

## DIOXINS

### PLENARY LECTURE AT DIOXIN '90, BAYREUTH, FRG

Christoffer Rappe  
Institute of Environmental Chemistry  
University of Umeå, S-901 87 Umeå, Sweden

#### INTRODUCTION

The concept of Toxic Equivalent Factors (TEFs) provides a useful method to estimate the hazard and dose-response of complex mixtures containing PCDDs and PCDFs. The levels of all the individual PCDDs and PCDFs are converted into one value of Toxic Equivalents (TEQs).

$$TEQ = \sum (TEF \times conc)$$

The two most accepted factors, the Nordic/87 and the I-TEF/89 (NATO) include both 17 discrete congeners and are almost identical. All the 17 congeners are fully chlorinated in the 2,3,7,8-positions. The TEF approach makes the assumption of additive doses, although this concept has not been confirmed.

Other closely related polychlorinated polycyclic compounds have been identified in environmental samples and technical products, but these compounds are presently not included in the TEF/TEQ system. These compounds include the polychlorinated biphenylenes, thiantrones, dibenzothiophenes, naphthalenes, pyrenes and alkylidibenzofurans. These other compounds are not discussed in this presentation.

#### ANALYSES

The analytical methods for PCDDs and PCDFs are based on HRGC/MS, primarily HRMS. The sample is extracted and the extract purified prior to the final analysis, using a multistep clean-up with a multitude of house-methods.

The accuracy and precision of these ultratrace analyses has been questioned and debated. For that reason several intercalibration studies have been performed, the most extensive by WHO/EURO where pooled and spiked samples of human milk and human blood were distributed to 30 laboratories around the world. In all 19 laboratories reported results, not all of them for both matrices. For the human milk sample 12 laboratories were considered to be qualified, their coefficient of variation for reproducibility and repeatability (C.V.) was about 30 % and for the blood analyses also 12 laboratories were qualified, and for this matrix the C.V. was about 45%.

The good accuracy could be attributed to the use of  $^{13}C_{12}$ -labelled stan-ards for the quantification of most congeners. Consequently the accuracy could be expected to be much lower in analyses where the total levels of PCDDs and PCDFs are reported. Air and flue gas sampling can also introduce additional errors due to losses during the sampling, which could be difficult to compensate correctly.

## SOURCES

The following main sources of PCDDs and PCDFs have been identified and discussed (primary or secondary)

- Contamination of pesticides
- Contamination of technical products
- Incineration of municipal waste (MSW)
- Incineration of hospital waste
- Incineration of chemical waste
- Production of iron, steel and other metals
- Car emissions
- Bleaching of pulp
- Production and use of chlorine
- Municipal sewage sludge

The absolute amount and relative importance of these individual sources will vary greatly from country to country. Based on limited data, the Swedish EPA estimated that in 1985 the total emissions of PCDDs in Sweden counted as TEQ was in the range of 400 - 600 g/year. After 1985 some of the major sources have been reduced, but new ones have been identified and added. This year (1990) the corresponding figure should be 200 - 300 g/y. Similar calculations with similar results have been performed in some other countries.

All combustion and incineration sources have primary their emissions into the air, the pulp bleaching, some metal production and sewage sludge give emissions mainly into the water.

The term *pattern* refers to the ratio between all isomers within a group of isomers, e.g. all 22 tetraCDDs or all 28 penta CDFs. It has been reported that the pattern for most incineration or combustion sources seem to be very much the same containing almost every isomer. This pattern has been identified in emissions from the combustion of MSW, hospital waste and chemical waste as well as in emissions from cars and steel mills.

The term *profile* refers to the sum of all isomers within a group, for instance all tetraCDFs as compared to all penta-, hexa-, hepta- and octaCDF. Available data indicate a larger variation in the profiles than in the patterns from different combustion sources.

It has also been found that pattern and profiles in the aqueous effluents from the pulp bleaching and Mg production are different from the combustion pattern.

## HISTORICAL ASPECTS

It is considered that PCDDs and PCDFs are the result of the more wide-spread use of chlorinated chemicals during the second half of this century, although this standpoint is disputed. A very limited number of historical samples have been analyzed including a few human samples. The reported results are close to the detection limit or the laboratory blank levels, consequently the interpretation of the results cannot solve the controversy.

Later during this conference we will report on a study on archived soil and herbage samples performed together with scientists in England. In these analyses we have used very sensitive congener specific analytical methods allowing quantification down to 1-10 pg/kg (ppq). The samples were collected during the period 1846-1986, and the following conclusions could be drawn

1. PCDDs and PCDFs could be found in all samples, including 2,3,7,8-tetraCDD
2. The levels increase over the time
3. All samples have a typical "combustion pattern", especially for the tetra- through hexachlorinated congeners
4. The ratio PCDDs/PCDFs indicates a change to be more dominated by the PCDDs for the younger samples, especially hepta- and octaCDD.

The results of this study are in agreement with a study on a sediment core from the Baltic Sea reported on during DIOXIN'89, performed in collaboration with scientists from the Swedish EPA.

## ENVIRONMENTAL TRANSPORT AND TRANSFORMATION

The aqueous emissions are transported by the water, and point sources like pulp mills can be identified in the bottom sediments at distances exceeding 100 km. Long range air transport has also been reported, but not quantified.

The environmental degradation of PCDDs and PCDFs is quite slow. Both photo-chemical and biological degradation have been studied under laboratory conditions, but at the moment it is difficult to quantify to what extent these reactions take place in the environment. The laboratory experiments are performed using single isomers, primarily 2,3,7,8-tetraCDD, although complex congener mixtures are normally found in the environment.

The environmental formation of PCDDs and PCDFs is not very much discussed, although laboratory experiments clearly show that both biological and photochemical reaction can yield these compounds.

## ENVIRONMENTAL SAMPLES

### Abiotic samples

Background levels have been reported in a series of abiotic samples like air, soil, snow, sediment and sewage sludge. The patterns in all these background samples are "combustion" patterns, but for the profiles in these samples some interesting differences can be noted.

In samples from combustion sources, the profiles are in general not dominated by any particular congener group, and this is also the case for most samples of ambient air. However, in soil, snow, sediment and sludge samples the profiles are dominated by hepta- and octa CDD. This is especially obvious for the sewage sludge samples, but also for samples of snow and vegetation collected close to highways and younger herbagesamples discussed above.

Presently the situation is not completely understood. The widespread use of chlorinated phenols like PCP during 1940-1985 has been suggested to explain these observations, however a few samples collected prior to the commercial introduction of PCP show the same feature.

The lower chlorinated congeners have a higher vapor pressure, a higher solubility than the hepta- and octaCDD, and the photochemical degradation is also faster for the lower chlorinated congeners as compared to the higher chlorinated congeners.

### Biota

The 2,3,7,8-substituted Cl<sub>4</sub>-Cl<sub>6</sub> PCDDs and PCDFs bioaccumulate and biomagnify like other lipophilic stable pollutants. The non 2,3,7,8-substituted are metabolized and/or excreted much faster and are normally not found in biological samples, exceptions are the classes of crustaceans and molluscs, where most congeners are retained. The hepta- and octachlorinated compounds are normally quite low in biological samples due to the low solubility.

The levels are much higher in aquatic animals than in terrestrial, and the levels in samples from the Northern hemisphere are higher than in samples from the Southern hemisphere.

For fish the levels of PCDD and PCDF depend on the species, organ, age, weight, fat content, sex, time of the year and location. The highest levels have been found in the Baltic Sea, the Great Lakes of America and in Newark Bay. The levels in the fish caught offshore are generally much lower than in those caught close to the coast.

## HUMAN LEVELS

It is now undisputed that background levels of PCDDs and PCDFs can be identified in the general population. In an effort to quantify this background, WHO/EURO has collected and compared the levels of PCDDs and PCDFs in human milk collected from selected and comparable mothers from many countries around the world. They should represent urban and rural areas in the respective countries, although the differences between these two categories were not remarkable.

On the other side the differences between the countries are interesting. The highest levels were found in Belgium, Holland, FRG and UK (30-40 pg TEQ/pg milk fat). The lowest levels were found for New Zealand, Hungary and Yugoslavia (5-12 pg TEQ/g milk fat) and Poland and the Scandinavian countries are in the middle. In all samples only 2,3,7,8-substituted congeners were found.

The hepta- and octaCDDs are always the highest in all samples from the general population. These congeners are normally low or absent in most food items, consequently there must be another route of exposure than via the food. These two compounds are known contaminants in commercial PCP.

Enhanced levels have been found in occupationally exposed persons as well as in persons with specific life style (very high fish consumption).

## MASS BALANCE CALCULATIONS

During his key-note lecture at DIOXIN '89 in Toronto Curtis Travis presented some mass balance calculations based on mathematical models. He came to the conclusion that the known identified sources contributed by only 10% to the total environmental burden of PCDDs and PCDFs.

Another way to perform similar calculations is by measurements of the ground deposition rate of PCDDs and PCDFs. This can be done directly or indirectly through the analyses of soil, sediment, snow and herbage samples.

The literature is very scarce of data that can be used for such calculations. However, available data indicate that the annual deposition rate is in the order of 2-20 ng TEQ/m<sup>2</sup>. Using the value 4 ng TEQ/m<sup>2</sup> and year and the area 450 000 km<sup>2</sup> for Sweden, the result is 1800 g TEQ/year. This value is about one order of magnitude greater than the calculated annual emissions in Sweden, in agreement with the calculations presented by Curtis Travis. The discrepancies can be explained by unidentified sources and/or by long range transport. Another possibility is that the estimation of the annual emissions is based on nonrepresentative samples.