FURTHER DEVELOPMENT OF THE FAST ANALYSIS FOR THE PCDD/F DETERMINATION IN SOIL AND SEDIMENT SAMPLES TO DELIVER RESULTS IN 48 HOURS – RESULTS OF MORE THAN 12,000 ANALYSES

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Introduction

At the Dioxin 2007 conference we presented the development and implementation of a Fast Analysis method to determine the PCDD/F distribution in the Upper Tittabawassee River floodplains and river sediments with a delivery time of 48 hours.[1,2] The investigation of the river floodplains is part of the Midland Offsite Corrective Action (MOCA)[3] project. In 2006 nearly 4000 samples were analyzed within four months in the upper section of the river. In 2007 the investigation of the Tittabawassee River floodplains was continued with the soil and sediment characterization of the middle and lower river sections in more than 8,000 samples. In total 12,192 samples have been analyzed with this method so far. To our knowledge it is one of the most comprehensive studies on PCDD/F in respect to a site investigation worldwide. In order to handle the increased work load in 2007, we successfully included a third laboratory. Further QA/QC requirements by the Michigan Department of Environmental Quality (MDEQ) were successfully implemented into the program.

Materials and Methods

Based on the Tittabawassee River floodplain results from 2005, the Environmental Analytical Support Laboratory of The Dow Chemical Company developed a method to rapidly measure the concentration of key PCDD/F contributors to the floodplain contamination and to estimate the Total-TEQ in order to deliver the results within 48 hours or less for 20 - 40 samples per day. The principles and details of this method which was approved by the EPA as method 1613 RT/TRP (Rapid Turnaround/Tittabawassee River Floodplains) were presented at the 2007 Dioxin conference[1,2]. In brief, the soil and sediment samples are extracted following the EPA method 1613b[4]. An aliquot of the raw extract is passed through a significantly shortened clean-up procedure and the final extract is analyzed with either GC/HRMS or GC/LRMS on a short DB-5MS GC column without any further confirmation analysis. The PCDD/F contamination in the floodplains is dominated by a distinct PCDF pattern which is related to the early days of chemical production in Midland and can be linked to the use of graphite electrodes in the Chloroalkali process[5]. Therefore the Fast Analysis is limited to the quantification of the major PCDF-components of this process which contribute to around 85% to the Total-TEQ: 2378-TCDF, 12378-PeCDF, 23478-PeCDF and 123478/123678-HxCDF (the latter congeners cannot be base line separated on the short GC-column). 2378-TCDD was included in the analysis as a potential indicator for the Trichlorophenol process. However the contribution of 2378-TCDD to the Total-TEQ in the floodplain samples is in general in the order of 2%. The sum of the TEQ-values (WHO-TEF 2005) of all analyzed PCDD/F-congeners is multiplied by 1.1, a factor derived from the initial floodplain investigation in 2005 to compensate for the contribution of those congeners not included in the Fast Analysis. Therefore the reported result from the Fast Analysis is an Estimated TEQ (E-TEQ).

For the 2007 investigation program the MDEQ requested more stringent threshold levels as to when the Fast Analysis data required confirmation. Furthermore it also requested the inclusion of 12378-PeCDD to the Fast Analysis as this congener is a main contributor to the TEQ burden in some fish tissues. Based upon the 2005 floodplain data the contribution of 12378-PeCDD to the Total-TEQ, like 2378-TCDD, is in the range of 2%. Therefore, in order not to increase the number of analytes per sample we chose the approach to double the 2378-TCDD concentration to cover this request.

Although the Chloroalkali pattern dominates in nearly all samples from the floodplains and in the sediments there are some cases where PCDD/F from the former Chlorophenol processes can contribute significantly to the TEQ and may lead to an underestimation of the E-TEQ[1,2]. To cover these cases several triggers were established which flag the E-TEQ of those samples as being potentially biased.

The following triggers were developed:

- If the E-TEQ is equal to or greater than 50 ng/kg d.w. and the E-TEQ contribution of 2378-TCDD is equal to or greater than 10 %, then the sample is flagged with a "T" for a potential bias due to PCDD/F deriving from the Trichlorophenol process
- If the E-TEQ is equal to or greater than 50 ng/kg d.w. and the concentration of 123478/123678-HxCDF is at least 1.7 times the concentration of 23478-PeCDF, then the sample is flagged with a "P" for a potential bias due to PCDD/F deriving from the Pentachlorophenol process
- If the E-TEQ is equal to or greater than 50 ng/kg d.w. and the ratio 124689-HxCDF to 123478/123678-HxCDF is above 0.9, then the sample is flagged with a "N" for a potential bias due to PCDD/F deriving from the Pentachlorophenol process
- Samples which had significant matrix interferences were also flagged as potentially biased

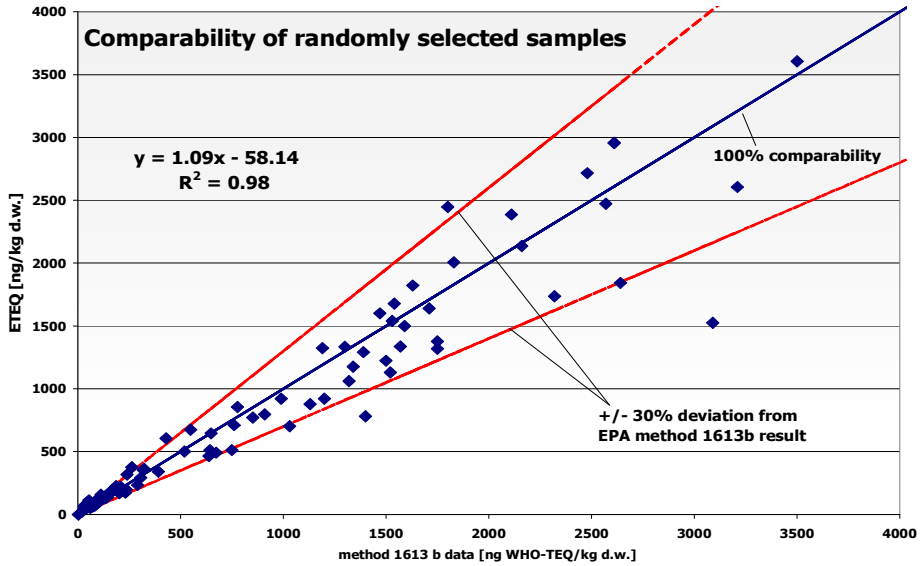
In consequence, the remainder of the raw sample extract from these flagged samples was additionally analyzed by the full EPA method 1613b. In total 386 Fast Analysis samples from 2007 were flagged by the laboratories for a comparability analysis. Furthermore, 129 samples were randomly selected for quality assurance purposes as requested by the MDEQ. For all 515 samples, the remainder of the raw extract was sent to Vista Analytical, El Dorado Hills, CA for analysis by method 1613b. All 2378-substituted Tetra- through HexaCDD and CDF congener results were confirmed on a second GC-column to avoid the co-elution problems for some 2378-substituted PCDF congeners[6,7].

Results and Discussion

From August to November 2007 more than 8000 samples were analyzed. For more than 1500 samples, the requested turn-around-time was 48 hours to support the field crews[1]. To achieve this goal a third laboratory, Analytical Laboratory Services (ALS), Burlington, ON, was included in this study in addition to Vista Analytical and the Dow laboratory. In order to be qualified for the Fast Analysis several quality assessments were made including the analysis of control samples, laboratory audit, proficiency tests, MDL studies, parallel analysis of selected samples within two months prior to the start of the project and an in-progress audit within the project.

As part of the extensive QA/QC program in the investigation which includes field, method and lab blanks, field and lab duplicates and OPR (ongoing precision and recovery) samples, 129 samples analyzed in any of the participating laboratories in 2007 were randomly selected for a comparability study of the Fast Analysis with the analysis according to method 1613b. The results of this comparability study are shown in Figure 1.

Figure 1: Comparability of randomly selected samples with the Fast Analysis and method 1613b



In Figure 1 the center line depicts the ideal comparability between the Fast Analysis method and EPA method 1613b and the upper and lower lines represent the +/- 30% deviation line. Only 2 sample results were clearly outside this control range. The R^2 for all sample data is 0.98.

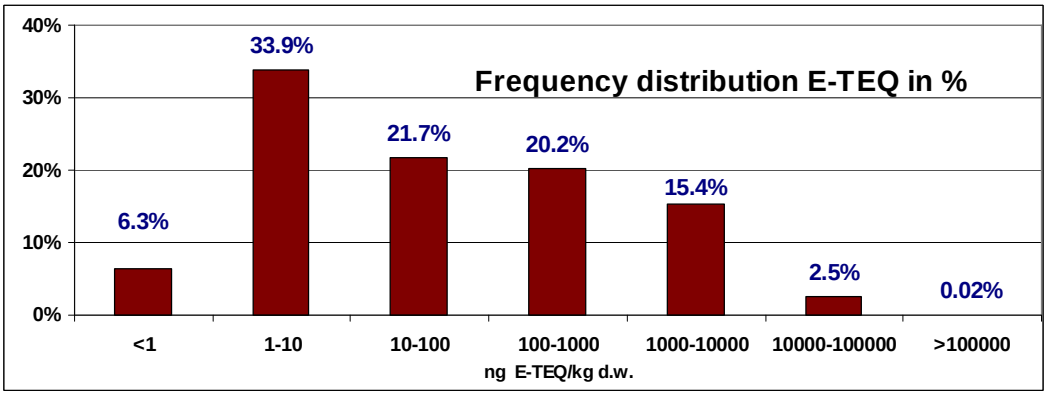
This data set allows also a separate performance comparison of all participating laboratories. The linear regression analysis data listed in Table 1 shows the excellent agreement of the results obtained with the Fast Analysis and the EPA method 1613b in the participating laboratories. It demonstrates the full comparability of the data regardless of the laboratory performing the analysis.

Table 1: Comparison of laboratories

laboratory	Linear regression	R^2
A	y = 1.00x - 38.82	0.99
B	y = 1.23x + 24.27	0.99
C	y = 1.08x - 57.47	0.98

In total 12,192 samples have been analyzed within 9 months in 2006 (4 months) and 2007 (5 months). This number of data points includes around 600 field and 600 laboratory duplicates which were analyzed on a regular basis. It does not include method blanks and OPR samples which were always processed in parallel to each batch of samples.

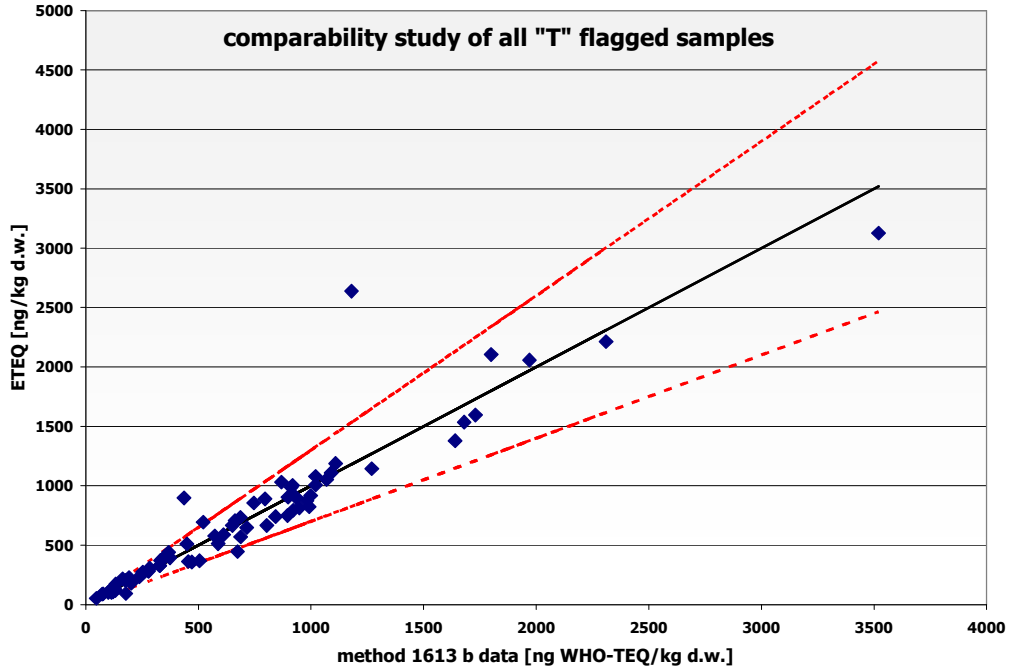
Figure 2: Frequency distribution of the E-TEQ based on 12,192 data points



More than 80% of the samples have E-TEQ values below 1000 ng/kg d.w. (see Figure 2). Values above 100,000 ng E-TEQ/kg d.w. were found in three samples only, with a maximum of 151,000 ng E-TEQ/kg d.w. The highest 2378-TCDD concentration was 2310 ng/kg d.w. while in more than 60% of the samples this congener could not be detected at all.

As shown in Figure 3 the comparability study demonstrates that Fast Analysis derived data which have an elevated contribution of 2378-TCDD to the Total-TEQ ("T"-flag) with the Fast Analysis do not lead to bias of more than 30% below the analytical data obtained by the regular method 1613b. The two data points lying outside the 30% line represent an over-estimation by the Fast Analysis which will not compromise the data. Based upon these data a comparability analysis of samples fulfilling the "T"-flag criteria alone is not necessary. However the "P" and "N" flagging, indicating potentially elevated contributions of higher chlorinated PCDD/F to the Total-TEQ is an important tool to avoid significant underestimation of the E-TEQ data. In 83 of all 316 "P" and/or "N" flagged samples (26%) the EPA method 1613b results were more than 30% higher than the E-TEQ results from the Fast Analysis (up to 7 times higher). With the combination of both flags not a single false negative value was determined.

Figure 3: Comparability of all "T"-flagged samples



The Fast Analysis is a reliable and proven method to analyze an enormous number of samples in a few months timeframe with rapid turn-around-time. Embedded in extensive quality assurance and control programs it can be easily adopted by other laboratories. With slight modifications of the target analytes, which must not necessarily be limited to the 2378-substituted PCDD/F congeners, it can also be applied to investigations with large numbers of samples having other sources of PCDD/F with different congener distributions. It can also serve as a suitable method for process control where short turn-around times for the data reports are required without compromising the data quality and it helps to substantially reduce the overall analytical costs even with the extra QA/QC requirements. This has been also acknowledged by EPA Region 4 which has requested the development of a screening method as part of the bidding for an extended site investigation[8].

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