Interlaboratory study of organophosphate ester injection ready test mixtures

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Introduction

Organophosphate esters (OPEs) are a group of flame retardant chemicals that have been in use for over 150 years (Andrae, 2007). OPEs have been applied to a wide range of commercial products such as: textiles, rubber, polyurethane foam (PUF), cellulose, cotton, electronic equipment cables, casting resins, glues, engineering thermoplastics, epoxy resins, and phenolic resins, to meet and comply with fire safety codes, standards, and regulations (van der Veen and de Boer, 2012). Other uses of OPEs have been reported; for example, tris(2-chloroethyl) phosphate (TCEP) is also used as a plasticizer in the production of polyvinyl chloride (Björklund et al., 2004). Contamination of indoor air and dust, outdoor gas and particle phase, lakes, river sediment, and lacustrine and marine biota, across Europe, USA and Japan is well documented (Marklund et al., 2003; Andresen et al., 2004; Björklund et al., 2004; Leonards et al., 2011; Salamova et al., 2016; Venier et al., 2016; Guo et al., 2017).

The aims of this interlaboratory study were: to evaluate, through the application of statistical analyses, the quality of the performance of the participant's measurement technology; to improve quality by supplying feedback to the participants; and to suggest general precautions that need to be taken during the analysis of OPEs. The overarching goal of this study was to contribute to improving the reliability and quality of the OPE data reported in literature. The study was designed to address the variability associated with OPE analyses and also to compare the precision and accuracy of data generated for both individual target analytes and different laboratories. Additionally, the use of specific analytical instrumentation and methodology were investigated to determine if particular analytical techniques were associated with better performance.

Materials and methods

Eleven participating laboratories were asked to analyze 16 OPEs (Triethyl phosphate (TEP); Tri-n-propyl phosphate (TnPP); Tri-n-butyl phosphate (TnBP); Tris(2-butoxyethyl) phosphate (TBOEP); 2-Ethylhexyl diphenyl phosphate (EHDP); Tris(2-ethylhexyl) phosphate (TEHP); Tris(2-chloroethyl) phosphate (TCEP); Tris[(2R)-1-chloro-2-propyl] phosphate (TCIPP); Tris(1,3-dichloro-2-propyl) phosphate (TDCIPP); Tris(2,3-dibromopropyl) phosphate (TDBPP); Triphenyl phosphate (TPhP); Tri-o-tolyl phosphate (TOTP); Tri-m-tolyl phosphate (TMTP); Tri-p-tolyl phosphate (TPTP); Tris(3,5-dimethylphenyl) phosphate (TMDPP); Tris(2-isopropylphenyl) phosphate (TIPPP)) in two injection ready solutions prepared and tested by Wellington Laboratories Inc. (Guelph, Ontario, Canada; certified ISO 9001:2008, ISO/IEC 17025:2005, and ISO Guide 34:2009). One solution had low concentrations, and the other had high concentrations of the target analytes, relative to a range of reported indoor and outdoor environmental concentrations. The test mixtures were prepared from stock solutions using calibrated NIST-traceable Class A volumetric glassware. All stock solutions were prepared gravimetrically (weight/volume) through the dissolution of an accurately weighed amount of the OPE in a suitable organic solvent.

The exact concentrations (reference values) in the test mixtures were not shared with the analyst until after the analysis. In order to aid in the selection of appropriate instrument settings, calibration curves, etc. approximate concentration ranges for each target analyte were provided.

All eleven participating laboratories are currently involved in the analysis of OPEs in environmental matrices. The samples were analyzed using each laboratory's routine methods. If any target OPEs were not included in their established suite of analytes, laboratories could choose to omit them from their analysis. Participating laboratories were asked to determine each test mixture in three independent replicates, report results individually in nanograms per milliliter (ng/mL), and provide details of instrumentation and analytical methods used.

In order to evaluate the overall performance of the participating laboratories and assess the precision and accuracy of the reported values, statistical analyses were performed on the collated data comparing the concentrations reported by each lab with the reference values provided by Wellington Laboratories Inc. Statistical analyses for consistency, repeatability, reproducibility, and bias were based on ISO 13528. All statistical analyses were performed using either Microsoft Excel 2013 or IBM SPSS Statistics 24. Laboratories are only identified by number/letter codes to preserve their anonymity.

Results and discussion

Target analytes with the highest mean absolute percentage bias and therefore poorest accuracy amongst laboratories were: TOTP and TMTP (both 10.3 %), TBOEP (18 %), and TPhP (21 %) for the low-concentration test mixture; and TOTP and TPhP (both 9.0 %), TnBP (9.2 %) and TMTP (14 %) for the high-concentration test mixture (Table 1).

Figs. 1 and 2 show the distributions, medians and reference values for the low- and high-concentration test mixtures analyzed by the 11 laboratories, respectively. Of particular note were discrepancies between the reference value and laboratory means for TCEP, TBOEP, TOTP and TDBPP.

Table 1 Exceedances of the 25 % percentage bias accuracy threshold by laboratory.

Lab #	Number of reported analytes	% exceedances - low concentration test mixture	Analytes for which accuracy threshold is exceeded	% exceedances - high concentration test mixture	Analytes for which accuracy threshold is exceeded
1	15	13	TnBP, TDBPP	0	
2	15	47	TBOEP, EHDP, TEHP, TPhP, TMTP, TPTP, TIPPP	0	
3	14	0		0	
4	14	7	TPhP	0	
5	6	50	TnBP, TBOEP, TCEP	17	TBOEP
6	16	44	TEP, TCEP, TCIPP, TPhP, TMTP, TPTP, TIPPP	13	TDBPP, TPTP
7	16	50	TBOEP, TEHP, TCEP, TCIPP, TDBPP, TPhP, TOTP, TPTP	13	TBOEP, TPTP
8	11	0		0	
9	14	36	TCIPP, TPhP, TPTP, TDMPP, TIPPP	50	TnBP, EHDP, TPhP, TMTP, TPTP, TDMPP, TIPPP
10	16	0		0	
11	16	6	TDCIPP	6	TDCIPP

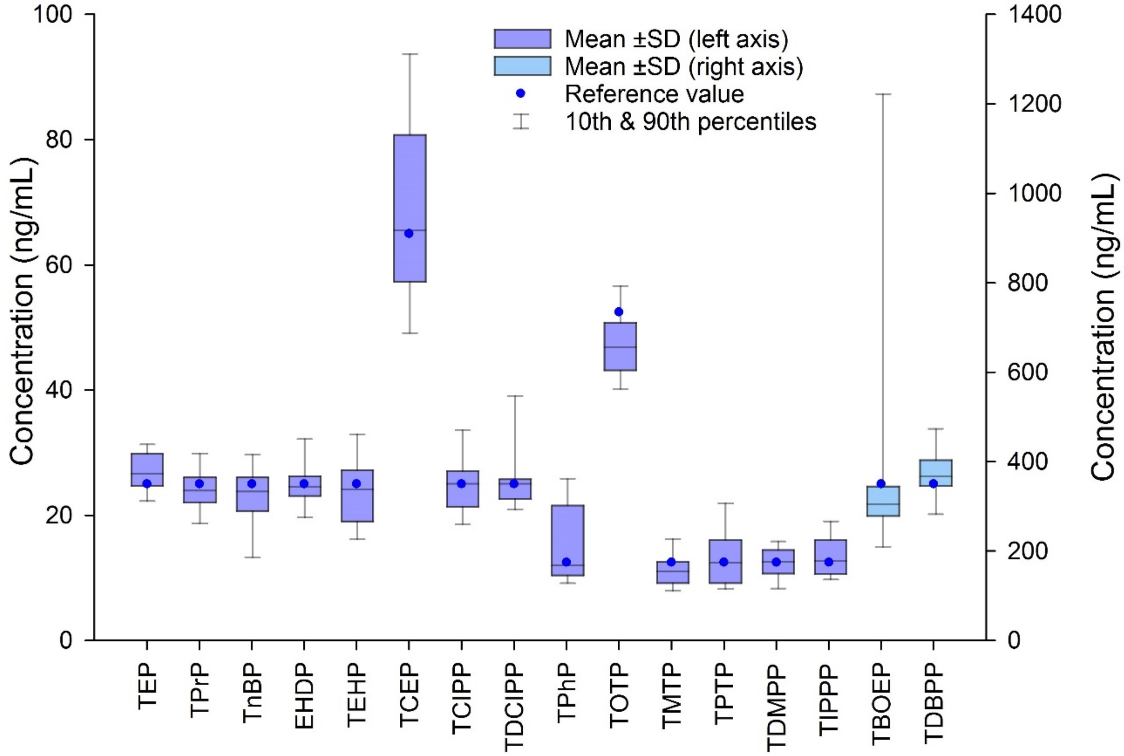

Figure 1 Comparison of the median of laboratory measurements (*black bar*) and actual test mixture reference values (*blue circle*) for low-concentration test mixtures. The *colored boxes* indicate the standard deviation for all laboratory measurements, and the whiskers indicate the 10th and 90th percentiles. TBOEP and TDBPP use the right axis.

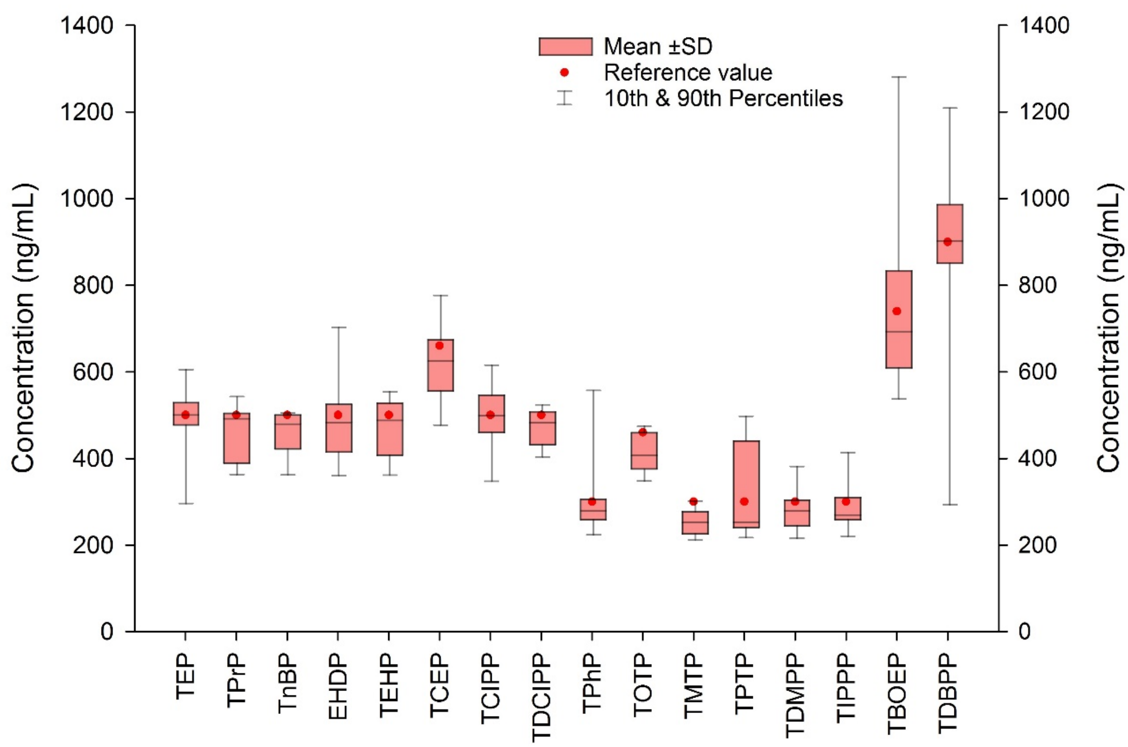

Figure 2 Comparison of the median of laboratory measurements (*black bar*) and actual test mixture reference values (*red circle*) for high-concentration test mixtures. The *colored boxes* indicate the standard deviation for all laboratory measurements, and the whiskers indicate the 10th and 90th percentiles.

In this interlaboratory study, TDCIPP performed relatively better for low-concentration test mixtures than for those reported in the INTERFLAB study for "novel flame retardants" (NFRs) (Melymuk et al., 2015). Overall absolute zeta-scores (ζ-scores) for TDCIPP were greatly improved with 68 % of laboratory scores within the satisfactory range, compared to just 30 % of laboratory scores in the INTERFLAB study. This perhaps suggests that recommended improvements to the analyses of this compound have been adopted by laboratories and that enhancements to analytical methodologies have taken place. However, the performance of TBOEP was poorer in this current OPE study than for the INTERFLAB one, with 70 % of laboratories scoring critical/unsatisfactory overall absolute zeta-scores, and a higher overall mean zeta-score of 11, compared to 5 in the NFR study.

Of the eleven participating labs, 5 reported using GC-MS, 2 GC-MS/MS and 4 LC-MS/MS. Labs using LC-MS/MS obtained the best performances for both accuracy and precision in both the low- and high-concentration test mixtures for analyzed OPEs.

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