POLYBROMO-DIPHENYLETHER IN HUMUS OF ALPINE FORESTS – SPATIAL DISTRIBUTION AND ALTITUDINAL VARIATION

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Introduction

Polybromo-diphenylether (PBDE) are bicyclic aromatic ethers. Dependent on bromine content, PBDE isomers cover a wide range of chemical and physical properties and are therefore suitable substances for the investigation of gas/particle air transport processes. 209 PBDE position isomers are possible, but as they are synthesized by electrophilic substitution of diphenylether, eight 2,2',4,4'-PBDE isomers dominate in the commercial formulations.

PBDE are widely used as additive flame retardants for plastics and textile back coatings. For this purpose the polymer material is blended with amounts from 5–30% w/w. PBDE are not chemically bound to the polymer and can therefore evaporate, separate or leach from the surface of treated products into the environment. Three commercial formulations exist: pentaBDE, octaBDE and decaBDE named after their average bromine content. PBDE are persistent and bioaccumulate and biomagnify in the food web. Their widespread use made them ubiquitous in abiotic and biotic samples. Increasing levels were analysed in sewage sludge, sediments, human plasma and milk[4, 11, 9, 8, 16]. PBDE are structurally similar to thyroid hormones and induce neurotoxicity when administered at a sensitive period of brain growth[4].

Therefore penta and octaBDE preparations have been banned in the EU since 15 August 2004[7] and are under review for Stockholm Convention. DecaBDE was exempt from this ban because it was believed to be hardly subject to long-range air transport[17] and to have a low bioaccumulation potential. Possible degradation of decaBDE under anaerobic conditions or in biota into more toxic forms was also not considered[6]. The European Court of Justice recently annulled the exemption from the EU Restriction of Hazardous Substances (RoHS) directive[5]. Effective from 1 July 2008 the use of decaBDE in electrical and electronic equipment will also be restricted.

For this study humus from remote Alpine forests was analysed for PBDE. The rough canopy of coniferous forests combs the bypassing air and gaseous pollutants diffuse into the wax phase of conifer needles whereas particles are deposited on their surface. The topsoil humus layers with their high organic carbon content accumulate persistent organic pollutants (POP) from wet (rain and snow) and dry (gas and particle bound pollutants incl. fall of needles) deposition over a long period[18].

This paper presents results from the **Mo**nitoring **N**etwork in the **A**lpine **R**egion for **P**ersistent and other **O**rganic **P**ollutants – **MONARPOP**[2, 14]. Its main goal is to investigate the actual contamination of the Alps and to understand the role of high mountains in the global atmospheric transport of POP [3, 15].

Materials and Methods

A total of 56 humus samples (31 sampling points in 1400 m a.s.l. and 7 height profiles consisting of 3 to 5 sampling points in increasing altitude) from remote Norway spruce (*Picea abies*) forest sites in the Alps were collected for PBDE analysis in autumn 2004. The entire humus layer O_L material included within a 30x30 cm metal frame was taken. The material from 4 to 10 pits along a 5x20 m rectangular grid was pooled to one sample, freeze-dried and grinded. An aliquot was sent to the Federal Environment Agency, Germany, where 20 g

were spiked with a $^{13}C_{12}$-PBDE standard mixture/solution, extracted, clean-up processed and quantified by GC-MID(EI+)HRMS. The analytical method was already described in detail[10].

Results and Discussion

The depth of the sampled humus layers ranged from 0.3 to 35.3 (median 3.4, n=482) cm. The organic carbon content was nearly constant with a median of 39.8% (n=28) and therefore all data are only presented on d.m. basis. Eight significant congeners for the three commercial PBDE formulations were determined. For pentaBDE $\sum_6$BDE28+47+99+100+153+154, for octaBDE BDE183 and for decaBDE BDE209. PBDE were detected in all humus samples, higher levels at the border of the Alps near potential sources decreasing to the centre (Figure 1). BDE183 dominates in the northeast Alps. It needs to be clarified if these higher concentrations which indicate a higher input are caused by a higher usage of octaBDE in Austria and/or neighbouring eastern countries. The concentrations in 1400 m a.s.l. range for $\sum_6$BDE from 210 to 1472 (median 524, n=31), for BDE183 from 14 to 662 (median 156) and for BDE209, for which multimedia models predicted a low long-range air transport potential, from 610 to 7610 (median 1440) ng kg^{-1} d.m.. All data are presented as box-whisker plots. To some maximum outliers also local but until now unknown sources may have contributed.

For comparison concentrations of PBDE from an investigation of moss from Norway range for Σ_6BDE from 11 to 190 (median 69, n=12), for BDE183 from <LOD to 37 (median 11) and for BDE209 from 105 to 1590 (median 693) ng kg^{-1} d.m.[12].

The dominating congener in humus is decaBDE209, followed by heptaBDE183, tetraBDE47, hexaBDE153 and pentaBDE99. HeptaBDE183 is a minor congener in most environmental samples. Its unexpected higher per cent contribution could be due to re-volatilisation of the congeners with less than seven bromine from humus to air or decreased relative deposition via atmosphere and litter fall.

The humus height profiles follow no common trend for all eight congeners investigated but a concentration maximum for hexaBDE153, hexaBDE154, heptaBDE183 and decaBDE209 at the same altitude of the local height profile is noticeable (Figure 2). For this observation the following explanation is proposed. Particle bound pollutants are normally dispersed into the atmosphere. During a thermal inversion with fog, a frequent weather condition in Alpine valleys, they become trapped on the surface of the inversion layer and deposited in the specific local and seasonable inversion height[13].

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References

1. Alpine Space Programme. <http://www.alpinespace.org/ (29 April 2008)>
2. Bassan R., Belis C., Heublein D., Iozza S., Jakl T., Jakobi G., Kirchner M., Knoth W., Kräuchi N., Levy-Lopez W., Luchetta A., Magnani T., Moche W., Oehme M., Offenthaler I., Perthen-Palmisano B., Schmid D., Schramm K.-W., Schrott H., Schröder P., Sedivy I., Simončič P., Uhl M. and Weiss P. *Organohalogen Comp* 2005; 67: 1839.
3. Daly G.L. and Wania F. *Environ Sci Technol* 2005; 39: 385.
4. de Wit C.A. *Chemosphere* 2002; 46: 583.
5. European Court of Justice 2008. Judgment of 1 April 2008 on joined cases C-14/06 and C-295/06. <http://curia.europa.eu/en/actu/communiques/index.htm (29 April 2008)>
6. European Union 2004. Risk assessment. CAS No. 1163-19-5, EINECS No. 214-604-9, 114 pp.
7. European Union. 2003. *Official Journal of the European Union* 2003; L42: 45.
8. Hale R.C., La Guardia M.J., Harvey E., Gaylor M.O. and Mainor T.M. *Chemosphere* 2006; 64: 181.
9. Hites R.A. *Environ Sci Technol* 2004; 38: 945.
10. Knoth W., Bassan R., Belis C., Jakobi G., Kirchner M., Kräuchi N., Mann W., Meyer R., Moche W., Nebhuth J., Offenthaler I., Sedivy I., Simončič P., Uhl M.,Vilhar U. and Weiss P. <http://www.bfr2007.com/abstracts/files/add37420.pdf (29 April 2008)>
11. Letcher R.J. and Behnisch PA, Ed.. *Environment International* 2003; 29: 663.
12. Mariussen E., Steinnes E., Gundersen H., Borgen A. and Schlabach M. *Organohalogen Comp* 2005; 67: 591.
13. Massachusetts Department of Agricultural Resources. <http://www.mass.gov/agr/pesticides/thermal_inversion.htm (29 April 2008)>
14. MONARPOP. <http://www.monarpop.at/ (29 April 2008)>
15. Vighi M., Ed. *Ecotoxicology and Environmental Safety* 2006; 63: 1.
16. Wang Y., Jiang G., Lam P.K.S. and Li A. *Environment International* 2007; 33: 963.
17. Wania F. and Dugani C.B. *Environ Toxicol Chem* 2003; 22: 1252.
18. Weiss P. Berichte BE-195. Umweltbundesamt GmbH, Wien, September 2002. ISBN 3-85457-616-1. 121 S.

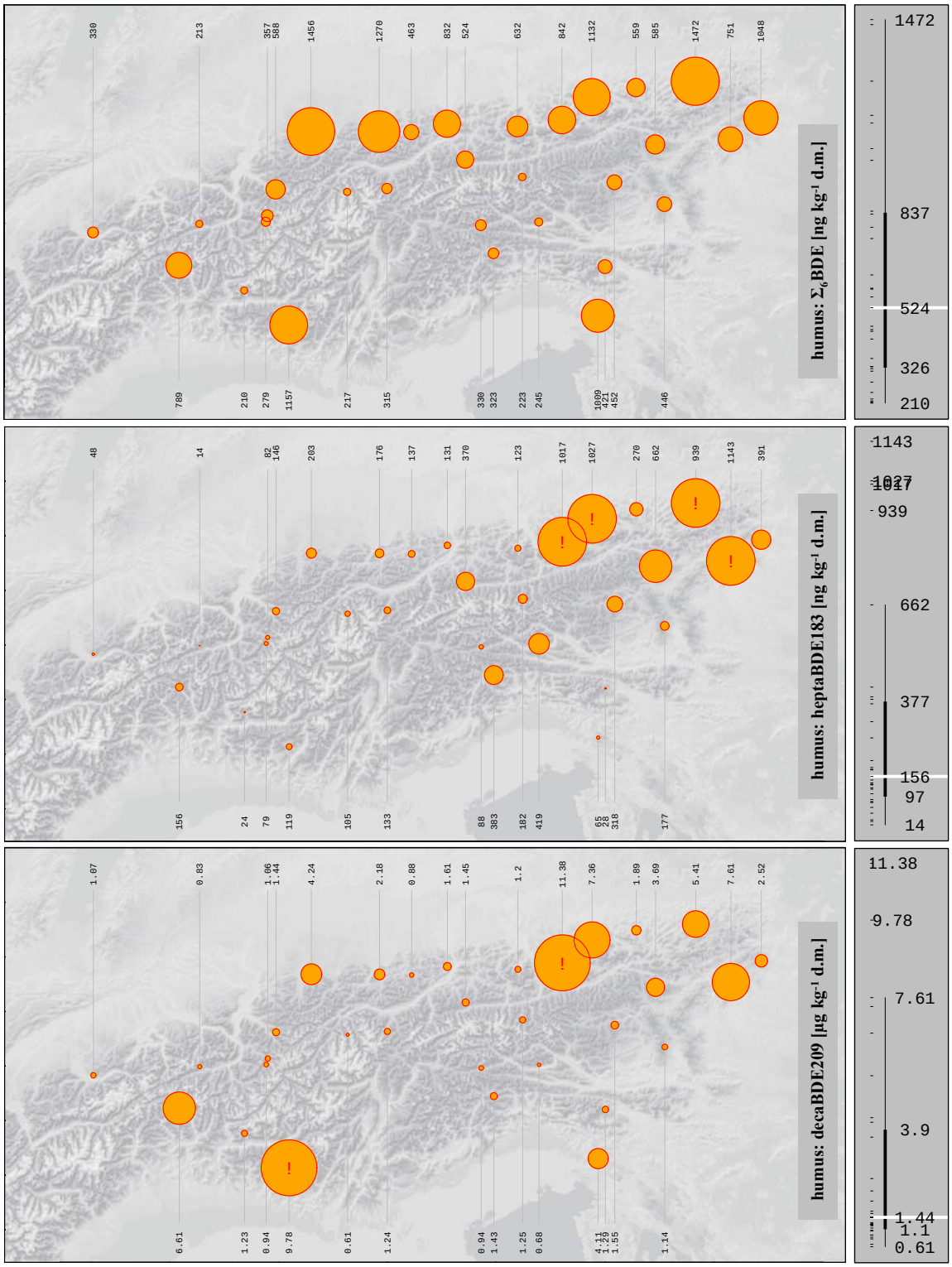

Figure 1: Spatial distribution of the concentration of Σ_6BDE28+47+99+100+153+154, heptaBDE183 and decaBDE209 (note concentration unit) and box-whisker plots (min-25%-median-75%-max-outlier !) in forest humus of the Alps

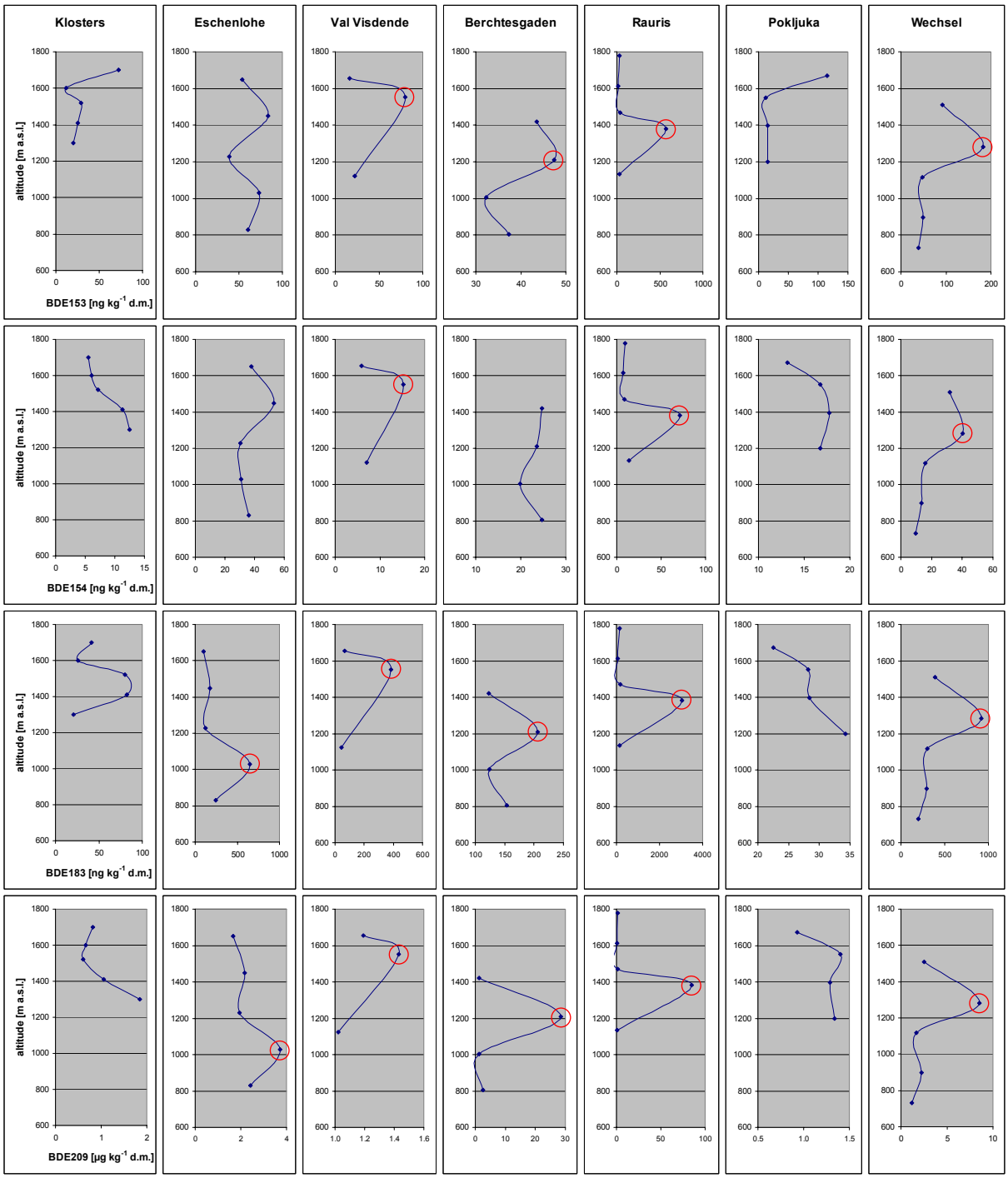

Figure 2: Altitudinal variation of the concentration of hexaBDE153, hexaBDE154, heptaBDE183 and decaBDE209 (note concentration unit) in forest humus of the Alps.◯…concentration maximum of this congeners at the same altitude of the local height profile e.g. 1381 m a.s.l. in Rauris