Pattern recognition for PCDD/PCDF and PCB in samples from primary and secondary sources

Heidelore Fiedler[1], Thomas Gräff[2], Andreas Höllriegl-Rosta[2], Gerlinde Knetsch[2]
[1] Örebro University, School of Science and Technology, MTM Research Centre, SE-701 81 Örebro, Sweden; [2]German Environment Agency, Dessau, Germany

Introduction

In a joint activity, the European Reference Laboratory with its National Reference Laboratories and the German Environment Agency (UBA) with the expertise of Örebro University in Sweden collaborated in the assessment of patterns and profiles of polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), and polychlorinated biphenyls (PCB) from primary and secondary sources. In order to identify the sources of contamination in the environment but also in food and feed, congener and homolog profiles have been assessed [1][2].

Materials and Methods

Congener profiles of 7 PCDD, 10 PCDF, and 12 dioxin-like PCB (dl-PCB) as well as 6 indicator PCB were compiled. Sum parameters including the toxic equivalent (TEQ) using the WHO2005-TEFs were computed as well. Contributions of each congener (or homolog) to the sum of the respective parameter was used for the assessment The database was maintained in MsExcel. For the recognition of typical patterns in the data, R programs for cluster analysis of the groups of PCDD/PCDF or PCB were developed.

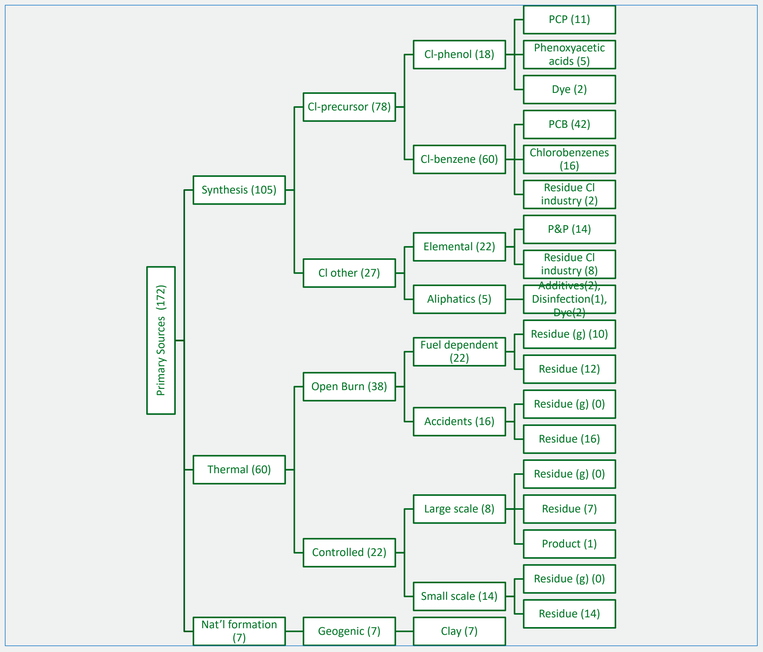

Figure 1: Grouping and classification of the primary sources (total of 172)

Results

In a first step, 278 datasets containing any of the PCDD, PCDF or PCB were grouped into primary sources and secondary sources. The evaluation grouped all primary sources into subgroups "thermal", "synthesis", "natural formation" and the secondary into "abiotic", "biotic" and "unknown" samples. From there two more levels of classification was done. Figure 1 displays the hierarchical structure of the primary sources and includes the number of datasets therein.

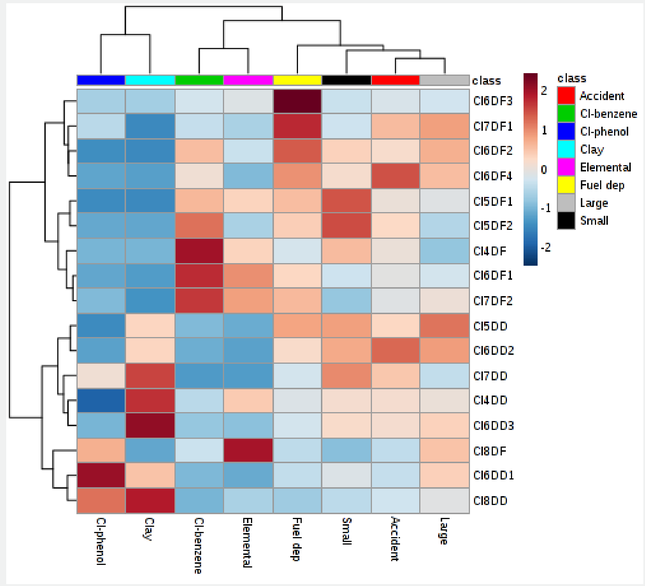

Figure 2: Dendrogram heatmap of average contribution of 17 PCDD/PCDF to the sum of PCDD/PCDF(17)

Figure 3 displays a dendrogram heatmap grouping similar profiles of 12 dl-PCB into five Groups and five Clusters. From the hierarchy of the 12 dl-PCB congeners, it can be seen that when scaling to the sum of the 12 congeners, PCB-118 by far has the largest contribution across all samples. When aplying the TEF concept and scaling to the TEQ_{PCB}., PCB-126 - due to its high TEF, is dominant in most samples,

Figure 2 displays a dendrogram heatmap grouping the eight level 2 groups according to contribution of the 17 PCDD/PCDF assigned a TEF. It can be seen that the chemical synthesis processes have distinct patterns dominated by the PCDF for the PCB (Cl-benzene group) or PCDD for the Cl-phenols. Statistically, the Cl-phenol group can be distinguished by the group from natural formation (e.g., ball clay). The combustion sources have less distinct profiles.

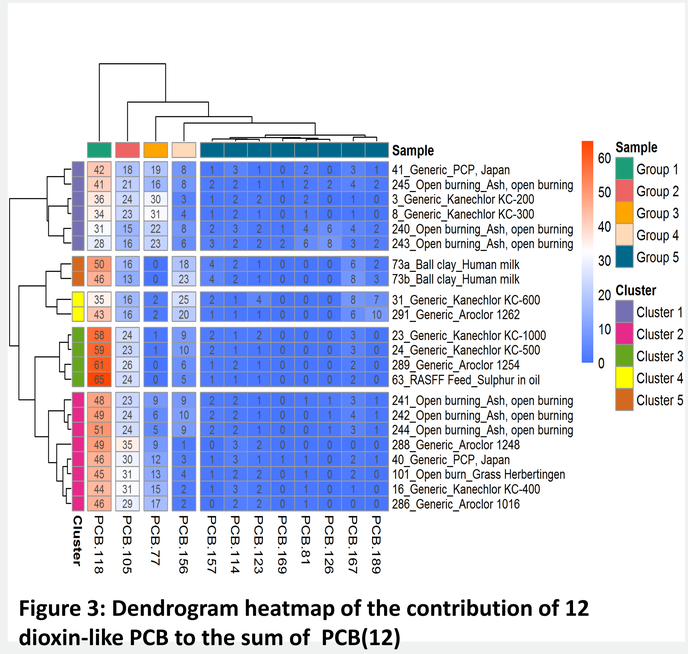

Figure 3: Dendrogram heatmap of the contribution of 12 dioxin-like PCB to the sum of PCB(12)

Conclusions

The use of this dataset will be for future assessments in two directions:

- German UBA – Sources or source pathways: To identify possible causes for contamination of environmental samples, technical products but also for food
- EURL/NRLs - Food and feed incidents/accidents: To identify the sources of contamination or contamination pathways but also identify similarities between cases even when the source could not be identified.

References:

[1] POP database of the German Environment Agency http://www.dioxindb.de/index-e.html
[2] Full report available https://www.umweltbundesamt.de/sites/default/files/medien/1410/publikationen/2019-04-04_texte_39-2019_gutachten_oru.pdf

Acknowledgement: This work was financed by Umweltbundesamt as Project No. (FKZ) 97932
Contact: Dr. Heidelore Fiedler, heidelore.fiedler@oru.se