DEVELOPMENT AND IMPLEMENTATION OF A FAST ANALYSIS FOR THE DETERMINATION OF PCDD/F TO DELIVER RESULTS IN 48 HOURS – PART I – BACKGROUND AND APPLICATION

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Introduction

At Dioxin 2006 we presented data about the PCDD/F distribution in more than 300 samples of the Tittabawassee River floodplains obtained from an intensive investigation in 2005 as part of the Midland Offsite Corrective Action (MOCA)[1] project. The PCDD/F distribution is dominated by 23478-PCDF, 2378-TCDF and 123478-HxCDF and can be attributed to the chloroalkali process of the early production years. Together with 12378-PCDF, about 85% of the Total-TEQ can be explained by these congeners in samples with a concentration range above 100 ppt TEQ. In 2006, ATS (Ann Arbor Technical Services) continued the investigation of the river floodplains with the GeoMorph® site characterization. The 6.5 mile characterization began at the confluence of the Chippewa River into the Tittabawassee River which is just upstream of Michigan Operations. The GeoMorph® investigation process iteratively evaluates the chemical, geologic, geomorphologic structures in the floodplain soils. In order to carry out this investigation most effectively, data about PCDD/F as the primary constituents of concern needed to be available in a time frame which is significantly shorter than the typical 2 -3 weeks turn-around-time.

Materials and Methods

Based on the 2005 Tittabawassee River floodplain results, the Trace laboratory of The Dow Chemical Company developed a method to rapidly measure the key contributors to the floodplain contamination and estimate the Total-TEQ in order to deliver the results within 48 hours or less for up to 20 samples per day. The principles are described in this paper, more details and QA/QC-data are presented in part II [2].

Results and Discussion

The PCDD/F contamination in the flood plains 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 chloro-alkali process[3]. Additional sources of PCDD/F were the Trichlorophenol (TCP) and Pentachlorophenol (PCP) productions. In all 2005 samples which had a Total-TEQ above 100 ppt, the chloroalkali pattern was clearly dominating and driving the Total-TEQ-value even if PCDD/F from the other contributing processes were present. A good analogy is that the chloroalkali pattern in all samples is like coffee and sometimes PCDD/F from additional processes contribute to the total pattern like cream or sugar added to the coffee.

Prerequisites for the method development were the reduction of the analysis to the determination of the key congeners only, the implementation of a factor to closely estimate the Total-TEQ-value from a limited number of PCDD/F congeners, and to use as many steps from method 1613b as necessary to produce a sample extract to be analyzed by GC-MS.

The principle concept is to extract the samples according to EPA method 1613b after spiking with ^{13}C-labelled standards of all seventeen 2378-substituted PCDD/F, split the raw extract and pass one portion through a shortened clean-up procedure. The extracts are analyzed with HRGC-LRMS or HRGC-HRMS. A key difference to the EPA method is the acceptance of recovery rates down to 5-10%. As long as the internal standard delivers

a quantifiable peak (a S/N ratio >10) then recovery rates even outside the EPA method limits are acceptable and allow a quantification of the internal standard as well as the target analytes. In order to achieve this, the amount of internal standard added prior to extraction was increased by a factor of 10.

Because it was anticipated to use a quadrupole instrument (Agilent 6890 gas chromatograph coupled with 5973N mass selective detector (GC/MSD)) for the analysis, the sample amount was increased to around 30 g (wet weight) in order to achieve a limit of detection (LoD) for each target component of 4 ng/kg dry weight. The moisture content was determined in a separate sub-sample.

After the extraction with benzene or toluene the extracts were concentrated to about 20ml and aliquoted. One half of the raw extract serves as a retainer for potential QA/QC check. In the event that analysis of this QA/QC retainer is required, the turn-around-time is significantly accelerated as the time consuming extraction step has already been performed. The sample analysis aliquot (other half of the concentrated extract) was passed through a silica gel column combined with silica gel/H_2SO_4 (44%) and drained directly into a carbon column. After the extract is completely drained onto the carbon column, the analytes are eluted in a reverse flow with 10 ml of n-Hexane/Dichloromethane (50:50). The clean-up extract is blown to dryness, dissolved in 20 µl of a nonane solution of ^{13}C-1278-TCDF at 50 ppb concentration and transferred to the HRGC-MS system.

Another key difference to the conventional method is the use of a 30 m DB-5MS column without any confirmation analysis, which allows reduction of the total run time to 20 minutes.

Based on the 2005 data, the quantification was limited to the determination of 2378-TCDF, 12378-PeCDF, 23478-PeCDF, 1234(6)78-HxCDF. The use of the short column made a baseline separation of 123478- and 123678-HxCDF impossible. But as both congeners have the same TEF this has no impact on the Total-TEQ. The quantification included also the corresponding ^{13}C-labelled standards and the ^{13}C-1278-TCDF injection standard. 2378-TCDD, although having an insignificant contribution to the overall TEQ in the flood plains was also added to the list of the key congeners (2378-TCDF, 12378-PeCDF, 23478-PeCDF, 1234(6)78-HxCDF) in order to detect the rare cases where the impact of Trichlorophenol production related PCDD/F had any significance on the PCDD/F residues (“white coffee”).

The lack of any confirmation analysis can lead in general to biased high data. In the case of 2378-TCDF which has to be confirmed on a polar column according to method 1613b the bias is negligible as the potentially co-eluting non-2378-substituted TCDF do not have a significant presence in chloroalkali related samples. Likewise, in the analysis according to method 1613b, biased high data are possible for 23478-PeCDF which cannot be sufficiently separated from co-eluting non-2378-substituted PeCDF congeners on a DB-5MS column[4,5]. For the Fast Analysis, this is acceptable under the conservative approach that the estimated results should not lead to an underestimation of the true value.

In order to estimate the Total-TEQ, the sum of the TEQ-values of all analyzed PCDD/F-congeners is multiplied by 1.1 and the result is expressed as E-TEQ (Estimated-TEQ). This factor was established based on the 2005 data for samples in the range above 100 ppt TEQ and expresses the average contribution of those 2378-substituted congeners in the typical floodplain pattern which are not measured with the Fast Analysis.

However, in some cases the chloroalkali pattern is overlapped with elevated PCDD/F-contributions from the chlorophenol processes (“coffee with cream and sugar”). In such cases the established E-TEQ factor is not sufficient to estimate the Total-TEQ and the E-TEQ can lead to significantly biased low data.

Therefore these samples had to be identified and flagged for an immediate analysis with the 1613b method. As the whole analytical process is highly automated, numerical criteria were developed to automatically flag these samples. Whenever the contribution of 2378-TCDD to the E-TEQ which is typically in the order of 2 % exceeds 20% in samples with an E-TEQ of 50 ppt or more, these samples are considered to have a potentially significant impact from Trichlorophenol related PCDD/F. The PCP process leads mainly to Octa- and HeptaCDD/CDF which are not quantified in the Fast Analysis and slightly elevated HxCDD/F. As TCDD/F and PeCDD/F are

typically non detectable in the PCP process, the ratio 1234(6)78-HxCDF/23478-PeCDF was calculated and used as a trigger for a potential PCP-related PCDD/F impact, whenever this ratio exceeds 1.7 in samples with an E-TEQ of at least 50 ppt.

A secondary criteria is that the ratio between the 124689-HxCDF/1234(6)78-HxCDF must be at least 0.9. 124689-HxCDF is characteristic for the PCP-process, elutes shortly before the analyzed 1234(6)78-HxCDF and was included in the quantification program.

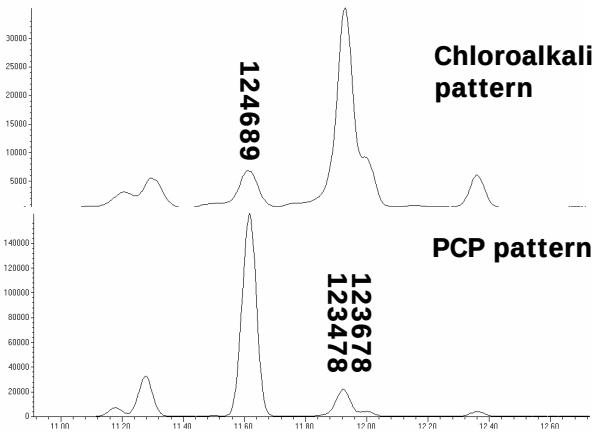

Figure 1: HxCDF mass chromatograms for a typical chloroalkali process related pattern and for an additional influence of HxCDF related to the PCP-process.

When both criteria are fulfilled the contribution of the higher chlorinated congeners which were not included in the Fast Analysis can exceed 20 % and bias low the estimated Total-TEQ. Therefore these samples were also automatically selected for a regular 1613b analysis. In some cases, mainly when the E-TEQ exceeded 30 ppb, on some ^{13}C-standard traces interferences may be present which cannot be separated with the LRMS and do not allow a quantification according to the Fast Analysis method. These samples were also selected for an analysis according to method 1613 b.

Nevertheless it is worthwhile to note that even in these few cases the estimated Total-TEQ-value from the Fast Analysis was still accurate enough that the sampling crews could proceed with the work based on the E-TEQ.

The complete procedure was summarized in a method which is in essence the method 1613b with modifications to accelerate the procedure where applicable but still include the essential QA/QC steps. The “Fast Analysis” method was presented to the EPA and approved for this investigation as 1613 RT/TRP (RT=Rapid Turnaround TRP=Tittabawassee River Floodplains).

In total, nearly 3700 samples have been analyzed between August and December 2006. Due to this workload, Alta Analytical (now Vista Analytical) was included in the process. On average, the analytical results of 20 samples were delivered within 48 hours from each laboratory.

An extensive QA/QC program was established in the development phase and along with the investigation of the floodplain samples (details are presented in part II of this publication[2]) which includes comparability studies with the EPA method 1613b, interlaboratory studies, field blanks, lab blanks, field duplicates and lab duplicates. Each set of analyses was accompanied by an OPR sample (ongoing precision and recovery), a method blank and a randomly selected laboratory duplicate. All injection sequences included two calibration standards at different levels (CS 1 and CS 3) and solvent blanks distributed over the sequence. 60 samples were also selected for a comparability study of the Fast Analysis with the analysis according to 1613 b which was performed by Alta Analytical. Results of the comparison between the Fast Analysis and the analysis of the same sample raw extracts according to method 1613b with and without confirmation of all 2378-substituted PCDF- congeners on a SP 2331-column are shown in Figure 2.

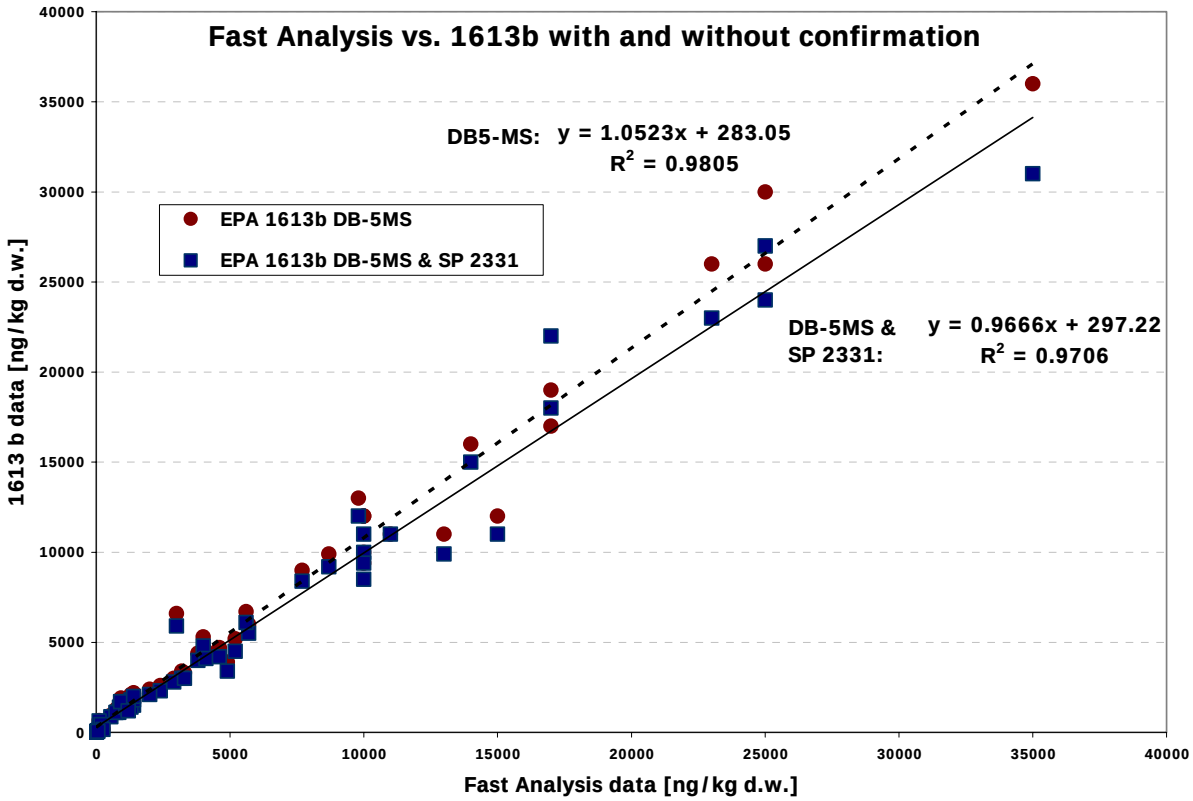

Figure 2: Comparison of Fast Analysis with EPA method 1613b with and without confirmation analysis

Besides the significant reduction in turn-around-time, the costs for the analysis were reduced to around 30% of the costs for a conventional EPA 1613b analysis.

In 2007 the investigation in the Tittabawassee River floodplains will continue with the next 11 river miles, so we anticipate to analyze around 6500 samples this year.

By carefully selecting the key congeners (not necessarily 2378-substituted PCDD/F) this method can be adapted to other cases where dominating PCDD/F pattern are present.

Acknowledgements

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References

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