Does the number of field blanks influence reported air POP concentrations in monitoring programs based on PUF-PAS?

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Introduction

Several monitoring programs developed to evaluate the presence of Persistent Organic Pollutants (POPs) in air are currently being conducted at different geographic scales, including worldwide and regional programs[1-5]. A significant number of these programs are based on the use of polyurethane foam disks for passive air sampling (PUF- PAS), mainly due to the logistical advantages this method presents. The "Guidance on the global monitoring plan for POPs"[2] establishes the need of field blanks to control potential undesired contamination during PUF-PAS sampling campaigns. Particularly, it indicates that "field blanks should be taken every several samples" and that "one field blank should be deployed at each site to assess potential contamination". However, to our knowledge, no clear specifications about the number and frequency in the use of field blanks have been included in the guidance. In agreement, published studies based on PUF-PAS from different monitoring programs have shown different field blank strategies, i.e. one field blank per sampling site and year although samples were collected seasonally each year, one field blank per sampling trip to different specific locations or one field blank per each sampling site and event[5-8]. In this study, we present a preliminary evaluation on the influence that the number of conducted field blanks can have over reported air POP levels. With that goal, data reported through the Spanish Monitoring Program on POPs (SMP) based on PUF-PAS for the characterization of POPs in air[5] will be used to evaluate different field blank scenarios.

Materials and methods

Blanks and samples: Concentrations of PCDD/Fs, dl-PCBs and PBDEs corresponding to a total of 262 samples and their associated 262 field blanks collected under the SMP every three months around each season's change (winter, spring, summer and fall) have been used in this study. Selected samples and blanks correspond to six consecutive years in which all samples were processed using the same analytical procedure. Samples and blanks were obtained from up to seven background (rural/remote) locations and up to five urban sites in Spain by means of PUF-PAS. Field blank PUFs were transported and handled as real samples at each sampling site and sampling season. Detailed information on the sampling and analytical determination of the studied POPs can be found in Muñoz-Arnanz et al. for PCDD/Fs and dl-PCBs[9] and in Roscales et al. for PBDEs[10].

Field blank data treatment: Since pollutant amounts in field blanks cannot be related to a reliable sampled air volume, POPs were reported as total pg/PUF for PBDEs and fg/PUF for PCDD/Fs and dl-PCBs. Field blanks were used to calculate the method detection limit (MDL) for each analyte at each sampling site as the mean POP amount + 3 SD[2]. When target analytes were not detected in field blanks, the limit of detection (LOD; 3 times signal to noise ratio) was used. Contaminant amounts below the MDL in real PUF samples were set to ½ MDL for PBDEs and to 2/3 MDL for PCDD/Fs and dl-PCBs[6]. Two different MDLs were calculated to evaluate the influence of the number of field blanks in the concentrations reported in real samples. First, we evaluated the effect of sampling year, season and site on the total amount of PCDD/Fs, dl-PCBs and PBDEs found in blanks. Based on this information, MDLs were calculated according to: (1) MDLs based on the whole dataset of field blanks (systematic scenario), (2) MDLs based on one field blank per year corresponding to the season when POP amounts in field blanks tended to show the lowest values (extreme scenario). These MDL scenarios were performed only for some analytes selected according to their detection frequency in the studied samples; commonly detected (OCDD, PCB-77 and -118, PBDE-47, -99 and 209), scarcely detected (TCDD, PCB-81 and PBDE-183). Thus, this is a preliminary evaluation that will be completed by including the whole data reported under the SMP (22 PCBs, 17 PCDD/Fs, 15 PBDEs, 3 HCHs, HCB and 6 DDTs).

Statistical analysis: IBM-SPSS 24 was used for data handling and analysis. General Lineal Models including sampling year, season and site and their pair-interactions were used to evaluate the influence of these factors on total amounts of PBDEs, PCDD/Fs and dl-PCBs in field blanks (separated response variables). Response variables were ln [concentration+1] transformed when necessary to achieve a normal distribution. Non-significant effects were progressively removed from the GLM to a final model retaining only significant effects. Repeated measures t-test was used to compare reported POP amounts depending on data treatment according to the MDL scenarios evaluated. In addition, the effects of sampling site, year and season in POP amounts in real samples were evaluated according to the two MDL scenarios separately by means of one-way ANOVA and *post-hoc* Bonferroni pairwise comparisons.

Results and discussion

Pollutant levels in field blanks: Total PBDE amounts (TPBDE) in field blanks (Figure 1) showed significant variations according to the sampling year ($F_{262,5}$=4.1, p<0.05). Due to the low p values obtained for sampling site this factor was retained in the final model and considered a marginally significant source of variation in PBDE concentrations ($F_{262,11}$=1.7, p=0.07). The rest of considered factors did not show a significant effect. These results suggest the need of conducting at least one field blank per year and sampling site to avoid significant shifts in reported air concentrations. Season did not result significant, but the lowest PBDE amounts mostly occurred in spring and this was the season that showed the greatest variance and range for TPBDEs (range: spring 13,620; fall 12,681; summer 8,086; winter 7,616 pg). Accordingly, spring field blanks were used to calculate MDLs for the extreme scenario.

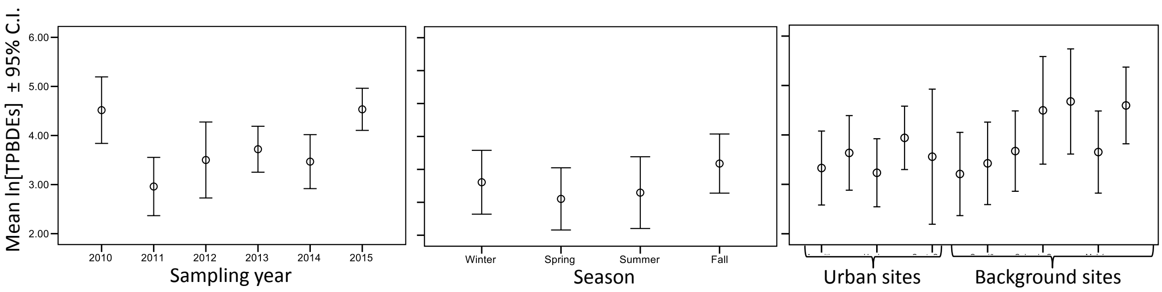

Figure 1. Log-transformed (ln) total PBDE amounts (pg) in field blanks according to the evaluated factors.

In the case of PCDD/F amounts in field blanks (Figure 2), sampling locality showed a significant effect ($F_{262,11}$=2.2, p<0.05) basically due to the greater amounts found in some of the cities studied here. Among the rest of considered factors, only the interaction sampling year*season resulted significant ($F_{262,22}$=3.6, p<0.001). In contrast to PBDEs, the interaction between sampling year and season indicates that PCDD/F amounts in field blanks vary according to sampling season, but these variations are not homogenous in all sampling years. Therefore, based on this result both factors, sampling year and season should be considered when conducting field blanks. In the case of PCDD/Fs, the lowest amounts in field blanks mostly occurred in winter but the greater variance and range were found in fall (range: summer 33.3; spring 47.9; winter 53.4; fall 81.5 pg). Winter field blanks were used to calculate MDLs for the extreme scenario.

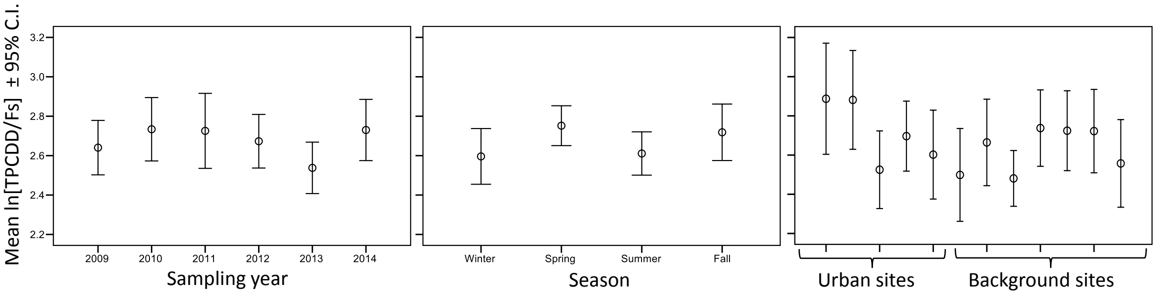

Figure 2. Log-transformed (ln) total PCDD/F amounts (fg) in field blanks according to the evaluated factors.

In the case of dl-PCBs (Figure 3), both sampling year ($F_{262,5}$=5.4, p<0.001) and season ($F_{262,3}$=13.8, p<0.001) resulted significant factors in the model. Besides their significant effects, based on F values and partial eta squared, these factors showed a much greater influence and explained a marked greater proportion of variation compared to that found for PCDD/Fs and PBDEs. According to these results, both sampling year and season should be field-blank controlled in the case of dl-PCBs but apparently, in contrast to PCDD/Fs and PBDEs, sampling site did not influence blank levels. As in the case of PCDD/Fs, the lowest dl-PCB amounts in field blanks were found almost in all cases in winter but the greater variance and range were found in fall (range: winter 337; summer 883; spring 887; fall 4887 pg). Winter field blanks were used to calculate MDLs for the extreme scenario.

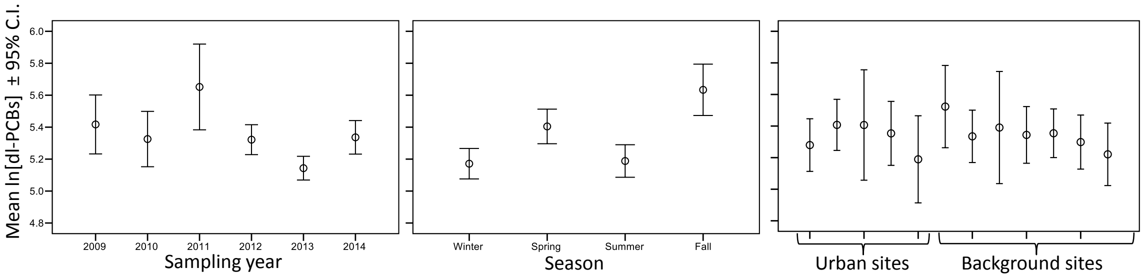

Figure 3. Log-transformed (ln) total dl-PCB amounts (fg) in field blanks according to the evaluated factors.

MDL scenarios and reported amounts of POPs in real samples: Variations in mean POP amounts reported in real samples according to the two MDL scenarios evaluated are presented in Figure 4. Mean values based on systematic MDLs for TCDD significantly (p<0.05) differed from those based on winter MDLs in 10 (3 cities and 6 background places) out of 13 localities and in four background sites in the case of OCDD. Neither mean value per year nor by season varied significantly between the systematic and winter MDLs for TCDD or OCDD. In spite of the significant effect in the studied sites, mean variation of TCDD values reported in real samples based on winter and systematic MDLs only exceeded 10 % in one urban site and three background places (Figure 4). In the case of OCDD, mean differences only exceeded 10 % of variation in two background sampling sites. Greater variations corresponded with those sites where PCDDs were found at the lowest levels with several cases below the MDL.

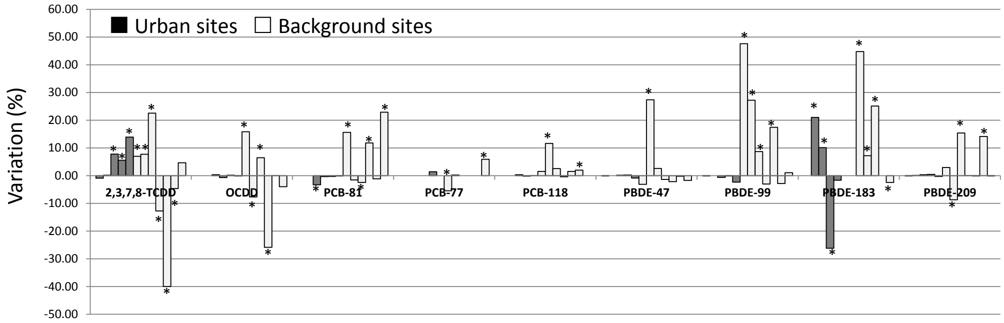

Figure 4. Variations (%) in total amount of selected POPs found in real samples between the two MDL scenarios evaluated. The * indicates significant differences (repeated measures t-test; p<0.05) between datasets.

Mean values according to sampling site varied significantly in five sites for PCB-81 and in two sites for PCB-77 and PCB-118 (Figure 4). Mean yearly values also varied significantly (p<0.05) in three years for PCB-81 and 118 and in one case for PCB-77. In the case of mean values according to season, significant differences were detected at least in one season for the three selected PCBs. In spite of the significant variations of PCBs according to different factors, variations (%) in mean values were usually lower than those found for PCDD congeners (Figure 4). Mean yearly and seasonal values based on winter MDL varied in less than 5% in relation to those based on systematic MDLs for the three selected PCBs. In the case of sampling site, mean value differences were lower than 10% for PCB-77 and -118 in all cases, but in the case of PCB-81 three remote sites showed variations greater than 10% (12-26%). As in the case of PCDDs, greater variations corresponded with those sites that showed the lowest PCB amounts.

Mean PBDE amounts based on the two MDL scenarios varied significantly in all years and seasons and in most sites for PBDE-183 (Figure 4). Mean yearly values varied significantly in three years for PBDE-99 and 209, and in no one for PBDE-47. Mean PBDEs per site varied significantly in four, three and one sites for PBDE-99, -209 and -47, respectively. Mean seasonal amounts varied significantly in three seasons for PBDE-99, in two for PBDE-209, and in no one for PBDE-47. The magnitude of all these variations strongly varied among PBDE congeners. Mean variation for PBDE-138 ranged from 1.8 to 51 %, being above 20% in most cases for the studied years, sites and seasons. In contrast, variations for PBDE-47, -99 and -209 were below 3% in most cases for sampling sites, years and seasons. As found for chlorinated compounds, significant variations in reported concentrations mainly occurred at sites where analytes where commonly found at very low levels

Significant differences were also detected when evaluating the effects of sampling site, year and season in data reported in real samples depending on the MDL treatment. For both datasets sampling site showed a significant effect ($p<0.001$) on TCDD. However, pairwise comparisons among sites differed among MDL treatments. Twelve significant pair comparisons were found for TCDD under the systematic scenario while twenty-one were found under the extreme scenario. Therefore, the significance level changed in the case of 9 pair-comparisons. In the case of OCDD only two pair-comparisons changed their significance between the datasets. Four or less pair-wise comparisons changed their significance depending on the MDL treatment for each of the studied PCBs. For PBDEs, changes in significant effects on pairwise comparisons between localities were detected in three, four and eight pair comparisons for PBDE-47, 209 and 99, respectively. In contrast, 32 pair comparisons changed in the case of PBDE-183. No changes in the effect of sampling year and season in reported amounts of the studied PCBs and PCDDs according to MDL treatments were detected. However, in the case of PBDEs, pair comparisons among years changed the significance in five cases for PBDE-183 and in one case for PBDE-209.

Our results suggest how the number of field blanks used in monitoring programs based on PUF-PAS can significantly influence the final reported results. Reported amounts in real samples show very low variations (%) for those analytes commonly found at high levels. In contrast, great variations in reported POPs took place for those analytes or sites showing very low levels. More importantly, reported data based on the two MDLs evaluated showed significant differences in the effects of sampling site and year. This could lead to important bias when evaluating spatial or temporal patterns in POP air concentrations. Our results clearly suggest that the number of field blanks can significantly shift reported POP concentrations in air based on PUF-PAS, at least for the target analytes studied here. However, further studies are yet needed to accurately evaluate the influence of the number of field blanks in other POPs, as well as in the total amounts of POP families reported under different MDL scenarios. With this information we will be able to optimize the number of blanks and reduce the economic cost and time consuming investment in the field blank treatment. Meanwhile, one field blank per obtained sample seems to be the most suitable procedure to avoid significant shifts in reported air POP concentrations.

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