Interactive data base of PCDD/F and PCB congener patterns to aid identification of contamination sources in feed and food

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Introduction

When contamination incidents with PCDD/PCDFs and/or PCBs occur in the food chain, an important immediate step is the interpretation of the occurrence pattern for identification of the source. Existing publications that summarize this process show the difficulties and complexity of this detective work [1, 2, 3, 4]. An important goal is the fast and efficient comparison of the pattern observed in a given contamination incident with those of known patterns of possible sources. Therefore, the network of the EU Reference Laboratory (EU-RL) and the National Reference Laboratories (NRLs) for dioxins and PCBs in feed and food established a core working group (CWG) "Dioxin patterns" for build-up of a database and development of tools for interpretation.

Based on an administrative agreement in Germany, data from monitoring and surveillance programs on levels of dioxins, PCBs and other POPs in food, feed and environmental samples have been collected since 1991. The data base runs in cooperation with the Federal States (Länder), the Federal Institute for Risk Assessment (BfR) and the Federal Office of Consumer Protection and Food Safety (BVL) and is coordinated by the German Federal Environmental Agency (Umweltbundesamt, UBA) [5]. In 2014 and 2016, results of two UBA projects were presented aiming at a compilation of typical profiles/fingerprints of the PCDD/F-PCB congener patterns for the environmental compartments (emission pattern of typical industrial branches, ambient air, soil, biota etc.) for

identification of sources. These data were also considered useful for source identification in incidents involving food and feeding stuff. Therefore, the CWG co-operated with UBA allowing the effective use of limited resources.

Materials and Methods

As basis, the seventeen 2,3,7,8-substituted PCDD/Fs, the 12 DL-PCBs and the 6 indicator PCBs congeners were included, if reported. Furthermore, if available, information on non-2,3,7,8-substituted PCDD/Fs, other PCBs and additional analytes was incorporated. Besides the information on the congener pattern, the characterisation of the source is of crucial importance. The congeners were included as raw data (on concentration basis) and also with their contribution to the TEQ.

PCDD/PCDF and PCB source and secondary contamination patterns which were already observed in incidents over the last two decades in the feed and food chain were collected by the EU-RL/NRL network.

In two work packages of the UBA projects, patterns for feed and food and environmental samples were collected. From these, the data with patterns found in chemical production processes and in thermal / combustion processes were used for inclusion in the current pattern data base.

Results and Discussion

The important basis for build-up of a database is the collection and inclusion of relevant and well described congener patterns for comparison. This includes the collection of contamination patterns (patterns in sources for contamination with PCDD/Fs and PCBs):

- Sources found already in the food chain (feed, food)
- Chemical production processes in general
- Thermal / combustion processes.

The general observation, that different sample batches (can) have different patterns, must be taken into account, when deciding which patterns can be included in the data base. The collection of as many different batch/pattern combinations for chemicals (incidents) increases the informative value.

The combined data base with about 140 patterns was structured allowing a differentiation as follows: PCB, PCP, chlorobenzenes, pesticides, other chemicals, kaolinite, feed, food of animal origin, food of vegetable origin, other matrices. There is an ongoing process of discussion on options for further amendments (reduction to fewer clearly differentiated patterns; inclusion of missing patterns, if available).

Four tools for evaluation were proposed and are being evaluated by the Core Working Group:

1. “Determinator” as decision support system

The “Determinator” platform was developed as decision support system for experts (the system does not decide, but supports the expert user¸ www.determinator.wur.nl). The core is a library, which as shell has a user interface (match, browse, filter, search, sort), library access and an engine with mathematical evaluation (for calculation of match percentages).

2. Options for visualisation

From a comprehensive database with reference vectors, the most similar reference vectors are identified and the data base is condensed to e.g. 15-20 reference cases. A list of 4-6 candidates is then selected and a well planned field sampling trial is carried out. Macros can then be used for comparison of the patterns of a selected sample with others.

3. Match factors as applied in NIST mass spectral libraries

This model is being developed.

4. Clustering

The evaluation of profiles and patterns can be based on normalization of 8 homologue groups from Cl_4 to Cl_8-congeners and of 17 PCDD/PCDFs and 12 dl-PCBs on a product basis and contribution to WHO_{2005}-TEQ. Multivariate analysis with hierarchical cluster analysis (HCA) and principal component analysis (PCA) can then be used to relate the observed contamination pattern with source patterns.

One or more of these tools will be selected and then subjected to validation by trial with patterns of known incidents where the source has already been identified.

Limitations in identification of sources arise in particular in cases where a number of congeners are not detected or occur at relatively low levels, for example, with chemical sources where kinetically governed processes yield only a few congeners.

Bioaccumulation factors influence the congener patterns significantly. The carry over factors "soil and air to fruits and vegetables" and in particular from feed to food of animal origin must be taken into account. It is also possible that during production processes the congener pattern changes. It is planned to include these factors in the data base in future amendments.

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