RESULTS FROM UNEPs 2ND GLOBAL INTERLABORATORY ASSESMENT: DIOXINLIKE POPs.

van Bavel B[1],van der Veen I[2], Nilsson H[1], de Boer J[2] and Fiedler H[3]

[1] Örebro University, School of Science and Technology, MTM Research Center, SE 70182 Örebro, Sweden
[2] VU University, Institute for Environmental Studies (IVM), De Boelelaan 1087, 1081 HV Amsterdam, The Netherlands
[3] UNEP Chemicals, Rue des Anemones, Geneva, Switzerland

Introduction

To assist laboratories to improve the quality of their analysis, UNEP has organized regional capacity building and training programs, which started in 2009. As part of this activity, the first round of the Global Interlaboratory Assessment on Persistent Organic Pollutants was organized in 2011-2012 [Abalos et al., 2013]. The "Report on International Intercalibration Studies" (UNEP 2005) emphasizes the importance of accurate results in POPs analysis, with an analytical variance to be as small as possible in order to make data acceptable and comparable between laboratories, countries, and regions, so as to allow sound decision making. Participation at international intercalibration studies is considered a prerequisite for existing and well established as well as for newly set-up laboratories because there is a need to permanently check the laboratory's performance and 'prove' their capabilities. From an international quality assurance point of view, world-wide international studies are preferred, but national initiatives could also improve the analytical quality in just that country or a region.

Interlaboratory assessment or proficiency testing (PT) programs can be used to assess both methodology and laboratory performance. UNEP has initiated such studies for the POPs on the Stockholm convention in several matrixes with the first round taking place in 2009/10 covering the traditional POPs [Abolas et al. 2013, van Leeuwen et al. 2013]. One of the aims of 2nd round of the UNEP assessment was to evaluate if the quality of the analysis of the Stockholm Convention POPs has improved globally and in different regions. This important in order to assure the quality of the data to be submitted to UNEP Global Monitoring Program [Fiedler et al. 2013]. Here we discuss the results of the dioxin-like POPs (dl-POPs) including both PCDF/PCDD and planar/mono-*ortho* PCBs.

Materials and methods

All laboratories were offered to register for a total of eight different matrices and six different groups of compounds including dioxin-like POPs (dl-POPs). The samples were distributed to the laboratories in December 2012 together with detailed instructions of required report format. The participants were encouraged to use their in-house methodology for the analysis of the target compounds and thus laboratories used their own extraction and clean up protocols, spiking schemes and QA/QC validation procedures. Often these protocols were based on standard methods such as EPA 1613 or EU1948. Upon completing the tests, each laboratory electronically submitted their data to the coordinators (MTM Research center, Örebro University, Sweden and VU University, Amsterdam, The Netherlands). All results were compiled and send back to the participants for a final control of transcription errors.

Samples

The sediment sample was marine sediment from the Netherlands, which was dried at 40 °C and sieved (0.5 mm pore size). After homogenization, individual plastic containers were filled with the test matrix and stored at room temperature until shipment. The samples were obtained from WEPAL. The fish material consisted of a pike-perch filet from the Netherlands. After cutting and homogenizing, individual glass jars were filled with the material. The jars were sterilized by autoclaving, which made it possible to store the fish sample at room temperature before opening of the jar. The mother's milk test material consisted of homogenized mother's milk from the Swedish mother milk bank in the Örebro region. Fifty mL milk was packaged in polypropylene bottles

and frozen prior shipment. The air extract was a raw polyurethane foam (PUF) extract in toluene, taken near one of Sweden's largest hazardous waste incinerations (HWI). The extract was diluted in 100 mL toluene. Of this extract, 1 mL was packaged in a sealed glass ampoule. In addition a standard solution with unknown concentrations of PCDD/DF and dl-PCB was send to all participants.

Results and discussion

The data assessment was carried out according to the principles employed in the data assessment of the QUASIMEME proficiency testing organisation (www.quasimeme.org). All data received from the participants were entered into a database and assessed using a standard procedure to allow direct comparison between participants. The approach of the assessment is based on the standard, ISO 13528 (2005), the IUPAC International Harmonised Protocol for Proficiency Testing (Advanced Draft) by Thompson et al. (2006). Additions or differences in the assessment from these standards are given or referred to in this report. However, the assigned value, the between-lab CV values and the laboratory assessment using z-scores are based on the Cofino Model (Cofino et al., 2000).

As an example the results for the standard solution is given in Figure 1 and 2 for the PCDD/DFs and dl-PCBs showing the interlaboratory variation , the UNEP criteria and the distribution of the laboratories per region. The results for the standard solution, the air extract, the sediment and the human milk sample were good to excellent based on the TEQ. However the fish sample caused major problems and no consensus value could be statistically calculated from the 38 entries for the PCDD/PCDF TEQ and 41 entries for the dl-PCB. The levels in the fish (concerning dioxins) were relatively low; however, with the use of high resolution GC/MS systems, this should not be a problem. A problem might be that dl-POPs levels are often reported on lipid basis, although in the instructions it was clearly stated that levels should be reported on wet weight to avoid error introduced by the lipid determination. For several of the dl-PCB (present at higher levels) a consensus value could be calculated but the CV varied from 29% to nearly 100%, again with the higher values for levels just above the LOD of most laboratories.

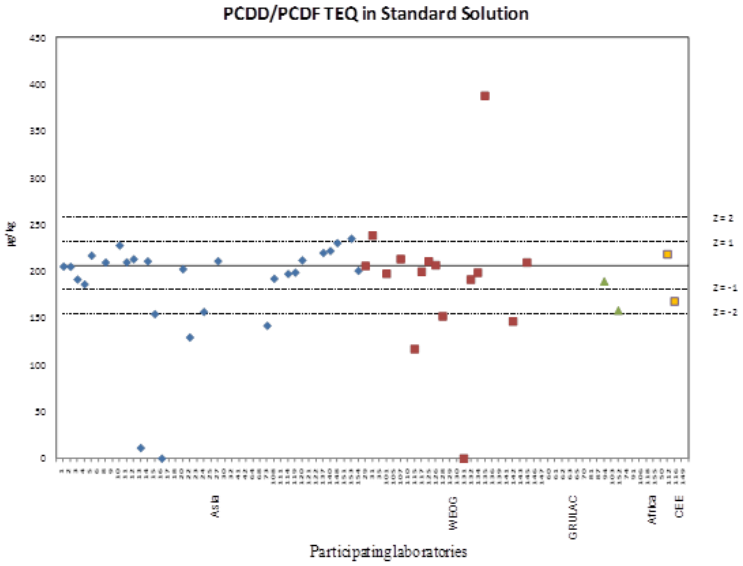

Figure 1. Results for the PCDD/PCDF TEQ in the standard solution. Laboratory code on the x-axis, concentration in µg/kg on the y-axis. The assigned value given by straight line, z = ± 1 (12.5%) and z = ± 2 (25%) are given by the dotted lines. The blue ♦ symbols represent Asia, The red ■ symbols represent WEOG, the green ▲ symbols represent GRULAC, the yellow ● symbols represent Africa and the orange ■ symbols represent CEE.

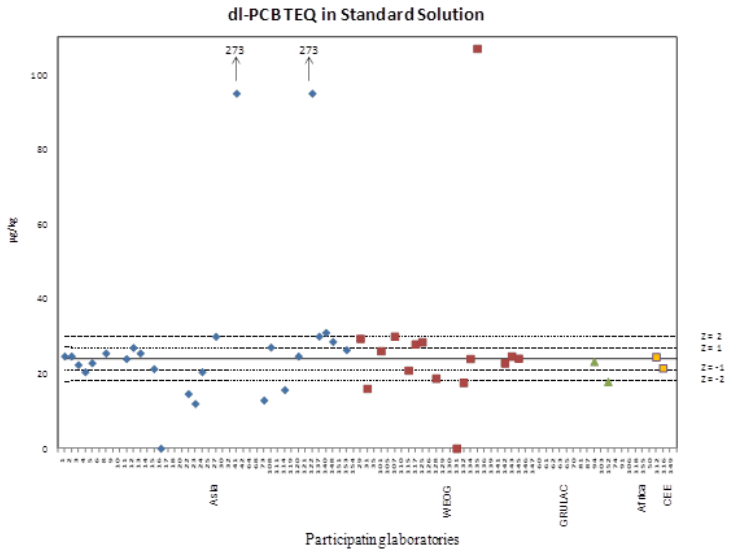

Figure 2. Results for the dl-PCB TEQ in the standard solution. Laboratory code on the x-axis, concentration in µg/kg on the y-axis. The assigned value given by straight line, z = ± 1 (12.5%) and z = ± 2 (25%) are given by the dotted lines. The blue ♦ symbols represent Asia, The red ■ symbols represent WEOG, the green ▲ symbols represent GRULAC, the yellow ● symbols represent Africa and the orange ■ symbols represent CEE.

The results for the standard solution for the TEQPCDD/PCDF were good in both studies - below 10% - and thus in agreement with the UNEP criteria of 12.5%. The results for the air samples improved substantially from over 20% to less than 10%. However, it should be noted that the sample for the second round was an extract compared to a fly ash sample in the first round. It has been found difficult to find a sample which would mimic a passive sampler PUF and to be distributed to a large number of laboratories. The results for the sediment sample were substantially better and improved to 12% for the second round. This is also in line with UNEPs criteria. These results are in agreement with several other studies on dioxin in standard solutions, sediments and incineration related samples (van Bavel and Abad 2008).

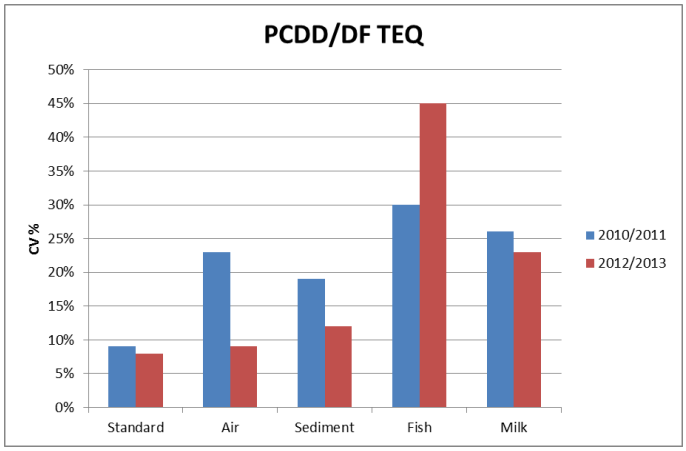

Figure 3: Comparison of the performance for the PCDD/PCDF TEQ analyses between the two ILS (% CV).

However, for the fish sample, the already large variation observed in the first round became even larger in the second round. The 45% variation is both disappointing and far from the UNEP guidelines. These results are not in agreement with other studies using fish samples (Becher at al. 2004) where better results were observed. No obvious reason could be found for the large variation in both studies. The level was high in the first fish sample and medium to high in the second. In an attempt to avoid variation of the lipid determination, all results were reported on wet weight basis but this did not seem to have any influence in either study.

It was further noted that levels in fish for dioxins are often reported in different units (with or without lipid normalization) and some misunderstandings might have resulted in reporting in the wrong unit. However all laboratories were allowed to change the unit after an initial inspection of the results. The results of the milk sample were good, taking into account the low levels of dioxins present in the sample from Sweden, indicating the decreasing trend in dioxin levels in the general population in western countries. The results are promising, also taking into account that 12 additional laboratories analyzed the milk sample, thus totaling 29. Although the results improved somewhat for a large number of laboratories, the CV is still 23% and needs to be improved to meet the UNEP criteria.

Conclusion

Results for the PCDD/PCDF on a TEQ basis were good and within the UNEP criteria for the standard solution, the air extract and the sediment. Results for the fish sample were unsatisfactory for both the PCDD/PCDF and dl-PCB TEQ. The results for the dl-POP for the milk sample were promising but still not within the UNEP criteria. For the dl-POPs it should however be noted that the majority of the participating laboratories were located in Asia (Japan and China) and the WEOG, while only 2 laboratories from the GRULAC and the CEE region and no laboratory from Africa participated.

Acknowledgements:

WEPAL, Wageningen, the Netherlands is gratefully acknowledged for providing one of the test materials. Prof. Wim Cofino is gratefully acknowledged for performing the statistical analysis.

References:

1) Abalos, M., Abad, E., Van Leeuwen, S. P. J., Lindström, G., Fiedler, H., de Boer, J., Van Bavel, B. (2013). First Worldwide interlaboratory study on persistent organic pollutants: Chlorinated dibenzo-p-dioxins and dibenzofurans. TrAC Trends Anal Chem, 46, 99-109.
2) Van Leeuwen, S. P. J., Van Bavel, B., De Boer, J. (2013). First worldwide UNEP interlaboratory study on persistent organic pollutants (POPs): with data on polychlorinated biphenyls and organochlorine pesticides. TrAC Trends Anal Chem, 46, 110-117.
3) H. Fiedler, E. Abad, B. van Bavel, J. de Boer, C. Bogdal, R. Malisch. The need for capacity building and first results for the Stockholm Convention Global Monitoring Plan Trends in Analytical Chemistry, Vol. 46, 2013.
4) Thompson, M., Ellison, S. L. R., Wood, R. (2006). The International Harmonised Protocol for Profi-ciency Testing of Analytical Chemistry Laboratories. IUPAC Technical Report. Interdivisional Working Party for Harmonization of Quality Assurance Schemes. Pure Appl Chem, 78, 145-196.
5) Cofino, W. P., Wells, D. E., Ariese, F., van Stokkum, I. H. M., Wegener, J.-W., Peerboom R. J. (2000). Chemometrics and Intelligent Laboratory Systems, 53, 37-55.
6) Becher, G., Haug, L. S., Thomsen, C. (2004).World-wide comparison on the quality of analytical determinations of PCDDs/PCDFs and dioxin-like PCBs in food. Talanta, 63, 1115-1122.
7) van Bavel, B., Abad, E. (2008). Long-Term Worldwide QA/QC of Dioxins and Dioxin-like PCB in Environmental Samples. Anal Chem, 80, 3956-3964.