2	0/2	0/2	0/2	0/2	0/2			
legacy target analytes	BDE47	2,2',4,4'-tetrabromodiphenyl ether	38.13	4.68	485.7914	79	366	368	370	1.3	1.9	66.8	2/2	2/2	2/2	2/2	0/2	0/2			
	BDE99	2,2',4,4',5-pentabromodiphenyl ether	42.93	5.10	564.6875	79	159	161	163	1.2	1.8	69.5	2/2	2/2	2/2	2/2	0/2	0/2			
	BDE100	2,2',4,4',6-pentabromodiphenyl ether	41.87	4.86	564.6875	79	159	161	163	1.2	1.7	68.7	0/2	0/2	0/2	0/2	0/2	0/2			
	BDE153	2,2',4,4',5,5'-hexabromodiphenyl ether	47.17	5.22	643.5836	79	159	161	163	1.2	1.9	70.0	2/2	2/2	2/2	2/2	0/2	0/2			
	HBBP	2,2',4,4',5,5'-hexabromobiphenyl	46.25	5.30	627.5843	79 <sup>68</sup>	627 <sup>8</sup>	629 <sup>8</sup>		1.3	1.8	69.8	0/2	0/2	0/2	0/2	0/2	0/2			

<sup>a</sup>Instrument limit of detection, LOD<sub>1</sub> (pg mL<sup>-1</sup>), of the standard mixture solution, eq. 3 in Section S7 of the Supporting Information. <sup>b</sup>Frequency of positive detection of the target analytes in the sediment samples collected at Sites 1 and 2 (see Figure 1). <sup>c</sup>Mass spectrum  $m/z$  values shown are from the present study, unless indicated otherwise. <sup>d</sup>First dimension GC×GC retention time. <sup>e</sup>Second dimension GC×GC retention time. <sup>f</sup>Kolic et al.<sup>43</sup> <sup>g</sup>Hoffmann.<sup>44</sup>

Table 2. Concentrations of the Quantified Br-PBPs in the Sediment Samples<sup>a</sup>

target analyte	concentration in the sediments of Lake Geneva (pg g <sup>-1</sup> ) <sup>b</sup>				literature values for other sediments (pg g <sup>-1</sup> )
	Site 1	Site 2	Site 3	Site 4	
4BBP	60	1.9 × 10 <sup>2</sup>	<4.0 <sup>c</sup>	<4.0 <sup>c</sup>	nd–40.0 <sup>d</sup>
PBEB	4.5	14	<4.0 <sup>c</sup>	<4.0 <sup>c</sup>	nd–32.0 <sup>e</sup> , nd–10.0 <sup>f</sup> , and nd–100 <sup>g</sup>
BDE99	66	90	<4.0 <sup>c</sup>	16	nd–10 000 <sup>f,g</sup> and 200–1600 <sup>h</sup>
BDE153	27	33	<4.0 <sup>c</sup>	5.2	nd–17 000 <sup>f</sup>

<sup>a</sup>TBB, HBB, BDE100, and HBBP were not detected in any of the sediment samples, whereas BDE47 was detected but not quantified. <sup>b</sup>The concentration is expressed per dry weight of the sediment sample. <sup>c</sup>The pollutant was detected in the sample; however, its concentration was lower than the sediment LOQ of 4.0 pg g<sup>-1</sup>. <sup>d</sup>Sediment samples of 14 rivers from Hai River Basin, China. <sup>e</sup>Sediment samples from Loselva River, Norway. <sup>f</sup>Sediment samples from Llobregat River, Spain. <sup>g</sup>Sediment samples from San Francisco Bay. <sup>h</sup>Sediment samples from Lake Thun, Switzerland. <sup>15–17</sup>

GC×GC-μECD and GC×GC-ENCI-TOFMS both successfully detected five of nine target Br-PBPs (4BBP, PBEB, 2,2',4,4'-tetrabromodiphenyl ether (BDE47), 2,2',4,4',5-pentabromodiphenyl ether (BDE99), and BDE153) in the extracts of the two sediments collected from Sites 1 and 2 (Table 1). Moreover, GC×GC-μECD and GC×GC-ENCI-TOFMS exhibited 100% agreement in both positive detections (indicating the presence) and negative detections (indicating the absence) of the nine analyzed Br-PBPs in both sediment samples (Table 1). In comparison, GC×GC-EI-TOFMS did not detect any of the nine target Br-PBPs in the same two samples. For both GC×GC-EI-TOFMS and GC×GC-ENCI-TOFMS, a target analyte was considered successfully detected in the sediment extracts if it met five criteria.<sup>29</sup> These were as follows: positive matches between the standard peak and sample analyte peak for retention times in both the first and second dimensions and positive matches between the standard peak and target peak for three *m/z* values, within a tolerance level of 5 mmu (Table S5). The lack of detection of any of the target analytes in the sediment extracts analyzed by GC×GC-EI-TOFMS was attributed to the lower sensitivity of EI-TOFMS for Br-PBPs. For GC×GC-μECD, an analyte was considered detected if there was a positive match of the retention times in first and second dimensions between the standard peak and suspect peak in the sample.<sup>29</sup>

Further confirming the above results, GC×GC-μECD and GC×GC-ENCI-TOFMS were both found to be more sensitive than GC×GC-EI-TOFMS by more than an order of magnitude for Br-PBPs (Section S7). GC×GC-μECD produced LOD<sub>i</sub> values that were 34–61 times lower than those achieved by GC×GC-EI-TOFMS for the nine Br-PBP analytes (Table 1). Similarly, GC×GC-ENCI-TOFMS gave LOD<sub>i</sub> values 22–40 times lower than those achieved by GC×GC-EI-TOFMS. The excellent sensitivity of GC×GC-μECD and GC×GC-ENCI-TOFMS for Br-PBPs thus enabled confident detection of several brominated analytes in sediment samples. This was not possible by GC×GC-EI-TOFMS with the sample preparation protocols employed here.

Finally, we employed GC×GC-μECD and GC×GC-ENCI-TOFMS for analysis of three passive sampler extracts deployed near the bed of the lake (191.5 m depth) during June, July, and August, 2011. Using the detection criteria discussed above, we successfully detected eight of nine target analytes in the water column of the lake. We observed 100% agreement between GC×GC-μECD and GC×GC-ENCI-TOFMS for both positive detections and negative detections for all individual Br-PBPs in all three analyzed passive sampler extracts (Table S5). As was found with sediment extracts (above), this procedure confirmed our ability to confidently detect Br-PBPs in the water column.

### Quantification of Br-PBPs in the Sediments and Water Column.

GC×GC-μECD has been employed previously for quantification of trace-level halogenated pollutants in complex environmental samples.<sup>29,30,33,40,45</sup> However, recent studies have revealed the importance of applying appropriate data processing to the GC×GC chromatogram prior to analyte quantification.<sup>29,46</sup> Therefore, all chromatograms were baseline-corrected with Eilers baseline,<sup>47,48</sup> using a freely available code<sup>49</sup> implemented in Matlab.<sup>50</sup> The three unitless algorithm parameters, *λ*, *p*, and *d*, were set to 10<sup>4</sup>, 0.02, and 2, respectively. The Eilers baseline is effective for eliminating poorly resolved background signals in complex samples analyzed by GC×GC.<sup>29,46</sup> After baseline correction, the analyte peaks were integrated with the inverted watershed algorithm implemented in GC Image software<sup>48</sup> (Table S4). This combination of baseline-correction and peak-integration algorithms was recently shown to give good performance for analyte quantification by GC×GC-μECD.<sup>29</sup> We used external standard calibration at five concentration levels, with three replicates at each level, for the quantification of the target analytes in the environmental samples.<sup>29</sup>

Using this approach, we successfully quantified up to four of nine target Br-PBPs in the four sediment extracts and up to seven of nine target Br-PBPs in the thirty passive samplers that had been deployed in the water column with GC×GC-μECD (Figure S2 and Tables 2 and S7). A target analyte was considered quantifiable if its integrated GC×GC-μECD signal in the environmental sample was more than three times the sum of the target analyte signal in the blanks. The effective limit of quantification (LOQ<sub>e</sub>) values were 3.5–4.0 pg g<sup>-1</sup> for sediment samples and 1.0–50 pg L<sup>-1</sup> for water column extracts, depending on the analyte (Table S5). The achieved LOQ<sub>e</sub> values in the present study were nearly 30× lower than the reported LOQ<sub>e</sub> values for conventional GC-MS with SIM.<sup>28</sup> Exceptionally, due to the apparent blank contamination (for water column extracts) and matrix effect (for sediment samples), we report BDE47 as nonquantified; see Section S8 of the Supporting Information for further explanation.

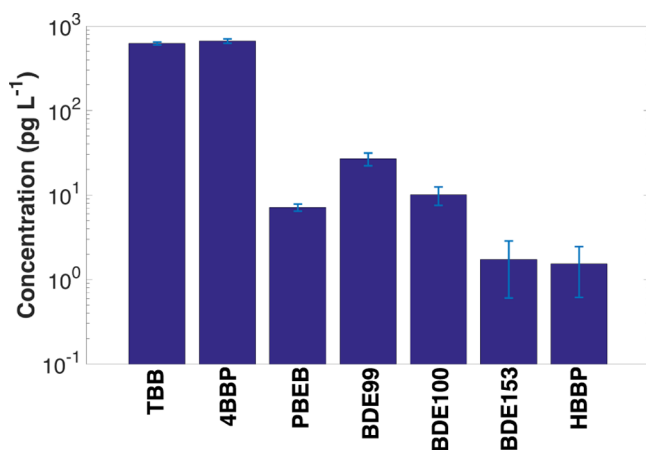
### Occurrence of Target Br-PBPs in Lake Geneva Sediments.

On the basis of analyte quantifications by GC×GC-μECD, the concentrations of 4BBP, PBEB, BDE99, and BDE153 in the sediment samples collected from the deep lake (Site 2) and near the urbanized area of Lausanne (Site 1) were elevated compared to the Br-PBP levels in samples collected from near the Rhône River delta (Sites 3 and 4), as shown in Table 2. The observed concentration distributions at these four sampling sites suggest that the Rhône River is not the principal input of these pollutants into Lake Geneva, as the Rhône is the major tributary that flows over Sites 3 and 4.



However, the observed concentration differences in the four analyzed locations may be confounded by the different sedimentation rates at these sites, and the results of the statistically small number of samples reported here should not be overinterpreted. The highest measured 4BBP concentration in the Lake Geneva sediment samples ( $187.0 \text{ pg g}^{-1}$ ) exceeded the highest 4BBP concentration reported in the River Daqing sediment samples in China ( $40 \text{ pg g}^{-1}$ ). For BDE99, we observed sediment concentrations in Lake Geneva samples ( $15.5\text{--}89.6 \text{ pg g}^{-1}$ ) to be lower than those in samples from some US, Canadian, and other European lakes and rivers (Table 2).<sup>15–17,51,52</sup> For BDE153, we observed sediment levels that were 3 orders of magnitude lower than those reported in Llobregat River, Spain ( $17\,000 \text{ pg g}^{-1}$ , Table 2).

**Concentrations and Trends of Target Br-PBPs in the Deep Water Column of Lake Geneva.** At Site 1, both TBB and 4BBP were found to have aqueous concentrations exceeding  $600 \text{ pg L}^{-1}$  in the deep water column ( $>70 \text{ m}$  depth), which is 1 or 2 orders of magnitude higher than the aqueous concentrations of the analyzed legacy pentaBDEs (Figure 2 and Table S7). The depth-averaged concentration of



**Figure 2.** Average measured aqueous concentrations ( $C_{\text{aq}}$  ( $\text{pg L}^{-1}$ )) of the target Br-PBPs at Site 1 (Figure 1). The error bars show the concentration variability ( $\pm 2$  standard deviations) over thirty water column samples taken at five different depths during three sampling periods (June, July, and August, 2011).

TBB was  $668 \pm 86 \text{ pg L}^{-1}$ , and the depth-averaged concentration of 4BBP was  $625 \pm 68 \text{ pg L}^{-1}$ , on the basis of measurements during three separate 1 month sampling periods (Figure 2). For PBEB, the concentration was  $7 \pm 1.8 \text{ pg L}^{-1}$ , and HBBP was not detected ( $\text{LOD}_e = 30 \text{ pg L}^{-1}$ ). By comparison, the measured aqueous concentrations of the pentaBDEs ranged from  $2 \pm 0.8 \text{ pg L}^{-1}$  (HBBP) to  $27 \pm 7 \text{ pg L}^{-1}$  (BDE99). These aqueous concentrations of pentaBDEs are comparable to those reported in the waters of all five Great Lakes<sup>10,55</sup> and in some rivers and lakes in Europe, including Lakes Thun and Greifensee in Switzerland.<sup>14,16</sup> Much higher aqueous concentrations of pentaBDE compounds have been reported in waters of Niuchao Lake, China ( $4020 \text{ pg L}^{-1}$  in winter and  $520 \text{ pg L}^{-1}$  in summer).<sup>56</sup>

We observed statistically significant vertical trends in the aqueous concentrations of both TBB and BDE100 over the sampled depth range of 70–191.5 m at Site 1 (Figure 3), on the basis of a linear regression of depth versus concentration for each Br-PBP. A vertical concentration trend was considered to

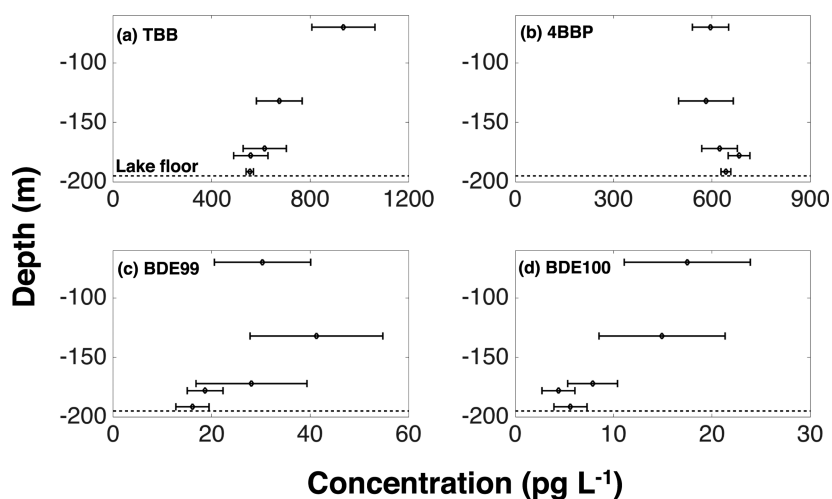
be present if the 95% confidence interval<sup>57</sup> of the regression slope parameter was found to not span zero. The remaining detected Br-PBPs, 4BBP, PBEB, and BDE99, did not exhibit a discernible trend at Site 1, on the basis of this criterion (Figures 3 and S3). Additionally, results from a nonparametric Kruskal–Wallis test<sup>58</sup> indicated that the concentration distributions of TBB, 4BBP, PBEB, BDE99, and BDE100 did not change significantly over the 3 month period of June, July, and August, 2011. The temporal stability of the water concentrations further supports the conclusion that the vertical concentration trends are statistically meaningful.

Spatial trends in contaminant concentrations are physically meaningful because they express processes that transport and/or degrade pollutants in the lake system. For example, the observed trends of decreasing concentrations of TBB and BDE100 with increasing depth may result from the active removal of these compounds by biodegradation in the anaerobic sediments at the lake floor. This interpretation is consistent with the finding that neither TBB nor BDE100 was detected in the sediments at any of the four sampling sites (Table 2), implying that their concentrations in the sediments were lower than those expected based on equilibrium partitioning with the water column (Table S8). Additional data and modeling analysis would be needed to attribute confidently the processes that explain the vertical concentration trends of the Br-PBPs in the water column at Site 1 in Lake Geneva.

Limited published data are available on the spatial concentration trends or gradients of hydrophobic compounds in aquatic systems, especially the deep water column, because the aqueous concentrations of these compounds are difficult to sample and quantify reliably. Published water column measurements of Br-PBPs in lakes are limited to surface samples having depths  $<10 \text{ m}$ .<sup>10,55,56,59–62</sup> However, previous modeling efforts have indicated that hydrophobic compounds could exhibit vertical gradients in large aquatic or marine systems, due to the simultaneous influences of currents and turbulent mixing, air–water exchange, atmospheric deposition, sedimentation, and/or transformation reactions.<sup>63–66</sup> The high sensitivity of GC×GC- $\mu$ ECD produced precise quantifications of Br-PBP analytes, and this allowed us to establish spatial trends of Br-PBP concentrations in the water column. This would have been more difficult (or impossible) with conventional analytical methods such as GC–MS.

**Potential Sources and Sinks of TBB and 4BBP in Lakes.** Little is known about the global production and distribution of TBB and 4BBP. Both chemicals have estimated global production volumes of  $>1 \text{ t year}^{-1}$ ,<sup>4</sup> and they are mainly produced in China.<sup>67</sup> TBB is used as a reagent in the production of different pharmaceuticals and personal-care products.<sup>68,69</sup> TBB is also used as an added flame retardant together with HBB during the production of organic polymers.<sup>70,71</sup> 4BBP is utilized in the industrial synthesis of other chemicals, including rodenticides, pharmaceuticals, and personal-care products.<sup>72–74</sup> TBB and 4BBP are additionally known to be anaerobic dehalogenation products of HBB and HBBP, after several successive dehalogenation reactions.<sup>75–79</sup> PBEB and HBB are currently still in use as NBFRs.<sup>3</sup>

The presence of TBB and 4BBP in Lake Geneva is unlikely to be explained by dehalogenation of higher brominated congeners. Although TBB and 4BBP are dehalogenation products of HBB and HBBP, respectively, they are not the main products of these pathways.<sup>75–79</sup> Additionally, in our



**Figure 3.** Aqueous concentration with respect to depth for (a) TBB, (b) 4BBP, (c) BDE99, and (d) BDE100 at Site 1. The error bars indicate the observed concentration variability (95% confidence interval) over the 3 month sampling period. The dotted line shows the depth of the lake bottom at the sampling site.

**Table 3.** Estimated Chemical and Physical Properties of the Investigated Novel Br-PBPs

properties	symbols	compound name			
		TBB	4BBP	HBB	PBEB
melting point	$T_m$ (°C)	122.8 <sup>a</sup>	72.9 <sup>a</sup>	327.0 <sup>a</sup>	138.0 <sup>b</sup> , 137.7 <sup>a</sup>
boiling point	$T_b$ (°C)	271.0 <sup>a</sup>	312.5 <sup>a</sup>	417.5 <sup>a</sup>	363.2 <sup>a</sup>
subcooled liquid vapor pressure	$P_L^*$ (mm Hg)	$7.5 \times 10^{-3c}$	$1.5 \times 10^{-3c}$	$1.58 \times 10^{-3c}$	$3.7 \times 10^{-6c}$
subcooled liquid aqueous solubility	$C_{w-L}^{sat}$ (mg L <sup>-1</sup> )	20 <sup>c</sup>	4.7 <sup>c</sup>	0.34 <sup>c</sup>	0.22 <sup>c</sup>
air–water partition constant	$\log K_{aw}$	-2.27 <sup>c</sup> , -2.17 <sup>a</sup>	-1.73 <sup>c</sup> , -1.86 <sup>a</sup>	-3.85 <sup>c</sup> , -4.06 <sup>a</sup>	-3.14 <sup>c</sup> , -3.49 <sup>a</sup>
octanol–water partition constant	$\log K_{ow}$	4.19 <sup>c</sup> , 4.66 <sup>a</sup>	4.96 <sup>c</sup> , 4.59 <sup>d</sup>	5.80 <sup>c</sup> , 5.85 <sup>a</sup>	5.97 <sup>c</sup> , 7.48 <sup>a</sup>
octanol–air partition constant	$\log K_{oa}$	6.12 <sup>c</sup> , 6.52 <sup>a</sup>	7.14 <sup>c</sup> , 6.82 <sup>a</sup>	9.61 <sup>c</sup> , 10.97 <sup>a</sup>	10.13 <sup>c</sup>
organic carbon–water partition constant	$\log K_{oc-w}$ (L kg <sup>-1</sup> )	3.58 <sup>c</sup> , 2.85 <sup>a</sup>	4.08 <sup>c</sup> , 4.01 <sup>a</sup>	5.55 <sup>c</sup> , 4.68 <sup>a</sup>	5.54 <sup>c</sup> , 6.49 <sup>a</sup>
dissolved organic carbon–water partition constant	$\log K_{DOC-w}$ (L kg <sup>-1</sup> )	4.05 <sup>c</sup> , 4.40 <sup>f</sup>	4.62 <sup>c</sup> , 4.84 <sup>f</sup>	6.33 <sup>c</sup> , 6.82 <sup>f</sup>	6.31 <sup>c</sup> , 6.96 <sup>f</sup>
polydimethylsiloxane (PDMS)–water partition constant	$\log K_{PDMS-w}$	4.84 <sup>h</sup>	4.84 <sup>e</sup>	6.21 <sup>g</sup>	6.64 <sup>g</sup>
bioconcentration factor (BCF)	$\log BCF$	4.60 <sup>c</sup> , 2.77 <sup>a</sup>	5.11 <sup>c</sup> , 3.12 <sup>a</sup>	6.61 <sup>c</sup> , 3.97 <sup>a</sup>	4.15 <sup>c</sup> , 6.62 <sup>a</sup>

<sup>a</sup>Estimated using EPISuite.<sup>105</sup> <sup>b</sup>Covaci et al.<sup>3</sup> <sup>c</sup>Estimated based on measured GC×GC retention times using the method of Nabi et al.; described further in the Supporting Information.<sup>84</sup> <sup>d</sup>Doucette and Andren.<sup>106</sup> <sup>e</sup>Estimated using the method developed by Kwan et al.<sup>23</sup> <sup>f</sup>Estimated using the LFER reported by Freidig et al.<sup>107</sup> <sup>g</sup>Estimated using the method developed by Booij et al.<sup>108</sup>

search of the GC×GC-ENCI-TOFMS data of the analyzed sediment samples, we failed to find the target ions for 1,3,4,5-tetrabromobenzene and 2,2-dibromobiphenyl (on the basis of the masses reported in literature<sup>78,79</sup>), which are the transformation intermediates that would be expected to produce TBB and 4BBP upon dehalogenation, respectively.<sup>75–79</sup> Therefore the surprisingly high levels of TBB and 4BBP in the water column are unlikely to be explained by in situ production of these compounds through the anaerobic dehalogenation of HBB and HBBP, respectively.

Anaerobic dehalogenation is likely to be a potential sink for both TBB and 4BBP in anaerobic lake sediments, on the basis of their structural similarities to BFRs that are known to degrade via this pathway.<sup>80–82</sup> Anaerobic dehalogenation has been measured in the laboratory for 4BBP.<sup>76,77</sup> No information is available concerning the rates of direct photolysis for either TBB or 4BBP. However, this process merits investigation, as structurally similar brominated compounds have environmentally relevant rates of direct photolysis (Table S10).<sup>67,83</sup>

**Bioaccumulation Potential, Long-Range Transport Potential (LRTP), and Arctic Contamination Potential (ACP) of TBB and 4BBP.** GC×GC presents a unique opportunity to analyze for Br-PBPs and simultaneously

estimate several environmentally relevant partitioning properties of these compounds. For TBB and 4BBP, few partitioning property data have been reported in the literature. Therefore, to expand upon the preliminary assessment of Howard and Muir,<sup>4</sup> we compiled several environmentally relevant property data based on the available literature data and multiple estimation methods, including a recently developed property estimation method based on GC×GC retention times<sup>84</sup> (Tables 3 and S10, Section S10). Both TBB and 4BBP meet the criteria for environmental persistence in aerobic environments, according to an estimated atmospheric oxidation half-life of >1 day and expert judgment (see refs 4 and 85). According to partitioning property estimates by GC×GC, TBB and 4BBP were found to have both LRTP and ACP, as defined by the following criteria:  $4 < \log K_{ow} < 8$ ,  $6 < \log K_{oa} < 9$ , and  $-3 < \log K_{aw} < 1$ .<sup>6</sup> TBB was identified previously as a potential Arctic contaminant by Wania.<sup>6</sup> Additionally, the previously reported detection of TBB in a snow core in Nunavut, Canada,<sup>9</sup> may be viewed as supporting evidence for its potential for long-range transport and associated Arctic contamination. Other target analytes, pentaBDEs, HBB, and PBEB, have been previously investigated for LRTP and ACP.<sup>9,18,59,86–88</sup>

According to chemical property estimates provided by GC×GC (Table 3), TBB and 4BBP meet the bioaccumulation potential criteria set by Howard and Muir,<sup>4</sup> defined as  $\log K_{ow} > 3$  and  $BCF > 500$ . These more conservative criteria compared to those in REACH (i.e.,  $BCF > 2000$ <sup>89</sup>) include a larger number of chemicals as potential bioaccumulative pollutants. 4BBP has been reportedly found in tissues of human cancer patients in China<sup>90</sup> and in human breast milk in Denmark and Finland,<sup>91</sup> which is consistent with its predicted tendency to bioaccumulate. Biotic occurrence data are absent for TBB. However TBB is the brominated analogue of trichlorobenzene, which is considered bioaccumulative and persistent.<sup>92</sup> PBEB, HBB, HBBP, and pentaBDEs have been found to bioaccumulate in the environment on the basis of both their properties and their previously reported occurrences in biotic media.<sup>25,51,52,86,88,93–104</sup>

**Implications.** The combination of GC×GC- $\mu$ ECD and GC×GC-ENCI-TOFMS was found to be a sensitive and selective analytical approach for the detection and quantification of Br-PBPs in complex environmental samples with limited cleanup. Conventional methods that are used for sample preparation and analysis of halogenated organic pollutants are optimized for specific chemical families. By comparison, the method proposed in the present study enables simultaneous analysis of a wide range of nonpolar halogenated target analytes, thanks to the limited cleanup step. The successful detection and quantification of TBB and 4BBP was made possible by the higher sensitivity and selectivity of GC×GC- $\mu$ ECD and GC×GC-ENCI-TOFMS for halogenated PBPs compared to those of GC×GC-EL-TOFMS and/or conventional GC-MS. Additionally, GC×GC enabled the estimation of several environmentally relevant chemical and physical properties for TBB and 4BBP. Finally, the mass spectrum data recorded by GC×GC-ENCI-TOFMS enabled retrospective analysis of both the passive samplers and sediment samples for additional suspect analytes, which enabled us to rule out debromination of higher brominated congeners as a potential source of TBB and 4BBP.

## ■ EXPERIMENTAL METHODS

**Selection of Target Analytes.** We performed a prioritization screening of the 65 novel Br-PBPs listed in the Howard and Muir study.<sup>4</sup> The screening criteria were that chemicals must be (1) amenable to GC- $\mu$ ECD without derivatization; (2) neutral; (3) thermally stable; (4) available as analytical chemical standards from research chemical suppliers; (5) registered in the European Union's Registration, Evaluation, and Authorization and Restriction of Chemicals (REACH) database; (6) and not banned from production in Europe. Applying these criteria led to four high-priority novel Br-PBPs: TBB, 4BBP, HBB, and PBEB. More details regarding the screening protocol are provided in Section S1 and Table S1 of the Supporting Information.

We additionally analyzed the legacy pentaBDE technical mixture, which consists of BDE47, BDE99, BDE100, BDE153, and HBBP. Throughout the present article we refer to this technical mixture as "pentaBDEs". These compounds had a historically high volume of production<sup>14</sup> and have been investigated widely in the environment in different parts of the world,<sup>14,18,109</sup> including Switzerland,<sup>14,18,109</sup> due to their toxicity,<sup>110,111</sup> bioaccumulation potential,<sup>16,25,112,113</sup> and persistence in the environment.<sup>12,14,18,26</sup> Our findings on pentaBDEs provide a point of comparison for interpreting the levels of

novel Br-PBPs in Lake Geneva. A list of chemical suppliers for all target analytes is given in the Supporting Information.

**Sampling Locations.** Lake Geneva is one of the largest fresh surface water resources in Europe, having a surface area of 580 km<sup>2</sup> and a maximum depth of 310 m.<sup>114</sup> It is the main drinking water source for more than 520 000 people (Figure S1).<sup>115</sup> Commercial and recreational fishing in Lake Geneva together amount to approximately 1000 tons of fish per year.<sup>116</sup>

We collected sediment cores from four locations of the lake (Figure 1), using either a Benthos gravity corer from a surface vessel (Sites 1–4) or a tube core from the robotic arm of a human-occupied Mir submersible (Site 2) during the Elemo field campaign in the summer of 2011.<sup>114</sup> The sediment samples were collected from locations having total depths of 192 m (Site 1), 310 m (Site 2), 236 m (Site 3), and 188 m (Site 4). Site 1 was located at 46.4945°N and 6.5796°E (World Geodetic System, WGS84), Site 2 was located at 46.4390°N and 6.6130°E, Site 3 was located at 46.4183°N and 6.7801°E, and Site 4 was located at 46.4345°N and 6.8551°E. Site 1 was at about a 2000 m distance from the lake shore and a 1200 m distance from the effluent discharge of Lausanne's Vidy WWTP, which serves a population equivalent of approximately 220 000 (Figures 1 and S1). The second sediment sampling site (Site 2) was located near the center of the deep lake. Sites 3 and 4 were located farther east and are likely affected by pollutant inputs from the Rhone river tributary and also the coastal cities of that region. All sediment samples, after collection, were brought immediately to the lab and stored at –20 °C until extraction for analysis.

We also sampled the deep water column of the lake by deploying passive samplers at Site 1 (Figures 1 and S1). This sampling location was chosen because it is likely influenced by pollutant inputs originating from urban runoff and the WWTP of the city of Lausanne. However, this location was sufficiently distant from the shore such that it also mixes regularly with the waters of the central lake, which are affected by other pollutant inputs, such as those from the Rhône River, agricultural runoff, cities of the French coast (e.g., Evian), and atmospheric deposition.<sup>42,117–120</sup> In the summer of 2011, during each of the months of June, July, and August, we deployed two passive samplers at five different water depths of 70, 132, 172, 178, and 191.5 m. Each passive sampler had an exposure time of 1 month. The deepest sampling point was 0.5 m above the sediment bed, which had a total water depth of 192 m. We were not permitted to place samplers at depths less than 70 m due to the operation of fishing trawlers. To deploy the passive samplers, we used a stainless steel chain connected to a buoy and a stainless steel bottom release. To protect the passive samplers from biofilm formation and bioturbation, the passive samplers were placed inside solvent-pretreated stainless steel cages. The cages were then deployed at the desired depths.

**Water Column Sampling.** Passive samplers are often employed for measurement of persistent and bioaccumulative pollutants in aquatic systems, due to their low expense, ease of storage and transport, and stability over time.<sup>121–124</sup> The rate constant describing pollutant uptake into the passive samplers from the water column ( $k_c$ ) was estimated based on the extent of disappearance of several performance reference compounds (PRCs) from the passive samplers during the sampling period (see eq 1 in Section S4 of the Supporting Information).<sup>125–127</sup> For further information, see the Sample Preparation and Cleanup section and also Section S4 of the Supporting Information.



**Sample Preparation and Cleanup.** *Extraction of Sediment Samples and Cleanup.* We culled sediment from the top 1 cm of each of the four collected sediment cores. Only the center section of the sediment core was taken, thereby excluding the sediment in contact with the plastic walls of the coring tube. The resulting sediment samples had a dry weight of approximately 5 g each. These samples were air dried and then homogenized (EPA method EPA-823-B-01-002, revision of October 2001). Each homogenized dried sample (0.5 g) was extracted using accelerated solvent extraction, which was a modified version of EPA Method 3545A, revision 1, February 2007.<sup>30</sup> We employed an extraction mixture of acetone and hexane that has been proposed previously for organochlorinated pesticides in sediment samples. We omitted the alumina, silica gel, and gel permeation chromatography (i.e., fractionation) and sulfur cleanup steps that would be usually applied with EPA Method 3545A so that the resulting extracts could be analyzed broadly for several classes of nonpolar halogenated compounds, including Br-PBPs. Further method details are given in Section S5 of the Supporting Information.

*Extraction of the Passive Samplers Deployed in the Water Column.* For passive sampling of the water column, we used PDMS sheets (AlteSil Laboratory Sheet, U.K.) of 5 mm thickness. PDMS exhibits linear mass transfer behavior over a wide range of sorbate  $K_{ow}$  values.<sup>128,129</sup> The PDMS sheets were cut into strips of  $10 \times 1 \times 0.05 \text{ cm}^3$ , each of which had a weight of  $1.98 \pm 0.20 \text{ g}$ . The strips were then cleaned using Soxhlet extraction with methanol for 24 h<sup>130–133</sup> and subsequently stored at  $-20 \text{ }^\circ\text{C}$ . Five cleaned strips were then immediately extracted, and these are referred to as the PDMS blank. Before field deployment, we loaded each of the PDMS strips with four PRCs (PCB 30, PCB 50, PCB 145, and PCB 204) to a concentration of  $20 \text{ ng g}^{-1}$  of each PRC. The details of the PRC loading process are explained elsewhere.<sup>127</sup> After the loading step, five strips were used to determine the initial PRC concentrations in the strips. After deployment in the lake, extraction of each of the deployed strips was carried out by soaking the strips in 20 mL of pentane for 8 h three consecutive times. The volume of the final extract (60 mL) was reduced to 1 mL by rotary evaporation and simultaneously solvent-exchanged to hexane. The final extract was stored at  $-20 \text{ }^\circ\text{C}$  until analysis. We did not perform any cleanup step on the final extract.

For quality assurance, we analyzed four different types of blanks. These were as follows: the five PDMS blanks (explained above); the solvent blanks, which were the solvents used for extraction (pentane and hexane); three field blanks, which were extracts of loaded strips brought to the field but not deployed; and the method blank, which was a solvent extract of the glassware used for the extraction and rotary evaporation.

**GC×GC- $\mu$ ECD and GC×GC-ENCI-TOFMS Analysis.** We analyzed our environmental samples with a Leco Corp GC×GC- $\mu$ ECD instrument equipped with a modified Agilent 7890A GC system having a split/splitless injector and a dual-stage, quadruple-jet modulator. The Leco GC×GC had a 30 m length, 0.25 mm inner diameter (i.d.), 0.25  $\mu\text{m}$  film thickness RTX-1 column (Restek, USA) as the first dimension and a 2 m length, 0.1 mm i.d., 0.1  $\mu\text{m}$  film thickness BPX-50 column as the second dimension (Restek).

GC×GC-ENCI-TOFMS and GC×GC-EI-TOFMS analyses were both performed using a Zoex (Zoex Corp.) instrument. This instrument was a modified Agilent 7890A GC system with a loop thermal modulator supplied by Zoex. The TOFMS was

made by TOFWERK, Switzerland, and it was equipped with both an EI source and ENCI source. The column set and temperature program were similar to those used for GC×GC- $\mu$ ECD measurements. When used with either an EI or ENCI source, the TOFMS exhibited a mass precision of  $\pm 5 \text{ mmu}$  for the target masses that we investigated. Further instrument details are reported in Section S6 of the Supporting Information. These analyses provided us with the bases for the comparison of the combination of GC×GC- $\mu$ ECD and GC×GC-ENCI-TOFMS with conventional GC×GC-EI-TOFMS.

**Chemical Property Estimation.** We compiled chemical property data for all analyzed Br-PBPs, including previously reported measurement values and also several model estimates. For TBB, 4BBP, PBEB, HBB, and BDE47, all of which have a boiling point of  $<402 \text{ }^\circ\text{C}$ , several partitioning properties were estimated from GC×GC retention times using a methodology that we have reported previously,<sup>84</sup> as described in Section 10 of the Supporting Information. Partitioning properties were also estimated for all investigated Br-PBPs with EPISuite.<sup>105</sup> We also assessed the Br-PBPs for aerobic persistence using BioWin<sup>105</sup> and the expert judgment criteria for biodegradability potential.<sup>4,85</sup> This provides a tabulation of environmentally relevant physical and chemical property estimates and/or experimentally measured values for TBB, 4BBP, PBEB, and HBB and the components of the pentaBDE technical mixture according to several different methods.

## ■ ASSOCIATED CONTENT

### § Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00440.

List of the screened chemicals; details for the passive sampling methodology; details about extraction and cleanup of the sediment samples; GC×GC instrument conditions; analytical procedure quality assurance; water column temperature profiles; aqueous concentrations of the target Br-PBPs; occurrence of target Br-PBPs in the Lausanne Vidy WWTP effluent; property estimation method details; and estimated physical and chemical properties of pentaBDEs (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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