Pattern database for identification of sources and transfers of polychlorinated dibenzo-*p*-dioxins, dibenzofurans and biphenyls

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Introduction

At Dioxin2017 in Vancouver, Canada, Malisch et al. [1] presented the initial results from a collaboration between the Core Working group "Dioxin Pattern" of the network of the European Union Reference Laboratory (EURL) with its National Reference Laboratories (NRLs) and the POP-Dioxin database maintained at the German Federal Environment Agency (UBA) [2]. Since 1991, the Germany Federal Environment Agency maintains a database of initially focused on PCDD/PCDF results from monitoring and surveillance programs coordinated by the Federal States (Länder), the Federal Institute for Risk Assessment (BfR) and the Federal Office of Consumer Protection and Food Safety (BVL). The original "dioxin database" has been expanded to include more persistent organic pollutants in relevant matrices such as environmental samples including (stack) emissions and residues of sources of POPs but also soils, sediments, ambient air and biota such as food and feed. The EURL and the NRLs are tasked with the surveillance and control of the EU limit values for feed and food and thus, have accumulated an abundance of measured data from official food and feed controls. Of special interest are feed or food samples that exceed the action levels for PCDD/PCDF, dl-PCB (on TEQ basis) or polychlorinated PCB (sum of six indicator PCB) and often are related to feed or food accidents. Such accidents have happened in the past and resulted in contamination "cases" or "crisis" inside and outside of the European Union [3,4]. Such accidents can have very different origin and some of the prominent examples include (1) the citrus pulp case from Brazil where lime from industrial use has been used in compound feed pellets for ruminants [5], (2) the Belgian dioxin crisis was caused by a feed additive heavily contaminated with improperly discharged PCB [6,7], (3) Guar gum from India contaminated with sodium pentachlorophenate, (4) several accidents involving ball clay or kaolinite as feed additive, a "natural" dioxin source [8-10], and (5) numerous incidents caused by improperly operated thermal processes such as open burning, drying or contaminated fuels. In this project, an attempt is made to join relevant datasets for PCDD/PCDF, and PCB from primary sources where these chemicals are formed and released with the secondary matrices such as fee and food or technical materials (paints, sealants) where contamination occurs. These datasets have been selected to establish typical patterns and profiles for the identification of sources of PCDD/PCDF and/or PCB contamination and thus, serve as an expert tools for rapid responses in case feed or food contaminations are discovered.

Materials and methods

The database for this joint project is composed of "technosphere" datasets from the Federal Environment Agency and amended by new datsets from literature found relevant for source identification and datasets from the food and feed controls provided by the EURl and the NRLs. The database is developed and maintained in MsExcel®; displaying one sample in one row. Each sample is charcterized by its unique sample number and descriptive qualitative information for identification and characterization as well as units and their basis (lipid, dry matter, fresh weight) and numeric results as mass concentrations for the following congeners and sum parameters:

- 17 2,3,7,8-substituted PCDD/PCDF congeners amended by the partial TEQ for PCDD, PCDF and the TEQ for PCDD/PCDF (WHO_{2005}-TEQ_{PCDD}, WHO_{2005}-TEQ_{PCDF}, WHO_{2005}-$TEQ_{PCDD/PCDF}$), and the sum of the 17 congeners (ΣPCDD/PCDF(17));
- 12 dioxin-like-PCB amended by the partial TEQ for non-*ortho* and *mono-ortho* PCB, the TEQ for the 12 dl-PCB,WHO_{2005}-$TEQ_{no\text{-}PCB}$, WHO_{2005}-$TEQ_{mo\text{-}PCB}$, WHO_{2005}-TEQ_{PCB}, and the sum of the 12 dl-PCB (ΣPCB(12));
- 6 indicator PCB amended by the sum of these six congeners (ΣPCB(6));
- Homologs for PCDD/PCDF (*tetra* through *octa*, Cl_4 through Cl_8) and the sum of the homologs ($\Sigma(Cl_4\text{-}Cl_8)$)
- Homologs for PCB (*mono* through *deca*, Cl_1 through Cl_{10}) and sum of these homologs ($\Sigma(Cl_3\text{-}Cl_{10})$).

The calculation of the sums and the TEQs was done through the "Function" tabs in MsExcel®; throughout the database, TEQs were calculated using the toxicity equivalency factors of the WHO expert group established in 2005 [11] [1].
Concentrations below the limit of detection or limit of quantification were entered as "<LOD/LOQ".
The references containing the original dataset are maintained in EndNote X7 (Clarivate Analytics, Boston, MA, USA).

Results and discussion

The datasets containing and congener- and homolog-specific values did undergo several rounds of quality control; all samples were checked against the reference (publication) and the original units were used. Corrections were made where necessary and duplicates eliminated. Finally, the database contained 280 datasets; of these 172 were assigned primary (prim) and 102 secondary (sec). The numeric information is compiled in 66 columns (17+4 for PCDD/PCDF, 12+4 for dl-PCB, 6+1 for indicator PCB, 10+1 for PCDD/PCDF homologs, and 10+1 for PCB homologs). It shall be noted that typically have information for all of the groups mentioned before. The distribution is shown in Table 1. As can be seen there is a substantial number of datasets that contain quantifiable concentrations of the 17 PCDD/PCDF congeners (95), dl-PCB congeners (21), indicator PCB (51) or PCDD/PCDF homologs (73). There was no dataset that contained values for all five groups of compounds. Given the low number of homolog-specific information for PCB, it was recommended to not further use this information in the test sets.

Table 1: Coverage of congener- or homolog-specific values of the 280 datasets in the database

Group	2,3,7,8-subst. PCDD/PCDF	12 dl-PCB	PCB(6)	PCDD/PCDF homologs	PCB homologs
# datasets	242	74	63	98	19
# datasets with all congeners/ homologs quantified	95	21	51	73	7

An initial hierarchy was developed for the primary sources as shown in Figure 1. From the chemistry in the source process, initial conclusions can be drawn as to the presence of PCDD/PCDF. For example: chlorinated phenols such as pentachlorophenol (PCP) are dominated by PCDD whereas PCB are dominated by PCDF, Therefore, secondary matrices such as treated wood will rather exhibit a PCP pattern than a PCB-pattern. For the PCB in applications, the PCB – independently of the producer or brand are quite similar and PCB with same number of chlorine have similar pattern for the six indicator PCB (Figure 2). Subsequently, secondary matrices either containing PCB such as sealants or paints or contaminated with PCB such as the feed during the Belgian chicken crisis contain the same patterns.

It has to be noted that there is quite a number of value below the limit of quantification (LOQ) such as for PCDD/PCDF with 242 datasets but "only" 95 having all congeners quantified. These datasets can still be used in the assessments, since for some sources it is expected that certain congeners are not present; *e.g.,* PCB

technical products should not contain PCDD/PCDF since it is unlikely that the C-C bond between the two phenyl rings be broken to insert oxygen and followed by ring closure with the insertion of the 2nd oxygen at position 5. Similarly, ball clay or kaolinit should not contain PCDF or food of animal origin (mammals) hardly have easily metabolized congeners present, *e.g.,* 2,3,7,8-TeCDF or 1,2,3,7,8,9-HxCDF.

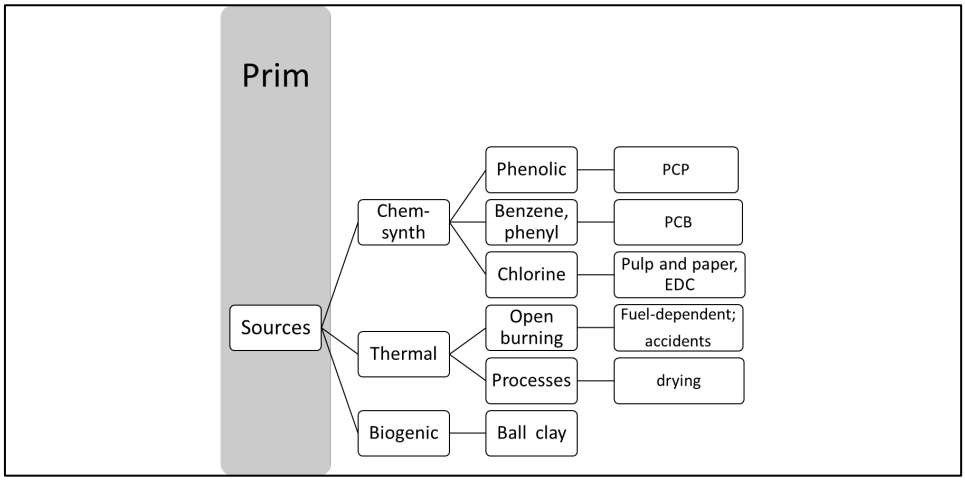

Figure 1: Main source groups and subsequent sub-groups that determine the pattern of the PCDD/PCDF

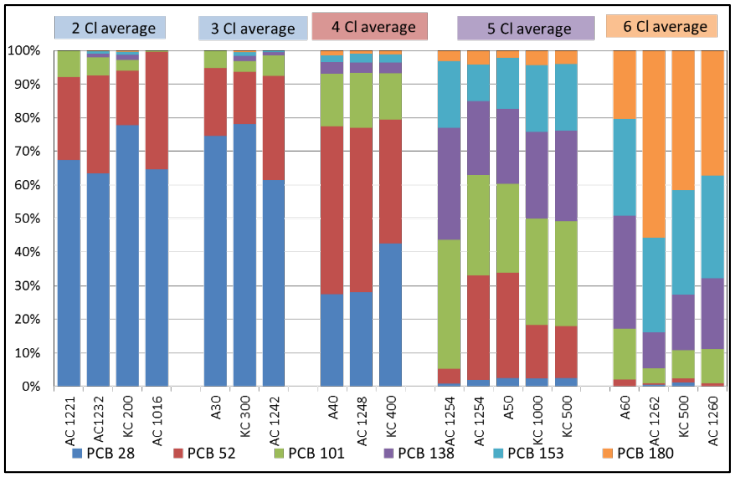

Figure 2: Indicator PCB pattern in commercial PCB according to number of chlorines (or chlorine content)

An important factor to consider are the data generators. It has been shown that despite highest qualifications including accredited laboratories, there are substantial differences between their mandates or research objectives. Among these the following: Historically, abiotic laboratories when analyzing matrices for the technosphere such as chemicals, ashes, industrial chemicals, contaminated soils) typically report 2,3,7,8-substituted PCDD/PCDF congeners but also homologs and other non-2,3,7,8-substituted PCDD/PCDF congeners whereas biotic labs analyzing foods of animal origin or humans "only" analyze the 17 2,3,7,8-substituted PCDD/PCDF. Today – due to enforcement – the analytical spectrum often is limited to 17 TEF congeners and therefore, important information as to the share of the 2,3,7,8-substituted congeners within a PCDD or PCDF homolog is

lost. This lack of information for source identification seems to be less relevant for food of animal origin (meat, dairy, eggs) but can be severe for feedstuffs or mollusks.
Another factor to consider is the very wide range of concentrations reported from mg/kg to fg/kg or fg/m³.

In order to use the database in future assessments, it has become clear that structurally the datasets have to be harmonized thoroughly as to the sequence of listing congeners or homologs, calculation of the sum parameters, treatment of values below LOQ or not analyzed congeners/homologs. QA/QC processes are to be applied for general acceptance of datasets into the base dataset. In addition, metadata have to be collected and maintained to categorize subgroups in the main groups of primary (source) and secondary (after transfer of contamination) maintained.
The use of this dataset will be for future assessments in two directions:

- 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.
- German UBA – Sources or source pathways: To identify possible causes for contamination of environmental samples, technical products but also for food.

Presently, work is ongoing to test these datasets between each other but also with "unknown" samples. Various approaches are being applied to match the profiles for further assessment.

Acknowledgements:
This work is funded by the German Environment Agency through a contract "Gutachten zur fachlichen Nutzung der Daten aus der POP-Dioxindatenbank für den Bereich Technosphäre" with Örebro University and the Core Working Group "Pattern of dioxins and PCB" by network of the EU Reference Laboratory and its National Reference Laboratories.

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