Biennial Global Assessment of POPs Laboratories, Second Round:

Workshop on Final Results and Training Course on Analysis of New POPs

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Prepared by:

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for

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Photo on title page: Participants at the final results workshop in Freiburg, Germany (in front of the “Haus zum Walfisch” [House of the Whale] where Erasmus of Rotterdam [1469 – 1536] lived during his exile because conflict with the Reformation). Photo courtesy of Dr. Rainer Malisch, CVUA Freiburg.

Annexes:

A) List of participants

B) Agenda Final Results Workshop

C) Final Agenda – Training Workshop on Analysis of New POPs

D) Summary of Discussion by Laboratories Present

Workshop on Final Results

1 OPENING OF THE WORKSHOP

1.1 Welcome by CVUA

The workshop on final results of the second round of the ´Biennial Global Assessment of POPs Laboratories´ was held on 24 and 25 June 2014, in Freiburg, Germany; there were 27 international participants from 18 different countries, four representatives from UNEP and eight scientists from the hosting institute (see Annex A). Mr. Rainer Malisch introduced the State Institute for Chemical and Veterinary Analyses of Food (CVUA) in Freiburg, which has multiple functions:

- Institute of the German Federal State "Baden Württemberg" for the official food control and animal health,
- European Union Reference Laboratory (EURL) for Dioxins and PCBs in Food and Feed,
- European Union Reference Laboratory (EURL) for Pesticides in Food of Animal Origin and Commodities with High Fat Content, and
- UNEP/WHO Reference Laboratory for POPs in human milk.

According to the EU legislation on official controls of feed and food, animal health and animal welfare, there are three levels of laboratories: (i) official laboratories; (ii) National Reference Laboratories (NRLs) and (iii) EU Reference Laboratories (EURLs). EURLs were established in 21 sectors for feed and food and 13 sectors for animal health and life animals. Main tasks are provision of scientific and technical support to the EU Commission and analytical support to NRLs, which support the official laboratories. For the proper implementation of official controls, the performance of laboratories is of outmost importance. Therefore, the EURLs organize proficiency tests (PTs) for NRLs and official laboratories annually. The successful participation in these PTs has to be documented. Results are discussed at annual workshops of the EURL/NRL network (for more details, see chapters 3.1 and 3.2).

1.2 Welcome and objectives of the UNEP workshop and training course

Ms. Heidelore Fiedler, Senior Scientific Affairs Officer at the United Nations Environment Programme (NEP) Chemicals Branch, DTIE and coordinator of the first and second round of the interlaboratory assessment, delivered some opening statements including welcome on behalf of UNEP, the European Union, who financed the interlaboratory assessment, and the Global Environment Facility (GEF), the second donor for this project. She expressed greetings from the secretariat of the Basel, Rotterdam and Stockholm conventions and the UNEP GEF coordination group at Chemicals Branch, who were invited to the workshop but unable to attend.

She then explained the objective of the workshop as well as the training course, namely to discuss the results of the second round of the interlaboratory assessment and lessons learned as well as to equip participants with the practical tools and knowledge to improve their performances in analysing POPs, respectively. She noted that the workshop and the training were the final activities of the second round of the interlaboratory assessment and the Global Environment Fund (GEF) Project ´Establishing the Tools and Methods to Include Nine New POPs into the Global Monitoring Plan´´. Ms. Fiedler also introduced the agenda of the workshop (Annex B).

1.3 Introduction of the participants

A round of introduction followed, during which the participants were given an opportunity to introduce themselves. A complete list of participants, including contact details, is provided in Annex A.

2 PRESENTATIONS ON THE INTERLABORATORY ASSESSMENT

2.1 Introduction and context

The workshop proceeded with Ms. Fiedler making reference to UNEP's capacity building programme for laboratories analysing POPs, which had been initiated in 2005 with GEF funding. She quickly introduced its various elements. As she outlined, the interlaboratory assessment was an essential component of this capacity-building programme and aimed to assist laboratories to improve their performance in analysing POPs. It implemented the recommendations by the Conference of the Parties to the Stockholm Convention (SC COP) as had been expressed in the guidance document for the Global Monitoring Plan (GMP) under article 16 of the Convention. She explained that the GMP required that POP laboratories must be capable, at any time, to analyse samples for POPs within a margin of ±25%.

Ms. Fiedler informed that the initial basic POPs and dioxin-like POPs (dl-POPs) had been analysed in seven laboratories in 2006/2007 during the UNEP Capacity Building Pilot Project for training and interlaboratory study of POPs. She also provided an overview of the first round of UNEP's ´Bi-ennial Global Interlaboratory Assessment on POPs´, including results for dl-POPs as well as basic POPs, which was implemented in 2010/2011. She highlighted that in this assessment, the results for dl-POPs had been unexpectedly good, most notably for standard solution. The weakest results had been obtained for fly ash. As regards basic POPs, she concluded that typically the instrumentation equipment in POPs laboratories around the world are capable to separate and identify individual POPs (although not all of them). Meanwhile, less than half of the laboratories performed satisfactory for naturally contaminated test samples.

Recognizing the importance of accurate data for the effectiveness evaluation to monitor changes of POPs concentrations in humans and the environment, the European Union through an ENRTP project and the Global Environment Facility through a medium-sized project to develop the tools and methods for the analysis of new POPs have financed the second round of the UNEP-coordinated "Bi-ennial Global Interlaboratory Assessment on Persistent Organic Pollutants", which was implemented in 2012/2013 together with international partners (MTM Research Centre Örebro University, Sweden and IVM VU Amsterdam, the Netherlands). For the second round, 105 laboratories participated in the so far largest proficiency test covering 23 POPs, seven standard solutions and seven naturally contaminated test samples. Of these, 89 laboratories from 48 countries and all UN regions had submitted results for this assessment, with Asia being the highest in number (Figure 1).

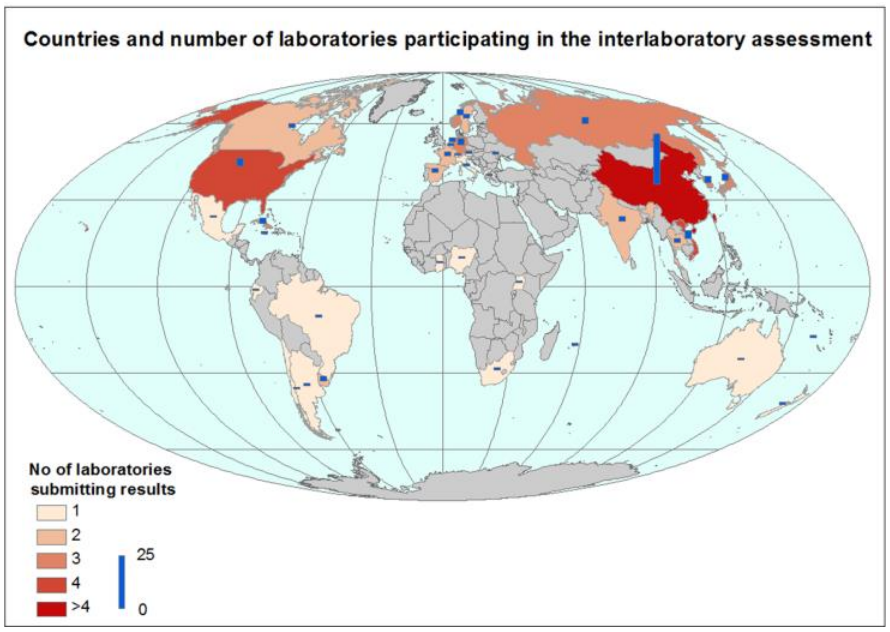


Figure 1: Graphical sketch representing the countries that had laboratories submitting results for the POPs interlaboratory assessment (in 2012/2013). Noteworthy, 25 laboratories from China but also good representation from OECD (including EU) countries.

Ms. Fiedler explained the origins and preparation of the naturally contaminated test samples (sediment, fish, mothers' milk, human blood serum, air extract, water and transformer oil) that had been submitted to laboratories for analysis in the second round.

Figure 2: Preparation of the water test sample using surface water from Amsterdam harbour Photo courtesy Dr. Jacob de Boer, IVM VU Amsterdam

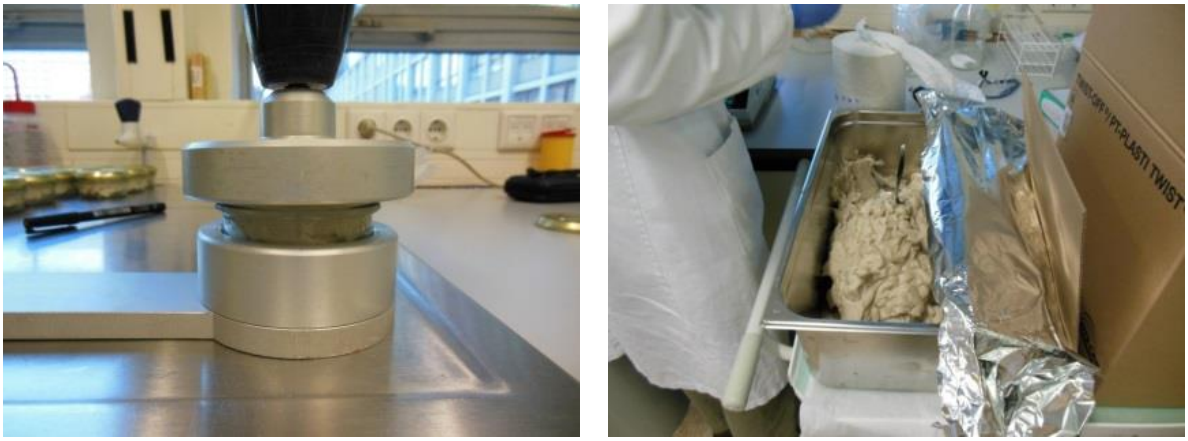


Figure 3: Preparation of the fish test sample for analysis of all POPs (courtesy of Dr. Jacob de Boer, IVM VU Amsterdam)

Figure 4: Mothers' milk test sample for analysis of all POPs as shipped to participating laboratories (photo courtesy of Dr. Bert van Bavel, MTM Research Centre, Örebro University)

Figure 5: Test samples were ampouled and shipped to laboratories; here: PFAS standard solution and human serum for PFOS analysis Photo courtesy of Dr. Bert van Bavel, MTM Research Centre, Örebro University, Sweden

She outlined how many of the 26 laboratories present at the workshop had submitted results for each of the samples and POPs, stressing that coverage had been complete only for the standard solution and generally weakest for human blood, followed by mothers' milk and air extract. According to POP, the highest turnout had generally been for OCP, followed by PCB, and the lowest for PFOS followed by PBDE. She stressed that the lowest number of laboratories reporting OCP had been in mothers' milk and air extract; for PCB in transformer oil followed by mothers' milk; for PCDD/PCDF in mothers' milk followed by sediment; for dl-PCB in mothers' milk followed by air extract; for PBDE in air extract followed by mothers' milk; and for PFAS in mothers' milk followed by human serum and air extract. She also emphasized that Africa had not submitted any results for PCDD/PCDF and dl-PCB. Very few laboratories from the Group of Latin American and Caribbean States (GRULAC), Africa and Central and Eastern Europe (CEE) had submitted results for PBDE and none of these had reported for PFAS.

She explained that the assessment had been made according to the ISO 17043 standard and that z-scores were calculated to assess performance in three categories: satisfactory, questionable and unsatisfactory. She provided an overview of the overall rate of satisfactory performance and then went into detail regarding the performance per group of POPs and test sample: For OCPs, performance had been most satisfactory for the standard solution. However, performance had been generally weak, with often far less than 50% satisfactory results for the large majority of analytes. As Ms. Fiedler concluded, naturally contaminated samples were a challenge for most laboratories. The variation in the data (as measured by the coefficient of variation (CV)) had been most pronounced for the sediment samples and generally in the case of endosulfan, indicating widespread problems in the analysis. For PBDE, performance had been best for sediment and worst for fish, but generally favourable with relatively low CV values. Looking at OCP in mothers' milk, the CV had been highest for endosulfans and lowest for HCHs. Chlordanes had the highest inclusion rate, indicating few outliers. For DDT, the rate of satisfactory results had been highest with 47%; however, 29% received extreme z-scores, potentially indicating errors in calculation or unit reporting. For the air extract, CV values had been lowest for drins and chlordanes, for which satisfactory results had also been most widespread. Meanwhile, the highest number of outliers had been observed for drins. Again, a considerable amount of highly irregular data had been reported for all analytes. For PCB, performance had been best. For PBDE, laboratories had most problems in analysis the fish sample and had been most successful when testing the sediment, as indicated by the CB and z-scores. For PFAS, laboratories had shown excellent performance in analysing human serum. The results were similarly satisfactory for the standard solution, although the CV value was much higher. The submitted results had been too few and too diverging, and there had been too many outliers to calculate z-scores for the air-extract data. For several other compound classes, too, no assigned value could be calculated. Ms. Fiedler concluded with acknowledgements, thanking those who contributed towards and participated at the interlaboratory assessment and the workshop. She highlighted that the funding had been provided by the EU and the GEF.

She concluded by stating that the results allow to draw the following conclusions: laboratories in developed and developing countries are aware of the importance of high quality POPs data and are willing to check their performance on regular intervals. The results provide clear indications where further training and capacity building is necessary and geographically where expertise in POPs analysis is located. For example, capacity and experience to analyse PFOS and precursors only exists in WEOG and some Asian countries (Japan and China), only one laboratory in Africa and GRULAC analysed brominated flame retardants. With respect to test sample type, most difficulties were encountered analysing fish samples and poorest results were for (simple) POPs pesticides such as DDT or endosulfan.

2.2 Overview on the intercalibration data of dioxin-like POPs (dl-POPs)

Mr. Bert van Bavel, from Örebro University, Man-Technology-Environment Research Center (MTM), one of the organisers of the interlaboratory assessment, presented an overview of the intercalibration data of dioxin-like POPs (dl-POPs). Mr. van Bavel began his presentation by re-iterating the objective of confirming a 50% decline in the levels of POPs within a 10-year period, as had been outlined in the guidance document for the GMP. He proceeded to briefly discuss the state of the art in the analysis of dl-POPs, referring to the many years of intercalibration studies for PCDD/PCDF with around 100 laboratories participating each year and providing more than 100,000 data points. These constitute an important tool for quality assurance and quality control (QA/QC). In 2010, the relative standard deviation (RSD) in dl-POPs analysis was below 20% for fly ash, below 15% for soil/sediment and below 10% for standard solution.

He then moved on to the second round of the interlaboratory assessment for POPs, listing the sample types and mentioning that laboratories had been asked to double-check their data, so as to avoid for instance calculation errors. He explained how the samples were packed and shipped to the laboratories and mentioned some problems that had occurred. Next, methodological issues regarding the analysis of dl-POPs were discussed. Mr. van Bavel emphasized the importance of internal QA/QC. He briefly talked about the reporting procedure for dl-POPs. Next, he explained the statistical analysis conducted for comparing the data. For data that do not follow a normal distribution, the 'Cofino' model, which included all data in the assessment, had been used. The assigned value had been based on the consensus value, provided by the Cofino model, without any trimming of the data. He explained the Horowitz equation.

Mr. van Bavel noted that 90 out of 105 participating laboratories had reported data and presented an overview of participation per compound class. Regarding dl-POPs most data had been received for the standard solution. He continued to discuss results for the standard solution for PCDD/PCDF and dl-POPs, emphasizing that there had been some extreme outliers, and discussed a summary of the standard solution for dl-POPs.

For the fish test sample, the results had been so scattered that no consensus value could be assigned (Cofino statistics). For human milk, although the concentrations had been lower, the performance had been better than for fish.

When comparing the results for coefficients of variation (CVs) from the first and second round of the interlaboratory assessment, Mr. van Bavel noted that the overall performance for PCDD/PCDF had improved significantly for the analysis air and sediments and slightly for standards and milk, whereas for fish samples a significant CV increase was observed which is a deterioration as result of a higher variation of these results. For dl-PCB, in all groups an increase of CV was observed, most notably so for the fish. Mr. van Bavel concluded on dl-POPs by stating that the results of the second round had overall been good and in agreement with other assessments. The results for the air test sample for both PCDD/PCDF as well as dl-PCB had been very good with very low RSDs. He emphasized the uneven distribution in terms of performance across regions, with the WEOG and Asia showing better performances. He also mentioned some areas for improvement, noting that more experience was needed, particularly for fish samples, and emphasizing the importance of frequent participation in interlaboratory assessments.

2.3 Overview on the intercalibration data of perfluoroalkyl substances (PFAS)

In his second presentation, Mr. van Bavel addressed the intercalibration data for perfluoroalkyl substances (PFAS) including perfluorooctane sulfonic acid (PFOS). PFOS has been listed in Annex B of the Stockholm Convention at its 4th meeting of the Conference of the Parties in 2009. In this interlaboratory assessment, the test samples of water and human serum was designed for PFOS analysis; no other POPs were included.

He noted that only eight laboratories had reported results for PFAS in human blood. For water and PFAS, 30 laboratories submitted, for sediments and fish nearly 20.

The test sample of air extract had been spiked with PFOS since it was assumed that the natural contamination may not have been high enough to allow for PFAS analysis. The results indicated that the variation for an extract had been relatively high. He stressed that the precursor compounds in the air (PUFs) needed improvement.

The following percentages of laboratories participated satisfactory (z-score < 2):

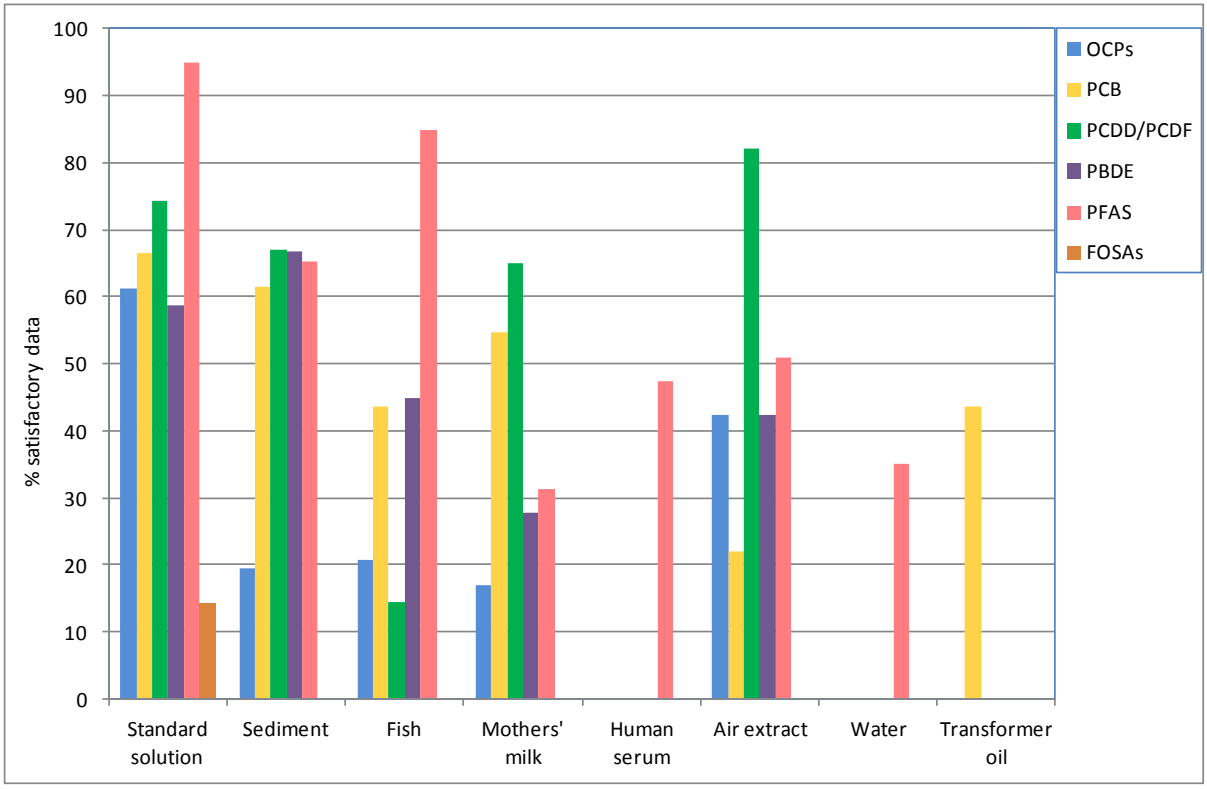
- Sediments: 89 % for PFOS, 42 % for FOSA (perfluorooctane sulfonamide)
- Fish: 84 % for PFOS, 86 % for FOSA
- Human milk: 63 % for PFOS, NA for FOSA
- Human blood: 50 % for PFOS, NA for FOSA
- Water: 19 % for PFOS, 10 % for FOSA
- Air: 44 % for PFOS, 57 % for FOSA

As a result, some improvements are needed. In general, capacity building is necessary in the three developing country regions (Africa, CEE, GRULAC) and large parts of Asia-Pacific region. UNEP's support would be needed to do so.

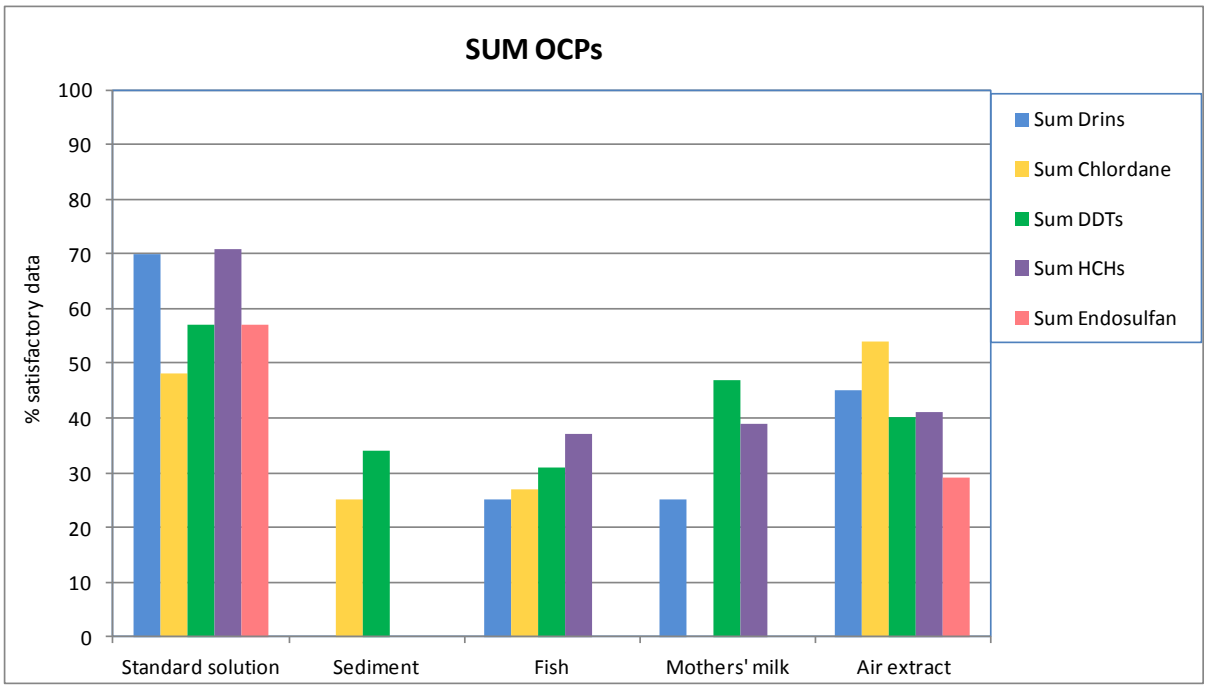
2.4 Overview on the intercalibration data of "basic POPs" and polybrominated diphenyl ethers (PBDE)

Mr. de Boer from the Institute of Environmental Studies (IVM), VU University, Amsterdam, continued with a discussion of results of the second interlaboratory assessment with particular focus on "basic POPs" (= initial POPs without dioxin-like analytes). He quickly discussed the test samples and target compounds and then proceeded to explain the statistical evaluation method, among others explaining how the z-score had been calculated and how it had been used to categorise performances.

The following figure summarizes the percentage of satisfactory z-scores for all analyte classes:



The following figure proves the need for improvement of the performance for ”basic POPs”, as only about 25 %– 55 % of the results for the test matrices were satisfactory.



Mr. de Boer stressed bad results for the indicator PCB in air (CV of 71%), whereas the CV for PCBs in other matrices had been in the range of 21% to 28%. With regard to high CVs for Dieldrin (in fish: 111 %, in sediments: 86 % - in air: 26 %), he assumed that there might have been a problem with the clean-up during the analysis of drins. As regards DDTs, the high CVs (range 43 %–79 %) may be

explained that glass wool has been used in the liner. He emphasized that certain DDTs would degrade.

He states that the performance of laboratories in the analysis of OCPs was still not satisfactory. For dieldrin in fish, only six laboratories had performed well. Laboratories in GRULAC had still problems with the DDT standard solution. p,p'-DDE is typically easier to analyse than the o,p'-congeners.

Mr. de Boer discussed the results for DDT for the standard soluton and the sediment sample across regions, stressing that the CV values had been very high for the standard solution for GRULAC as compared to Asia and WEOG. No CV could be calculated for Africa and CEE. As regards the sediment, the performance of Asian laboratories was more problematic. In the case of chlordanes in standard solution, WEOG and Asia showed very good performance.

He compared the performance based on CVs with regard to PCB between the two rounds, noting that the results had improved for all samples, except the standard solution. In the analysis of OCP, the performance had improved slightly improved for sediments and slightly deteriorated for fish and mother's milk. In the case of OCP in mothers' milk, laboratories had less difficulties with drins and DDT than in the previous round, while with chlordanes they scored substantially worse in the present one.

He mentioned that there had been an issue with the clean-up of fatty samples, especially fish. Subsequently, some discussion was about using gel permeation chromatography (GPC) according to EU reference methods, which was mentioned by CVUA. This method avoids treatment with sulphuric acid. If well done and GC two columns used, even determination by ECD can be an effective method.

Mr. de Boer ended his presentation with a number of conclusions: He stressed that regular interlaboratory studies and trainings (including internal ones) as well as better instrumentation were important elements in improving performances in the analysis of POPs, especially for new POPs such as PBDEs and PFOS. He noted that the results of the air extract had been good for most compounds. Meanwhile, he called for additional investigation regarding the poor results in the analysis of fish samples. Moreover, better and more data was necessary for some compound classes. Finally, he re-iterated the call for QA/QC.

2.5 Discussion of analytical aspects and performance

Led by Mr. van Bavel and Mr. de Boer, the group went through the matrices and POPs for all laboratories present by commenting on the test sample types, the POPs analysed, the instrumentation used, the frequency of analysis, and other relevant issues, including a self-evaluation. The outcome of this exercise is shown in Annex D.

At the end, Mr. de Boer outlined possible mistakes in analysing OCPs. Further details are available in the presentation "Discussion on second worldwide UNEP inter-laboratory study on POPs"

Discussion points were mainly around the following topics:

1. Standards
2. Quality charts
3. Clean-up methods: manually vs. automated extraction
4. Separation of OCPs

3 PROFICIENCY TESTING IN OFFICIAL FEED AND FOOD CONTROL IN THE EU

3.1 Proficiency Tests in the field of pesticides (with focus on determination of analytes now classified as old or new POPs in food of animal origin)

Mr. Ralf Lippold from the CVUA Freiburg informed participants about the EU proficiency tests (EUPTs) for pesticides organized by the four EU Reference Laboratories for pesticides (for fruits and vegetables; for cereals and feedingstuffs; for food of animal origin and commodities with high fat content; for analytes to be determined by single residue methods). Each of these EURLs performs at least one PT per year. The aim of these EUPTs is to improve the quality, accuracy and comparability of the analytical results generated by EU Member States within the frame of the EU co-ordinated control and national monitoring programmes. At the same time laboratories can assess their analytical performance and scope and make a comparison with other participating laboratories, which will hopefully result in additional efforts for improvement.

Participation is mandatory for all National Reference Laboratories (NRLs) and all laboratories analysing samples for the official control of pesticide residues as long as the scopes of the EUPT and the laboratory overlap. In the last years around 100 laboratories participated in EUPT AO.

The organization and performance is based on the requirements of ISO/IEC 17043, ISO 13528 and IUPAC Technical Report on Proficiency Testing. In addition, one protocol describing the general procedures for all EUPTs can be downloaded from the EURL website www.eurl-pesticides.eu. EUPTs are organized by the individual EURLs. One common scientific committee (with an advisory group and an independent quality control group) supervises the harmonized approach including preparation of sample material, evaluation of results and reporting.

For performance of these PTs, the EURL is accredited by the Deutsche Akkreditierungsstelle GmbH (DAkkS) attesting the competence as provider under the terms of DIN EN ISO/IEC 17043:2010 to carry out proficiency testing/ inter laboratory comparisons (Accreditation number: D-EP-18625-01-00).

For all EUPTs target pesticide lists were provided (about 10 -12 weeks before the samples are shipped). The pesticides listed (about 70 to 90) are mandatory to be analysed. For each pesticide and the relevant compounds included in the residue definitions, a MRRL (Minimum Required Reporting Level) was set. These MRRL values were the levels that laboratories were expected to achieve. The MRRL values were established by the organiser and confirmed by the EURL Scientific Committee.

For reporting results a web-based database was used.

The median was used as the estimation for the assigned value. The median is the central value of all measured results, i.e. the number separating the higher 50% of the results from the lower 50%. For an even number of measured values it is the arithmetic mean of both central values. For a normal distribution, and after removal of outliers, the median and the mean are almost identical.

Because for many parameters the results from a few laboratories deviated significantly from the median, the calculated standard deviation would have been larger than the target standard deviation calculated according to European Proficiency Testing schemes (25 % of the median, see below).

Additionally, for all pesticides the robust standard deviations Q, using the algorithm as described in DIN 38402-45:2003, were calculated. The algorithm minimises the influence of outlying results and provide good estimations of the standard deviation.

68.3% of the values used for the calculations are in the range of ±1 standard deviations. From the results of ten previous European Proficiency Tests on pesticides in vegetable or fruit matrices, a fit-for-purpose relative target standard deviation (FFP RSD; $\%s_{EUPT}$) of 25 % was estimated.

The z-score is calculated from the fit for pupose standard deviation as follows:

$Z = (m - M)/s_{EUPT}$

with:

Variable	Description
Z	Value of the z-score
M	Result of the laboratory
M	Median
S_{EUPT}	Fit-for-purpose standard deviation from European Proficiency Tests

The z-score therefore is a factor of the fit for purpose standard deviation by which the laboratory result differs from the assigned value. Therefore, the value of the z-scores can be used to assess the analytical results:

Range	Evaluation
0 - 2	The analysis fulfils the requirements - acceptable (at the normal distribution and the level of confidence 95 %)
> 2 - 3	The analysis should be checked - questionable
> 3	The analysis does not fulfil the requirements – unacceptable (at the level of confidence 99.7 %)

Results for pesticides reported by the laboratories as “analysed” but without reporting numerical values although they were used by the organiser to treat the Test Item and were detected by the organiser and the majority of the participants that had targeted these specific pesticides, at or above the MRRL have been considered to be false negative results. Results reported as <RL (RL= Reporting Limit of the laboratory) are considered as not detected and are judged as false negatives if the assigned value of the analyte is at or above the MRRL.

For false negative results, z-scores were calculated using

- the MRRL value in cases where the Reporting Limit (RL) of the lab was higher than, or equal to, the MRRL value.
- the RL value in cases where the RL of the lab was lower than the MRRL value.

The real problems are caused by false positive results, *i.e.*, a pesticide is reported to be present above MRL but is not present in the sample. Results reported for pesticides that were included in the target pesticide list, but which were
(i) not used in the preparation of the spiked test material and
(ii) not detected by the organiser (even after a repeated analysis with lower detection limits) were assigned as false positive results - if they were reported at concentrations at, or above, the MRRL value as stipulated by the organiser. No z-score values were calculated for these results.

According to their results the laboratories are classified into two categories - A or B. Currently, laboratories that have detected and quantified a sufficiently high percentage of the pesticides present in the Test Item (e.g. at least 90 %) and reported no false positives will have demonstrated 'sufficient scope' and can therefore be classified into Category A. During the last EUPTs AO about 60 % of the participating laboratories were classified in category A.

During the last 5 EUPTs it was observed that the scope of the laboratories and the quality of their results increased. However, due to the large workload of the laboratories the number of errors during reporting of results increased (e.g. typing errors, mismatches in the result submitting pages).

When a NRL does not perform satisfactory, generally the EU-Commission is informed as well as the Member State. EURL will visit the laboratory and evaluate the reasons for the low performance. In some cases a correlation between budget and performance can be observed: Laboratories with smaller budgets often do not have the equipment for analyzing all pesticides.

It should be noted that a Member State can transfer the responsibilities for NRL-functions and official analysis to other Member States or can contract private laboratories (esp. small Member States follow this approach).

Particular observations from analysis of "basic POPs" and "new POPs" can be drawn from the PT of 2012 with raw poultry meat. Acceptable results were mostly in the range of 60 %– 70 % for levels mostly in the range of 0.01 mg/kg–0.05 mg/kg product.

3.2 Proficiency Tests in the field of PCBs and PCDD/PCDF

Mr. Alexander Kotz from the CVUA continued with the discussion on the EUPTs in the field of PCBs and PCDD/PCDF for the official control of feed and food. Two EU regulations fix criteria and requirements for laboratory performance in these areas (Commission Regulation 159/2009 [feed] and 589/2014 [food]). Essential requirements for laboratories comprise the accreditation according to EN ISO/IEC 17025 and the continuous successful participation in interlaboratory studies.

Analytical methods are based on physical-chemical methods with determination of the individual congeners of interest and subsequent calculation of the sum parameters (TEQs; sum of 6 indicator PCBs) or on bioanalytical screening methods with determination of bioanalytical equivalents (BEQs). Physical-chemical methods can be used as "confirmatory methods" as their results are suited to confirm the exceedance of maximum levels (with consideration of the measurement uncertainty) for legal measures. Instrumentation of confirmatory methods for PCDD/PCDF and dioxin-like PCBs includes High Resolution Mass Spectrometry (HRMS) and MS/MS.

Important criteria for screening methods are: (i) false-compliant rate < 5 %; (ii) repeatability (RSD_r) < 20 %, (iii) within-laboratory reproducibility (RSD_R) < 25 %. Important criteria for confirmatory methods are: (i) trueness – 20 to + 20 %; (ii) within-laboratory reproducibility (RSD_R) < 15 %.

The EURL for Dioxins and PCBs performs two PTs per year. The participation of NRLs is mandatory. The PTs are also open for official laboratories of EU Member States and in certain cases also for commercial laboratories. The organization and performance is based on the requirements of ISO/IEC 17043, ISO 13528 and IUPAC Technical Report on Proficiency Testing. For performance of these PTs, the EURL is accredited by the Deutsche Akkreditierungsstelle GmbH (DAkkS) attesting the competence as provider under the terms of DIN EN ISO/IEC 17043:2010 to carry out proficiency testing/ interlaboratory comparisons in the testing field of chemical analysis and bioanalytical

methods for determination of PCDD/Fs and PCBs in food and feed (Accreditation number: D-EP-18625-01-00). 15 interlaboratory studies and proficiency tests were performed between 2006 and 2014 requesting for confirmatory methods the determination of 4 sum parameters (WHO-PCDD/F-PCB-TEQ, WHO-PCDD/F-TEQ, WHO-PCB-TEQ, sum of six indicator PCB), 35 individual congeners, lipids and moisture; for bioanalytical screening methods 3 BEQs as sum parameters (Total-BEQ, PCDD/F-BEQ and PCB-BEQ).

z-scores are calculated based on the following target standard deviations: 10% for WHO-TEQ, 15% for sum of six indicator PCB (PCB_6), and 20% for congeners; for BEQ-TEQs as determined with bioanalytical screening methods: 20 %. The target standard deviations are in same cases stricter than those applied by other providers.

Based on ten PTs performed between 2006 and 2013 with inclusion of 18 matrices, 3386 matrix/analyte combinations were evaluated. As result, 80 % of all parameters were between -2 and +2 z-scores. This shows a high degree of reliability.

A complex positive scoring system was developed based on the importance of the parameters for results (contribution of individual congeners to the sum parameter; sum parameter). A laboratory participates successfully in a PT, if the criteria for the reported analytes are met for each PT test sample.

Furthermore, the application of measurement uncertainty is evaluated: All sum parameters have to be reported with their corresponding measurement uncertainty, and with consideration of measurement uncertainty, the laboratory has to report whether the result exceeds the legally binding maximum or action levels.

For bioanalytical screening methods the main criterion is the ability to identify compliant samples and samples suspected to be non-compliant with established legal limits.

As the continuous successful participation in PTs is an utmost important criterion for performance of NRLs, the long-term evaluation of z-scores is recorded. For this, for each laboratory the z-scores of the different PTs are plotted over time allowing a better picture of the overall performance for different matrices and a long time.

Finally, the determination of lipids is a permanent issue: In some cases it was observed that the determination of the lipid content caused problems and as a consequence the performance on wet weight basis was satisfactory but not on lipid basis. In the future, some criteria may be defined to address the lipid determination.

4 DETAILED DISCUSSION OF ANALYTICAL ASPECTS AND PERFORMANCE

4.1 PBDE and PBB in standard solution, sediment, air extract, fish, human milk

Mr. van Bavel provided insights on the analysis of brominated flame retardants (BFRs). PBDE had been identified in 1997 in whales from the Faroer Islands (however, the results had not been published). He outlined that there were two methods for the identification and quantification of PBDE: (i) EI and (ii) NCI. Higher sensitivity is obtained with negative chemical ionisation. Chromatograms, mass spectra and levels were reported for a number of findings in whales.

Mr. de Boer presented results from the interlaboratory assessment report for the analysis of PBDE. He noted that for the sum PBDE, the CV (23-51; most around 30) was better than for the OCP and that the inclusion rate of the results in the assessment was also relatively high, particularly for fish and mothers' milk. He continued with a regional comparison of the results for each PBDE analyte for the standard solution, fish and sediment. For each of these, it had not been possible to calculate the CV and the inclusion rate for GRULAC, Africa and CEE due to a lack of data. He went into more detail for PBDE 47 and stressed the existence of some extreme outliers. Both for the sediment and the standard solution, Asia generally had a higher CV than WEOG.

Laboratories – at last in Asia and WEOG – have a method available for PBDE but less labs for PBB-153.

Discussion on new POPs for listing: Ms. Heidi Fiedler mentioned that PBDE-209 is at initial stages with the POPs Review Committee. Other candidates that are at later stages are pentachlorophenol, chlorinated naphthalenes, and hexachlorobutadiene.

The participants were invited to discuss their questions with the experts present. This provided an opportunity for participants to seek advice on challenges specific to their laboratories and thus to improve their performance in the analysis of POPs in the future.

5 CLOSURE OF THE WORKSHOP

5.1 Future needs and next steps

Ms. Fiedler briefly summarized which deliverables will be provided from the workshop and elaborated on the next steps. She brought it to the participants' attention that the all relevant information will be available on UNEP's website at www.unep.org. Also, participants would be provided with a USB, containing the presentations held during the workshop as well as other relevant materials, including the draft report of the second round of the interlaboratory assessment and its annexes. She also said that the final report and laboratory certificates would soon be available. She discussed the second phase of the POPs GMP and other upcoming issues, including the plan to continue implementing interlaboratory assessments on a bi-ennial basis.

5.2 Concluding Remarks

After the customary exchange of courtesies, the workshop was closed at 4:45 p.m. Workshop participants which were interested and would not participate at the training course were given a tour through the POPs laboratories at CVUA Freiburg, including explanations of the instrumentation used at the CVUA.

Training Workshop

6 ANALYSIS AND QA/QC ASPECTS OF NEW POPS

The training workshop on analysis of new POPs was opened on 26 June 2014, at 9:00 a.m. in Freiburg, Germany at the facilities of the CVUA. It was attended by nine participants from developing countries, *i.e.*, China (three laboratories), Ecuador, Moldova, Russian Federation, South Africa, Uruguay, and Vietnam. These laboratories had analysed a number of new POPs in the interlaboratory assessment and therefore, received some further and more detailed training on new POPs analysis.

6.1 Determination of PFOS

Mr. Bert van Bavel and Ms. Samira Salihovic, MTM Research Centre, Örebro University, covered the analysis of PFOS and other PFAS. This included background information as to identity and occurrence of PFOS and related compounds, an introduction to PFOS and precursors analysis, and insights on instrumental analysis and quantification of PFOS and related compounds.

PFCs have been detected after a request from 3M company to look into the blood concentrations of their workers. Soon, PFAS and especially PFOS were detected in all blood samples.

State of the art analysis in 2005 comprised:

- Clean-up methods:
  - ✓ included ion-pair extraction
  - ✓ different types of solid-phase extractions
  - ✓ dispersive active carbon clean up
    - ➢ Powley method 2005
- Analysis and detection:
  - ✓ LC-ESI-MS/MS (triple quad)
  - ✓ LC-ESI-MS/MS (ion trap)
  - ✓ LC-ESI-MS (single quad)
  - ✓ LC-ESI-TOF-MS
- Quantification:
  - ✓ extracted or non-extracted standard curves
  - ✓ external and internal standards
  - ✓ nearly all laboratories report the sum of the branched and linear isomers

Levels of PFAS are, when compared on a volume basis, significantly higher than chlorinated and brominated POPs (comparison as ng *per* mL of human blood). Among the PFAS, the most abundant is L-PFOS (highest observed concentration of 13.4 ng mL^{-1}). Via the food chain, most of the PFAS comes from eating fish/seafood followed by dairy products and others. Water can be a source of exposure; *e.g.*, filters (Teflon-based) in drinking water purification.

A Swedish study (PIVUS study) with 1016 participants revealed that almost all target compounds were detected in > 70 % of the study participants. Men have higher concentrations of PFHxS than women, whereas women have higher L-PFOS than men.

Due to the low lipid solubility of PFAS in fat, the concentrations in human milk are lower than the concentration in the blood. There is a linear relationship for PFOS and PFHxS between human milk and blood. The calculation of correlation factors for PFOA is disturbed by high procedural blanks.

Sample preparation and instrumental analysis was discussed in more detail covering various aspects such as SPE extraction and clean up using a Waters Oasis® WAX SPE Colum, laboratory contamination, analytical schemes, possible interferences by TDCA as well as other cholic acids for PFOS detection, UPLC separation and MS spectra.

It should be noted that the distribution between linear and branched PFAS is not the same: for example, PFOA in human blood contains 1% or less of branched isomers whereas for PFOS, the share is 30 % (60 %–70 % L-PFOS, 10 %–20 % for 3/4/5-PFOS respectively 6-PFOS). It also seems that between countries and at different times, the composition of the PFOS isomers (linear vs. branched) different.

6.2 Determination of PBDE

Mr. Alexander Kotz from CVUA shared insights on the determination of polybrominated diphenyl ethers (PBDEs) in biological matrices.

Current EU regulations and directives on maximum and/or action levels for contaminants in food and feed matrices don't set any legal limits for PBDEs. Commission recommendation on the monitoring of traces of brominated flame retardants in food of 3 March 2014 (2014/118/EU) defines a monitoring programme on the presence of brominated flame retardants in a wide variety of food samples reflecting human consumption. The compounds to be monitored include PBDE 28, 47, 99, 100, 138, 153, 154, 183 and 209. It should be noted that PBDE 209 is not (yet) listed in annexes of the Stockholm Convention. The limit of quantification for the monitoring is set as 0.01 ng/g wet weight or lower.

Methods for sampling and analysis are not defined in EU regulations, but criteria for PCDD/Fs and PCBs can be used as indication. EPA method 1614A describes the analysis of brominated diphenyl ethers in water, soil, sediment and tissue by HRGC/HRMS. It defies extraction, concentration, clean-up; clean-up, and GC-MS measurement (resolution here at >5,000).

The analytical method for PBDEs applied at CVUA includes sample pre-treatment, extraction of analytes of interest and clean-up with gel permeation chromatography, multi-layer silica column and Florisil column. With this method the analysis of PBDEs can be combined with PCDD/PCDF and PCB.

When starting PBDE analysis, it is advisable to avoid direct contact of solvents with plastic or rubber parts. Teflon part, glassware or stainless steel parts cause considerably less problems especially regarding blank levels. All adsorbents shall be thoroughly cleaned before use.

For sample pre-treatment freeze-drying or mixing of the sample with drying agent is applied. Freeze-drying can be used for almost all types of food and feeding stuffs. It reduces the amount of water in the sample using mild conditions and makes it easier accessible for the extraction solvent. But it has to be taken into account, that the depending sample amount the freeze-drying process is quite time consuming and possible contamination of the sample with PCB, e.g. from cable coatings has to be monitored.

As alternative sample-pretreatment the mixing with a drying agent is possible, but needs to be adjusted to the sample, water content and extraction solvents. E.g. sodium acrylate/vinyl alcohol

copolymer showed a good water retention and applicability for various solvents and solvent mixtures.

The extraction of the analytes of interests is a critical step in PBDE analysis especially regarding extraction efficiency of different combinations of sample pre-treatment and extraction techniques. The Twisselmann or hot Soxhlet extraction shows high extraction efficiency for nearly all kind of matrices, but needs not be combined for wet samples with an appropriate drying process (freeze-drying or mixing with drying agent) and suitable extraction solvent or solvent mixture. As alternative extraction method with shorter extraction times compared to Twisselmann extraction (maximum of 8 h for food and feed) pressurized liquid extraction can be applied. Also for pressurized liquid extraction suitable extraction solvents in combination with effective drying agents (e.g. polyacrylates) have to be applied. In addition cross contamination in the extraction system, the limited cell size and possible influence plastic or rubber parts need to be considered.

For quantification of PBDEs isotope-dilution analysis can be applied as unlabeled and 13C-labeled standards for most relevant congeners are available. Internal standards can be added at the very beginning of the analytical method prior to extraction and sample pre-treatment or to the extracted fat (e.g. for food of animal origin with high fat content). In both cases proper validation of extraction procedure and efficiency is necessary. For long-term storage of standard solutions suitable bottles (e.g. capillary bottles) and regular control of concentrations is necessary.

General principles of the clean-up method for PBDEs comprise the removal of interfering matrix, separation of the analytes of interest and the concentration of the final extract to an appropriate volume. For removal of interfering matrix components gel permeation chromatography or sulphuric acid-silica columns can be applied. For separation of PCDD/Fs from PCBs and PBDEs Florisil deactivated with 5 % of water is used.

At the CVUA identification and quantification of PBDEs are performed on a GC-HRMS system with monitoring of molecular ions or M-2Br. As alternative also GC-MS/MS or GC-LRMS (with monitoring of molecular ions or M-2Br in EI-mode or Br^- in NCI-mode) are applied. For gas chromatographic separation of PBDEs (except for PBDE 209) a 30 m 95%-methyl-5%-phenylsiloxane phase can be used. For reduction of thermal degradation the use of short columns with higher carrier gas flows is advisable for PBDE 209.

6.3 Lipids and their determination in products of the food chain

Mr. Rainer Malisch, CVUA, presented various methods for the determination of lipids. Due to bioaccumulation (“extraction” of apolar contaminants by lipids), concentrations of these contaminants are higher on lipid basis than on product basis. Normalization on lipid basis is the best way to compare levels of apolar substances in samples. Otherwise (if compared on product basis), also the variation of the lipid level between samples would have a significant influence. This was shown with the example of beef meat samples, the calculation of their dioxin levels on product basis and lipid basis and comparison with maximum levels in the EU.

A “true” fat content does not exist. The value depends more or less on the method used for determination. Fat is the proportion of food and feed (i) belonging to the group of lipid compounds (i.e. the total of lipids, scientific definition) or (ii) soluble in solvents of low polarity (pragmatic definition). Lipids comprise a wide number of substances such as triglycerides, di-, monoglycerides, (free) fatty acids, phospholipids, carotenoids, lipoproteins, wax, wax alcohols (aliphatic alcohols), paraffins, sterols (cholesterol, …) and esters, vitamins, terpenes, tocopherols, or contaminants.

In the Stockholm Convention, the definition of lipophilic contaminants requires that the bioaccumulation factor in aquatic species is greater than 5,000 or in absence of such data that log K_{ow} (octanol / water - coefficient constant)is greater than 5.

An overview was given on the lipid composition of the most important groups of food of animal origin (eggs, milk, meat) and the analytical methods established at CVUA Freiburg for extraction and clean up. Standardized methods for determination of pesticide residues (including lipophilic pesticides) in Germany are based on a modular system allowing a combination of single steps (extraction, clean up and determination). After drying of the product, extraction is mainly based on Soxhlet, Twisselmann (Soxtherm, Soxtec), ASE (accelerated solvent extraction) or PLE (pressurized liquid extraction) techniques. Solvents can be apolar (e.g. hexane, ethyl acetate, cyclohexane, toluene), polar (e.g. acetonitrile, acetone, 2-propanol) or mixtures. Depending on the analyte of interest, clean-up steps comprise gel chromatography, silica column, Florisil column or Carbopack columns and were established as manual or (fully or partly) automated procedures.

As conclusion, the determination of lipophilic analytes at trace levels in food and feed is a complex problem. Specific knowledge of “food and feed chemistry” is required (biological samples different from environmental samples). There is not only one „true“ analytical approach. The criteria approach for performance is important and a complex quality control required.

6.4 Determination of chlordecone

Björn Hardebusch, CVUA, informed participants about the determination of chlordecone in human milk as performed at the CVUA. Chlordecone was used as a pesticide in the 1960s and 1970s. It was used extensively in the tropics for the control of banana root borer. Chlordecone is analogous to mirex and therefore it can be expected that the analytical determination is possible with the routine method for pesticides using GC; however, the recoveries were low. The response factor for the standard solution was 5-times lower than for mirex. Furthermore, the distribution between lipid phase and polar phases is different.

The QuEChERS method is a fast method for determination of pesticides, in particular for more polar pesticides. It is based on LC/MS-MS and does not include the step of concentration with nitrogen. The method was validated with cow’s milk, and the SANCO criteria were fulfilled.

With an LOQ of 0.5 µg/kg lipid, so far no chlordecone was found in human milk.

6.5 Determination of alpha-HCH, beta-HCH, gamma-HCH, PeCBz and HBB as part of the analysis of POPs (extraction, clean up, GC-ECD, GC-MS, different GC columns, validation)

Ms. Karin Kypke, CVUA, gave an overview on the determination of OC POPs, including clean-up and extraction methods.

For milk, completely different extraction approaches were established such as the AOAC method (Liquid-liquid partition using methanol and diethyl ether/light petroleum), column extraction (extraction in a column using n-hexane/acetone), liquid-liquid partition (using n-hexane/acetone) or centrifugation with subsequent removal of the cream layer after centrifugation (raw milk, human milk).

For meat and fish, extraction can be based on column extraction (extraction in a column using n-hexane/acetone), Soxhlet extraction (light petroleum or diethyl ether), hot solvent extraction (light petroleum), liquid-liquid partition (using n-hexane/acetone and sodium sulfate solution) or centrifugation (cold centrifugation using n-hexane).

The following clean up-procedures were presented and discussed

- Liquid/ liquid partition with acetonitrile and chromatography on a Florisil column,
- Liquid/ liquid partition with dimethyl formamide and chromatography on a Florisil column,
- Column chromatography on activated Florisil,
- Column chromatography on partially deactivated Florisil,
- Column chromatography on partially deactivated alumina oxide,
- Gel permeation chromatography (GPC),
- Gel permeation chromatography (GPC) and column chromatography on partially deactivated silica gel,
- High pressure GPC (HPGPC).

6.6 Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed

Mr. Lippold explained the implications laid down in the EU Document SANCO 12571 (2013) on Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed, which was issued in 2013. The document can be downloaded via the EURL website www.eurl-pesticides.eu. This guidance document describes the **method validation and analytical quality control requirements** to support the validity of data used for checking compliance with maximum residue limits, enforcement actions, or assessment of consumer exposure to pesticides in the EU. He also highlighted that this guidance document is not only used in the European Union but also in Latin America for accreditation.

7 END OF TRAINING

After the customary exchange of courtesies, Mr. Malisch closed the training at 5:30 p.m.

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9 ANNEX B: AGENDA FINAL RESULTS WORKSHOP

Tuesday, 24 June 2014		
8:30-9:00	Registration	
9:00-10:00	Opening of the Workshop	
	Welcome	Rainer Malisch, CVUA
	Welcome and Objectives of the UNEP Workshop and training course	Heidelore Fiedler, UNEP
	Introduction of the participants	
10:00-10:30	Summary and context of the interlaboratory assessment	Heidelore Fiedler
10:30-11:00	*Coffee break*	
11:00-11:45	Overview on the intercalibration data of dl-POPs and PFOS (includes discussion)	Bert van Bavel, MTM Centre Örebro
11:45-12:30	Overview on the intercalibration data of basic POPs and PBDE (includes discussion)	Jacob de Boer, IVM VU Amsterdam
12:30-14:00	*Lunch*	
14:00-15:30	Detailed discussion of analytical aspects and performance	
	1. POPs pesticides in standard solution, sediment, air extract, fish, human milk 2. Indicator PCB in standard solution, sediment, air extract, fish, human milk, transformer oil	Jacob de Boer and Bert van Bavel (leads)
15:30-16:00	*Coffee break*	
16:00-17:30	Detailed discussion of analytical aspects and performance cont'd.	
	3. Dioxin-like POPs in standard solution, sediment, air extract, fish, human milk 4. PFC in standard solution, air extract, human blood, water	Bert van Bavel
17:30	*End of first workshop day*	
20:00	Reception	

Wednesday, 25 June 2014		
9:00-9:45	Proficiency testing in official food control in the EU in the field of pesticides (with focus on determination of analytes now classified as old or new POPs in food of animal origin)	Ralf Lippold, CVUA
9:45-10:30	Proficiency testing in official food control in the EU in the field of PCBs and PCDD/Fs	Alexander Kotz, CVUA
10:30-11:00	*Coffee break*	
11:00-12:30	Detailed discussion of analytical aspects and performance cont'd.	
	PBDE and PBB in standard solution, sediment, air extract, fish, human milk	Jacob de Boer and Bert van Bavel (leads)
12:30-14:00	*Lunch*	
14:00-15:30	Open discussion, questions and answers by participants and coordinators	
15:30-16:00	*Coffee break*	
16:30-17:30	Future needs and next steps	Heidelore Fiedler
	Concluding Remarks, end of Workshop	Heidelore Fiedler

10 ANNEX C: FINAL AGENDA - TRAINING WORKSHOP ON ANALYSIS OF NEW POPS

Freiburg, Germany, 26-27 June 2014

Thursday, 26 June 2014		
09:00-12:30	Determination of PFOS	Bert van Bavel Samira Salihovic
12:30-13:30	*Lunch*	
13:30-15:30	Determination of PBDE	Alexander Kotz
15:30-16:00	*Coffee break*	
16:00-17:30	Lipids and their determination in products of the food chain	Rainer Malisch
17:30	*End of day 1*	
Friday, 27 June 2014		
09:00 -10:00	Determination of chlordecone	Björn Hardebusch
10:00-10:30	*Coffee break*	
10:30 – 12:30	Determination of alpha-HCH, beta-HCH, gamma-HCH, PeCB and HBB as part of the analysis of POPs (extraction, clean up, GC-ECD, GC-MS, different GC columns, validation)	Karin Kypke Björn Hardebusch Ralf Lippold
12:30-13:30	*Lunch*	
13:30 – 15:30	Determination of alpha-HCH, beta-HCH, gamma-HCH, PeCB and HBB as part of the analysis of POPs (extraction, clean up, GC-ECD, GC-MS, different GC columns, validation) (continued)	Karin Kypke Björn Hardebusch Ralf Lippold
15:30-16:00	*Coffee break*	
16:00 – 17:30	Determination of alpha-HCH, beta-HCH, gamma-HCH, PeCB and HBB as part of the analysis of POPs (extraction, clean up, GC-ECD, GC-MS, different GC columns, validation) (continued)	Karin Kypke Björn Hardebusch Ralf Lippold
17:30	*End of training*	Rainer Malisch Heidelore Fiedler

11 ANNEX D: SUMMARY OF DISCUSSION BY LABORATORIES PRESENT

Name and contact	Test Samples	Compounds	Interval	Instrumentation	Comments
Argentina					
Mariana Ruiz de Arechavaleta INTI Argentina Buenos Aires	Standard	PCB/OCPs		GC/ECD	Happy with result Future human milk Problem with customs
	Sediment	PCB/OCPs	Monthly	GC/MS	
	Oil	PCB	Monthly		
Brazil					
Rafael Pissinatti Laboratorio Nacional Agropecuario – Lanagro/Mg Pedro Leopoldo	Standard	dl-POPs		GC/HRMS	Units for reporting results different from units in interlab (*e.g.*, pg/g)
	Fish	dl-POPs	Weekly		
	Air	dl-POPs	Rarely		
Canada					
Dave Hope Pacific Rim laboratories Inc. Surrey	Standard	dl-POP	Daily	GC/HRMS	For PBDE: EPA 1668 Better result with isotope dilution results
	Sediment	OCPs	1-2/year		
	Fish	PCB	Weekly		
		PBDE	Weekly		
China					
Hongping Gong Zhejiang Environmental Monitoring Center Hangzhou	Standard				Environmental laboratory EPA 1613 Happy with results
	Air	dl-POPs	Weekly	GC/HRMS	
	Sediment	dl-POPs	Monthly	GC/HRMS	
	Water	PFOS	Monthly	LC/MS/MS	
Lei Zhang China National Center for Food Safety Risk Assessment Beijing	Standard	dl-POPs/OCPs/PBDE/PFAS/PCB	2/year	GC/HRMS OCPs (GC/MS/MS)	Food laboratory
	Fish	dl-POPs/OCPs/PBDE/PFAS/PCB	Weekly		
	Milk	dl-POPs/OCPs/PBDE/PFAS/PCB	Weekly		
	Serum	PFAS	Monthly		
Dr. Minghui Zheng	Standard			GC/HRMS	Environmental

Name and contact	Test Samples	Compounds	Interval	Instrumentation	Comments
Research Center for Eco-Environment Sciences Chinese Academy of Sciences, Beijing	Air	dl-POPs	Weekly	GC/HRMS	EPA 1613 Happy with results
	Sediment	dl-POPs	Monthly		
	Water	PFOS	Monthly	LC/MS/MS	
Dr. Liyan Liu Harbin Institute of Technology School of Municipal and Environmental Engineering Harbin	Standard	PCB/OCPs/PBDE	Weekly	GC/MS	Problems OCPs, dirty iron source Most of results ok Method from Environment Canada
	Air	PCB/OCPs/PBDE	Weekly		
	Sediment	PCB/OCPs/PBDE	3 months		
	Water	PCB/OCPs/PBDE			
	Fish	PCB/OCPs/PBDE	6 months		
	Serum	PCB/OCPs/PBDE	1/year		
Hongliang Jia College of Environmental Science and Engineering Dalian Maritime University, Dalian	Standard	PCB/OCPs/PBDE	Weekly	GC/MS	Problem with DDT Method from Environment Canada
	Air	PCB/OCPs/PBDE	Weekly		
	Sediment	PCB/OCPs/PBDE	3 months		
	Water	PCB/OCPs/PBDE			
	Fish	PCB/OCPs/PBDE	6 months		
	Serum	PCB/OCPs/PBDE	Yearly		
Sukun Zhang South China Environmental Monitoring Analysis Center South China Institute of Environmental Science, MEP, Guangzhou	Standard	dl-POPs, PCB, PBDE, OCPs, PFOS	Weekly	GC/HRMS	Good result But not happy for DDT, mirex Missing toxaphene and chlordecone Also waste /fly ash analyzed
	Sediment	dl-POPs, PCB, PBDE, OCPs, PFOS	Monthly	GC/MS	
	Water	PFAS	Monthly	LC/MS/MS	
	Air	dl-POPs, PCB, PBDE, OCPs	Weekly		
Cuba					
Dr. Carlos M. Alonso-Hernandez Centro de Estudios Ambientales de Cienfuegos Pollutants Laboratory, Cienfuegos	Standard	PCB/OCB		GC/ECD	Needs CRM and standards Disappointed wit results
	Sediment	PCB/OCB	Weekly		
	Fish	PCB/OCB	Monthly		
Ecuador					

Name and contact	Test Samples	Compounds	Interval	Instrumentation	Comments
Dr. Olga Pazmino Morales Laboratorio De Plaguicidas De Agrocalidad Quito	Standard	PCB/OCPs	Monthly	GC/ECD	New GC/MS Agree with results Training new people Need standard OCPs
	Milk				
Ghana					
Archibold Buah-Kwofie Ghana Atomic Energy Commission Nuclear Chemistry and Environment Research Centre, Legon	Standard	OCPs/PCB		GC/ECD	Timing in the middle of moving Agree with results but can perform better Other samples fruit/vegetables Control samples to GC/MS lab in Ghana Use MTM protocol Training possibilities outside Ghana Needs ref material and standards
	Air	OCPs/PCB	1/month (Monet)	(GC/FID)	
	Fish	OCPs/PCB	10-20/week		
	Sediment	OCPs/PCB	10-20/week		
Modolva					
Dr. Anna Cumanova State Hydrometeorological Service Chisinau	Standard	PCB/OCPs		GC/ECD	
	Sediment	PCB/OCPs	Weekly		
	Water		Monthly		PCB in water
	Air	PCB/OCPs	Monthly		Problems with clean up of fish Try dl-POPs this year Drins because of H_2SO_4 clean up
	Waste				
	Fish	PCB/OCPs	On request		
	Oil	PCB			
Netherlands					
Dr. Jacob de Boer Institute of Environmental Studies (IVM)	Standard	PCB/OCPs/PBDE	2-3 x year		
	Sediment	PCB/OCPs/PBDE	2-3 x year		

Name and contact	Test Samples	Compounds	Interval	Instrumentation	Comments
VU University, Amsterdam	Fish	PCB/OCPs/PBDE	2-3 x year		
	Air	PCB/OCPs/PBDE/PFAS	2-3 x year		
	Water	PFAS	Weekly		
	Milk	PCB/OCPs/PBDE	2-3 x year		
	Serum	PFAS	2-3 x year		
Norway					
Kine Baek Norsk Institutt for Vannforskning	Standard	PFAS/PBDE/PCB/OCPs			
	Fish	PFAS/PBDE/PCB/OCPs	Monthly		OCPs problems; More discussion on BDE methods (oversestimation?) New LC/QTOF instrumentation Twin lab overest
	Sediment	PFAS/PBDE/PCB/OCPs	Monthly		
Nanna Margrethe Bruun Bremnes Norwegian Institute of Public Health Oslo	Standard	PCB/OCPs			Calculation error
	Milk	PCB/OCPs	300/year		Discontinued
	Serum	PFAS	1000/year		Results Ok
Russia					
Dr. Zarema Amirova Environmental Research & Protection Centre Ufa	Standard	dl-POPs	Weekly	GC/HRMS	
	Sediment	dl-POPs	Weekly		Many soil samples Also other human samples and feed and food
	Air	dl-POPs	Weekly		
	Water		Weekly		
	Fish	dl-POPs	Weekly		
	Milk	dl-POPs	Weekly		
	Serum		Weekly		
South Africa					
Dr. Okechukwu Jonathan Okonkwo Tshwane University of Technology	Standard	PBDE	Quarterly	GC/HRMS	
	Sediment	PBDE	Quarterly	GC/MS	More experiments with GPC

Name and contact	Test Samples	Compounds	Interval	Instrumentation	Comments
Pretoria	Fish	PBDE	Quarterly		
	Mothers milk	PBDE	Quarterly		
Spain					
Dr. Esteban Abad Laboratory of Dioxins IDAEA CSIC Barcelona	Standard	dl-POPs/OCPs/PCB/PBDE	Total 1000 samples /year	GC/HRMS GC/MS (GC/ECD) for some OCPs/PCB	
	Fish	dl-POPs/OCPs/PCB/PBDE			Different sample and compounds
	Sediments	dl-POPs/OCPs/PCB/PBDE			
	Air	dl-POPs/OCPs/PCB/PBDE			
	Milk	dl-POPs/OCPs/PCB/PBDE			
Sweden					
Dr. Bert van Bavel Dr. Samira Salihovic MTM Research Laboratory, School of Science and Technology Örebro University, Örebro	Standard	dl-POPs/OCPs/PCB	30-1000 year	GC/HRMS	
	Fish	dl-POPs/OCPs/PCB/PBDE		GC/MS/NCI	
	Sediments	dl-POPs/OCPs/PCB/PBDE		GC/MS	
	Air	dl-POPs/OCPs/PCB/PBDE			
	Milk	dl-POPs/OCPs/PCB			
	Serum	PFAS			
	Water	PFAS			
Switzerland					
Dr. Luiz Felipe Alencastro Dr. Dominique Grandjean Ecole Polytechnique Federale de Lausanne Lausanne	Standard	OCPs/PCB/PBDE/dl-PCB	30-100 /year	GC/MS/MS Isotope dilution	Many types of samples 3r individual results Satisfied with results PCB 123
	Fish	OCPs/PCB/PBDE/dl-PCB			
	Sediment	OCPs/PCB/PBDE/dl-PCB			
Uganda					
Emmanuel Kaye Directorate of Government Analytical Laboratory Pesticide Residue Laboratory, Kampala	Standard	OCPs/PCB	Weekly	GC/MS	Not all DDTs or isomers present in standards Background problems (high LOD)
	Fish	OCPs/PCB	Monthly	GC/ECD	
	Air	OCPs/PCB	1-2/year		

Name and contact	Test Samples	Compounds	Interval	Instrumentation	Comments
					Explanation of high LODs
Uruguay					
Alejandra Torre Laboratorio Tecnológico del Uruguay (LATU) Montevideo	Standard	OCPs/PCB		GC/MS	Improvement ! But more improvement needed
	Fish	OCPs/PCB	Seldom	(GC/ECD)	
	Milk	OCPs/PCB	Seldom	(GC/MS/MS)	
	Sediment	OCPs/PCB	Monthly		
Vietnam					
Trinh Khac Sau Vietnam-Russian Tropical Center, Hanoi Chemical and Environmental Department Hanoi	Standard	dl-POPs	Weekly	GC/HRMS	Need CRM Serum Happy No Comment!
	Sediment	dl-POPs	Weekly		
	Fish	dl-POPs	Monthly		
	Milk	dl-POPs	Annually		
	Air	dl-POPs	Weekly		
Dr. Nguyen Hung Minh Dioxin Laboratory Project Vietnam Environment Administration, Hanoi	Standard	dl-POPs	Weekly	GC/HRMS GC/MS (screening)	Different air samples, need more info on approx. concentration (ambient/emission) And other food items
	Sediment	dl-POPs	600/year		
	Air	dl-POPs	100/year		
	Milk	dl-POPs	60/year		
	Fish	dl-POPs	150/year		
	Water	PFOS	40/year	LC/MS/MS	