PATTERN RECOGNITION IN FLOODPLAIN SAMPLES

Wilken, M[1], Martin G[1], Lamparski L[1], Denney P[2], Baker B[2]

[1]The Dow Chemical Company, Analytical Sciences, 1602 Bldg., Midland, MI, 48674
[2]The Dow Chemical Company, 47 Bldg., Midland, MI, 48674

Introduction

The Dow Chemical Company has manufactured products in Midland, MI since 1897. Located on the Tittabawassee River, a comprehensive effort is underway to understand the impact of dioxins and furans that may have emanated from certain production processes in the early 20th century. As part of the Midland Offsite Corrective Action Program (MOCA), more than 300 soil and sediment samples were taken from the Tittabawassee River and its floodplain. Samples, their duplicates and matrix spikes were analyzed for polychlorinated Dibenzodioxins (PCDD) and Dibenzofurans (PCDF). This paper describes the contribution of the 2,3,7,8-substituted congeners for the floodplain and sediment samples and how patterns found are consistent with chloro-alkali production that began already in the late 19th century.

Materials and Methods

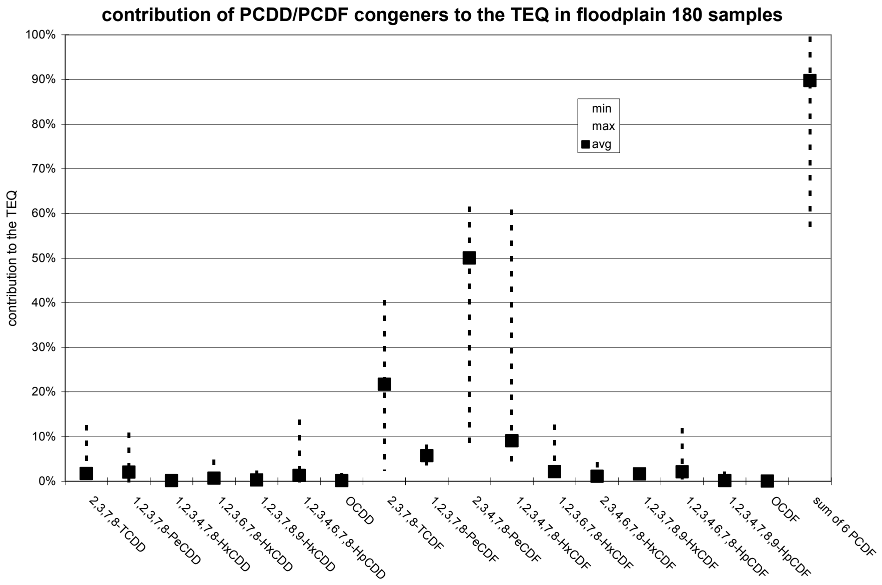
All PCDD/F analysis was performed by Alta Analytical, Inc. following EPA Method 8290, as outlined in the Quality Assurance Project Plan (QAPP) submitted by The Dow Chemical Company under the Tittabawassee River Floodplain Scoping Study to the Michigan Department of Environmental Quality. All reported data were externally reviewed according to EPA Level III guidelines, including 10% of the samples which received a Level IV data validation review.

Results and Discussion

For the data evaluation all duplicates, matrix spikes and matrix spike duplicates were excluded so that a total of 180 soil and sediment samples remains.

Figure 1 describes the average and the min-max range contribution of each of the 17 2,3,7,8-substituted congeners to the WHO-TEQ (TEQ). On average, more than 90% of the TEQ-concentrations in all samples relate to the PCDF. The dominant contributor to the TEQ is the 2,3,4,7,8-PeCDF-congener, contributing an average of 50 % to the TEQ concentration, followed by the 2,3,7,8-TCDF (21%) and 1,2,3,4,7,8-HxCDF (9%) congeners. The total contribution of these three congeners to the TEQ is more than 80 %.

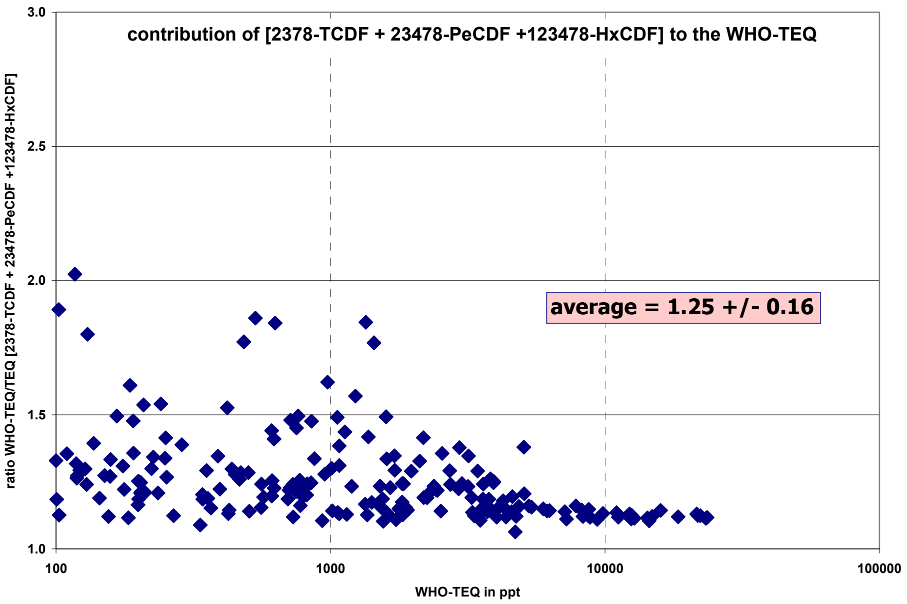
Figure 1: Contribution of PCDD/PCDF congeners to the TEQ in 180 floodplain/sediment samples



*sum of 6 PCDF: 2378-TCDF, 12378-PeCDF, 23478-PeCDF, 123478-HxCDF, 123678-HxCDF, 234678-HxCDF

In samples with TEQ concentrations above 100 ppt, the TEQ contribution of these three congeners can be multiplied by a factor of 1.25 (SD=0.16) to estimate the total TEQ (Figure 2).

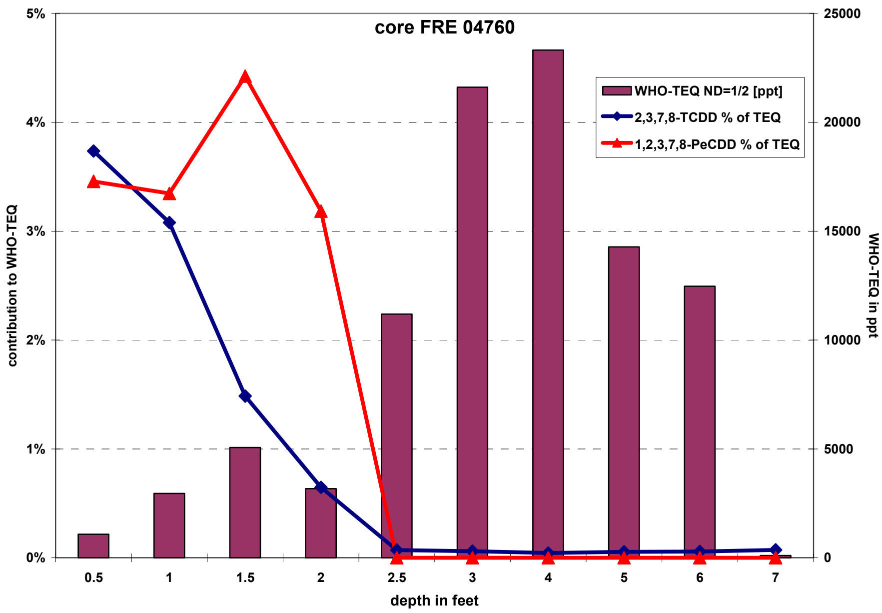
Figure 2: Contribution of three 2,3,7,8-substituted PCDF-congeners to the TEQ



Overall, 2,3,7,8-TCDD does not contribute significantly to the TEQ in these samples. In only two out of the 180 samples, the contribution of the 2,3,7,8-TCDD congener is slightly above 10%. The other 2,3,7,8-substituted PCDD congeners do not contribute significantly to the TEQ.

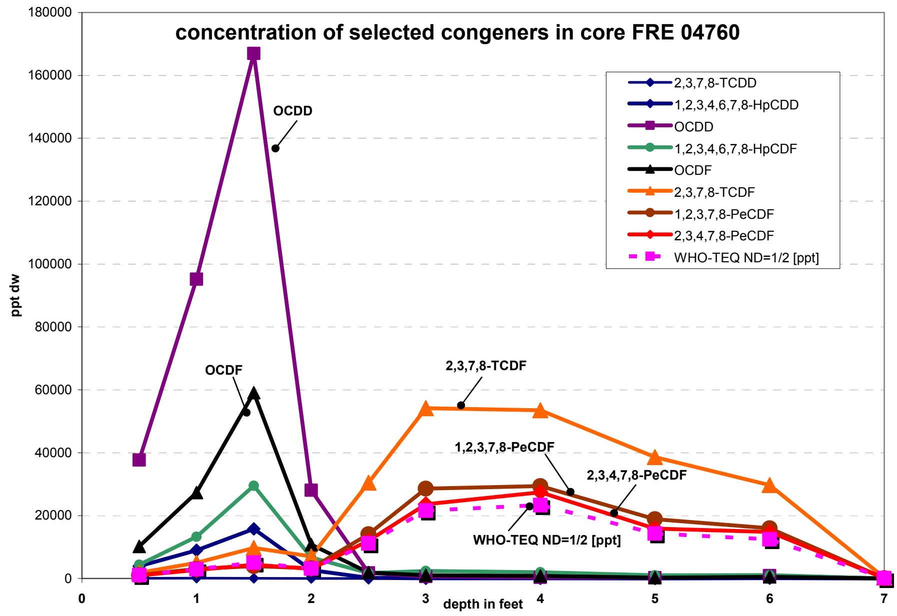
At several locations core samples were taken in distinct intervals in order to determine the vertical distribution of PCDD and PCDF. Figures 3 and 4 highlight congener profiles/patterns from one core sample (FRE 04760). Figure 3 describes a vertical distribution profile where the bars represent the TEQ value and the lines represent the relative contribution of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD to the TEQ. Within these core samples measurable PCDD/F concentrations were detected down to 6-ft with the highest concentrations below 2-ft. Between 2 and 2.5–ft, a noticeable change in the concentration, distribution and congener profile was observed. The samples below 2 ft depth showed no significant levels of PCDD, but exclusively PCDF with a pattern which is similar to PCDF-profiles known from the chloro-alkali process[1,2,3].

Figure 3: TEQ-distribution and 2378-TCDD and 12378-PeCDD TEQ-contribution in layers of a core sample



In all core sub-samples PCDF are the driving force for the TEQ levels although in the layers above 2.5 ft OCDD becomes the most dominating compound in terms of concentration. The patterns in the upper layers show also elevated levels of OCDF, 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF and are consistent with deposition related to PCP-production (Figure 4). Similar patterns could be observed also in other core samples.

Figure 4: Concentration profile of selected congeners in the layers of a core sample



A review of the production history may help to explain these patterns. More than 100 years ago, the first production process in Midland was the electrolysis of local brine in tar-coated wooden cells with graphite electrodes that discharged directly to the river. Tars and graphite, such as was used in the original manufacturing process, contain considerable amounts of dibenzofurans which can react in electrolytic cells to form polychlorinated dibenzofurans with a very specific congener distribution resembling a "chloro-alkali pattern". This original manufacturing process was abandoned in 1915. In the 1930s sedimentation ponds went into operation which significantly reduced the amount of contaminated solids discharged into the river. During the 1930s, the production of chlorophenols went into operation, forming PCDD as a byproduct.

Given this information, it is possible to "date" the lower soil or sediment layers with the higher TEQ values to the first decades of the 20th century and to identify the earliest production processes as a potential source of elevated PCDD/F levels found in the floodplain.

References

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