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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric deposition of polybromodiphenyl ethers in remote mountain regions of Europe" *by* L. Arellano et al.

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Background:

The distribution and deposition profile of polybrominated diphenylether (PBDE) flame-retardants (BFR) is assessed in the here presented comprehensive overview, based on a combination literature information and own relevant research. Specific emphasis is laid upon deposition properties in remote, high altitude (alpine) locations, as key sampling sites for the elucidation of altitudinal as well as longitudinal transport properties for BFRs. The PBDE distributions (patterns and concentrations) were determined in bulk deposition samples. The levels and patterns were discussed for four remote, alpine, European mountain areas. BDE 209, 47 and 99 were identified as the pre-

dominant PBDE compounds in the analysed samples. Site-specific flux calculations were done for all sites resulting in 100 ng m−2 mo−1 (Alps), up to 190 ng m−2 mo−1 (Tatras). A transcontinental transfer of these brominated pollutants from North American sources into Europe remote alpine sites is assumed based upon meteorological trajectory estimations. The fluxes of the identified secondary emissions were temperature dependent and correlated the to total particle (dry) and wet deposition (mainly rainfall). Photochemical transformation processes are considered as significant alteration pathway of the originally emitted PBDE profile, ultimately changing the PBDE patterns in the deposition samples towards lower brominated congeners.

General Comments:

Sampling and methods: Please provide detailed information on sampling period, type of deposition sampler (type, version, provider, city and country of origin) and all consumables/ chemical's used for field- and laboratory work (incl. type, quality, provider, city and country of origin) or refer to an earlier peer-reviewed paper where the unmodified methods is described in detail as required for scientific descriptions. The here cited Carrera et al 1998 paper is only describing the SPE sample preparation method but not the detailed deposition sampling procedures. The dimensions, sampling schedule and origin/type of sampling units were not adequately described.

Please explain in detail, why 12C instead of 13C standards (for recSTD as well as ISTD) were applied for the GC/MS quantification. There are plenty of commercial 13C labeled PBDE standards available for this type of quantification methods. PBDE209 (Deca) was analysed in parallel with 13 other PBDE congeners. Usually the analysis of PBDE 209 is done differently compared to less brominated congeners. Short-columns must be used for a reliable quantification due to well known analytical restrictions. In addition, PBDE 209 is highly photosensitive and tend to decompose in standard solution after rel. short time. Please reflect on these specific challenges in the introduction as well as the QC section. In order to provide a reliable threshold for the flux calculations (the entire discussion is based upon these values), the application and active

usage of a limit of quantification (LOQ), usually defined as 5 x individual blank is advised (discuss this in the QC section).

Detailed comments:

P22852/L25: “pre-weighed Whatmann glass fiber..” 1.) Type, please change to “Whatman”. 2.) Please provide information on the pre-cleaning procedures for the GFFs as wella as the C18-disks and our sampling devises including the bulk samplers (cleaning/ rinsing procedures etc). P22853/L25: “..dried over anhydrous sodium sulfate.” Add information on the drying procedure as well as the quality/ origin of the Na2SO4 applied.

P22854/L12: “SGE-BPX5 MS” Please, provide information on the origin of this capillary column (incluing film thickness, provider, city and country of origin).

P22854/L24: “PBDE determinations were performed by the internal standard method.” This sentence is difficult to understand. The expression Performed by the internal standard method” is easy to be misinterpreted. I suggest changing the sentence to “The target PBDEs were quantified with the above mentioned internal standards”.

P22854/L26:” . . . was filtered and solid-phase extracted as a real sample” . This sentence is difficult to understand. The sentence should be changed to “filtered and solid-phase extracted like a real sample.” P22855/L4:” 0.66 to 47 ng $m-2$ $mo-1$” This dimensions imply flux-calculations. I don’t see that such a dimension make sense for LOD determinations! I assume that this is a typo and you mean ng total or ng/m2, If not! Please recalculate the LOD values in ng/m2

P22860/L3:” Highest photodegradation is expected to occur at highest altitude and the results of the above..” Please Discuss why PBDE209 is still found in considerable levels at the high-altitude sites although the compound is known to be highly photosensitive.

P22862/L10: “Such particle diversity is also a likely cause for the lack of correlation between BDE209 and total particle deposition”. The GFF method used for particle collection in the here presented study is not sufficient to quantitatively collect the complete

particle fraction deposited onto the ground. Usually GFF (Whatman) has a limiting “cut-off” (most GFFs used for High-Volume air sampling for POP analysis have a cut-off of 50 μm). Thus, the fine fraction is not accounted for at all. In addition, the particle composition is not examined as well (neither with denuder techniques nor with SEM based examination). Therefore this scientific speculation cannot be supported by the here provided data material and should thus be omitted.

P2873/L31: “sYstem” Typo

NO SUPPLEMENTARY MATERIAL AVAILABLE FOR EVALUATION

Evaluations:

Scientific Significance: Good Scientific Quality: Good Presentation Quality: Good/Fair

The here presented study represents an interesting and well performed study on fluxes and deposition profiles for a selection of 14 PBDE congeners (incl. PBDE209) in European high Altitude (alpine) remote environments. The here provided information on the methods as well as a few concluding remarks need obvious clarification (see above). I therefore recommend the manuscript for publication in “Atmospheric Chemistry and Physics” after major revision

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 22847, 2013.