SUPPORTING INFORMATION for

UV induced formation of bromophenols from polybrominated diphenyl ethers

Paul Bendig and Walter Vetter*

University of Hohenheim, Institute of Food Chemistry, Garbenstrasse 28, D-70599 Stuttgart, Germany

*** Corresponding author:**

Walter Vetter

fax: +49 711 459 24377

Email: walter.vetter@uni-hohenheim.de

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GC/ECNI-MS analysis of bromophenols in the presence of PBDEs

All di- and triBP standards eluted prior to BDE-1 (i.e. the first eluting PBDE congener) and they could be easily analyzed by GC/ECNI-MS [1]. The GC/ECNI-MS spectra of di- and triBP standards featured the molecular ion ($[M]^-$) as the base peak followed by $[Br]^-$ which reached about 50% of the abundance of $[M]^-$ (Fig. S1). BP congeners not available as standard compounds were determined by means of the molecular ion. The isomer structure information was derived from the retention data on DB-5 like columns [2]. The mass spectra tetra- and pentaBPs (Fig S1c,d) compared well to those published by Stemmler and Hites [3]. These were characterized by highly abundant $[M-Br]^-$ and $[M-HBr]^-$ fragment ions which enabled us to distinguish them from mono- to tribrominated diphenyl ethers with which they shared the GC retention time range. In addition, the absence of *m/z* 159/161 (these ions were included in the SIM method) which is characteristic for PBDEs can be used for the verification of BPs in the presence of the lowly brominated PBDEs as they exclusively formed $[Br]^-$ and $[HBr_2]^-$ [4]. Additionally, 2,4,6-tribromoanisole and 2,3,5-triBP coelute on the DB-5 like GC phase but could be distinguished by means of their mass spectra.

In addition, the BP analysis required a very clean GC/MS system. After a couple of injections of pg amounts of pure BP standards the BP peaks became broader and the signal intensity was decreased. The effect was not observed for non-phenolic compounds such as 2,4,6-tribromoanisole or 2,4-dibromoanisole (Fig. S2). Throughout the study, frequent instrumental maintenance was necessary (e.g. exchange of the inlet liner and column cutting). These effects were less pronounced when higher amounts (>1-10 ng BP on column) were injected.

Figure S1

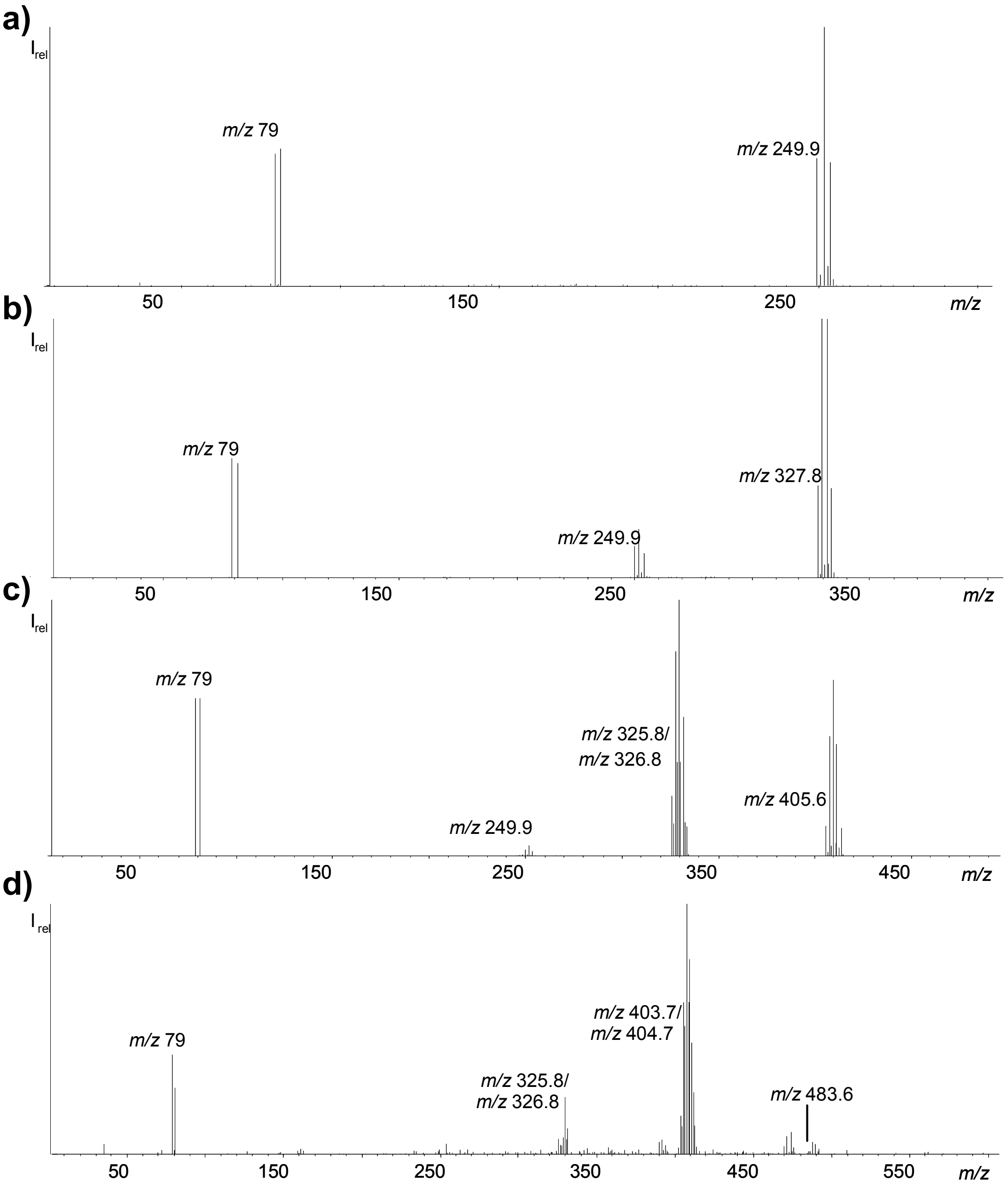

Figure S1: GC/ECNI-MS spectra of a) 2,4-dibromophenol, b) 2,4,6-tribromophenol, c) tetrabromophenol and d) pentabromophenol

Figure S2

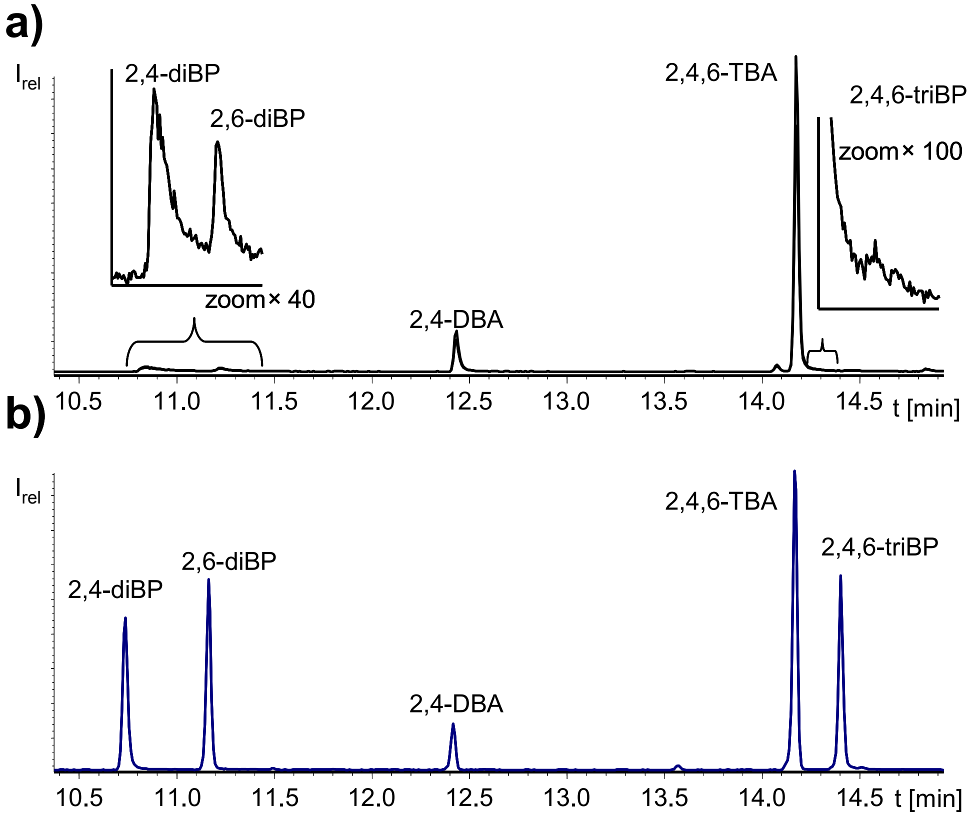

Figure S2: GC/ECNI-MS chromatograms (TIC of *m/z* 79, 81, 172, 174, 249.9, 251.9, 253.9, 327.8, 329.8 and 331.8) of a standard mixture of 2,4-, 2,6-dibromophenol (diBP), 2,4-dibromoanisole (DBA), 2,4,6-tribromoanisole (TBA) and 2,4,6-tribromophenol (50 pg each), a) before and b) after system maintenance

Figure S3

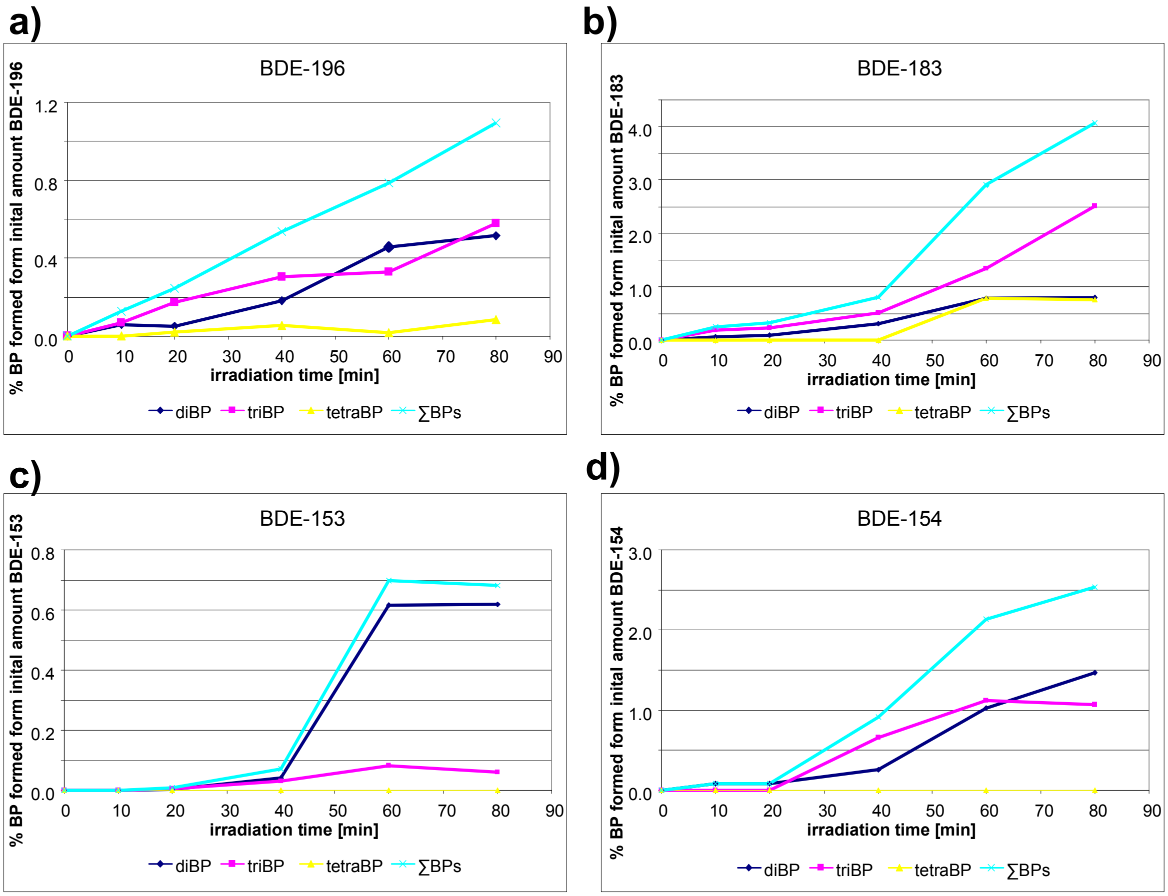

Figure S3: Formation of di-, tri- and tetrabromophenols with from a) BDE-196, b) BDE-183, c) BDE-153 and d) BDE-154 in dependency of irradiation time.

Figure S4

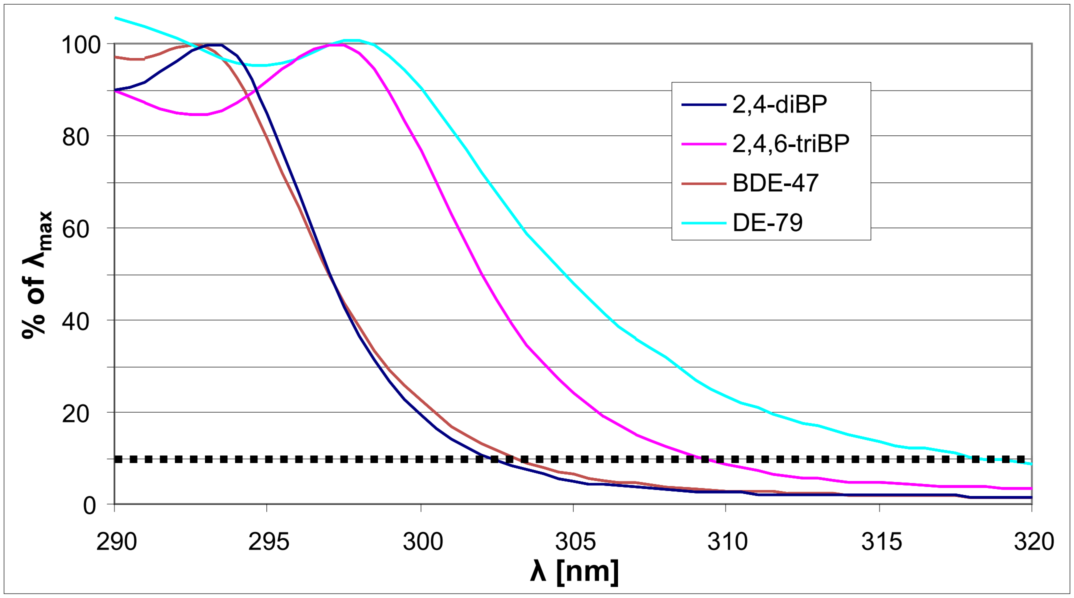

Figure S4: UV absorbance spectra of BDE-47, DE-79,m 2,4-dibromophenol, and 2,4,6-tribromophenol, normalized to λ_{max}. 10% of λ_{max} is marked with a dotted line.

Figure S5

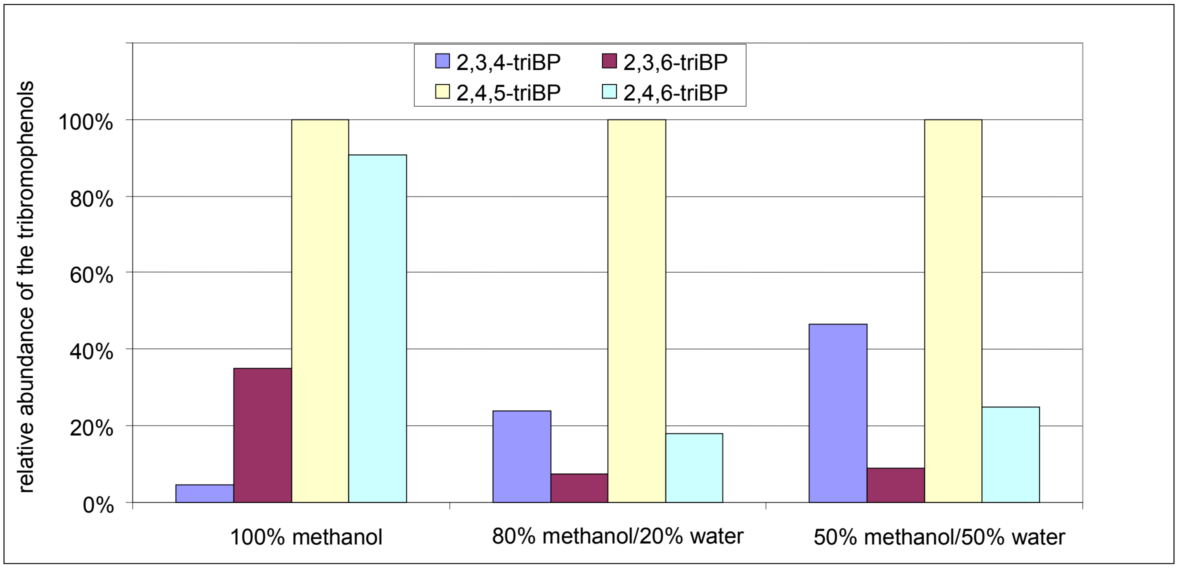

Figure S5: Abundances of tribromophenols (triBPs) relative to 2,4,5-triBP, after 80 min irradiation of BDE-183 in pure methanol, methanol/water (80/20) and methanol water (50/50)

Figure S6

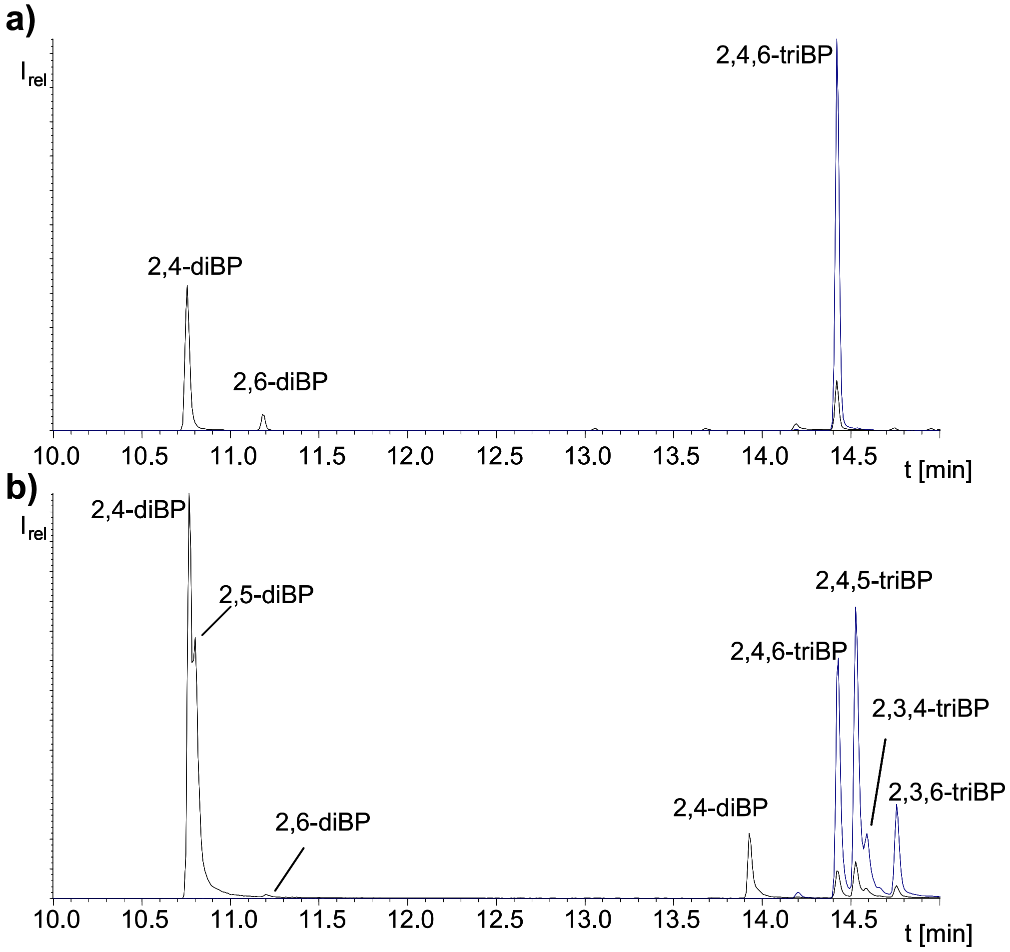

Figure S6: GC/ECNI-MS SIM chromatograms of *m/z* 252 (black ion trace) and *m/z* 330 (blue ion trace) of a) a passive water sampler extract from the Great Barrier Reef (Australia) and b) BDE-183 irradiated for 60 min.

REFERENCES

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(3) Stemmler, E.A. and Hites, R.A. *Electron Capture Negative Ion Mass Spectra of Environmental Contaminants and Related Compounds.* VCH: New York, 1988.

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