SOURCES OF EXPOSURE, ENVIRONMENTAL LEVELS AND EXPOSURE ASSESSMENT OF PCDDs AND PCDFs

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INTRODUCTION

Environmental contamination by PCDDs and PCDFs can be attributed to a series of primary sources to be described below, while human exposure is due to secondary sources including food intake, drinking water, inhalation and skin contact.

SOURCES

The primary sources can be divided into four different categories

1. Chemical reactions which have resulted in the contamination of pesticides and technical products including chlorophenols, chlorophenoxy herbicides and PCBs. The production and use of these chemicals are nowadays banned or strictly regulated in most countries, but during the 1960s and 1970s these products were widely used and hence a major source of PCDD/F contamination in the environment. Other chemical processes generating PCDDs and PCDFs result from the bleaching of pulp using chlorine and the production of chlorine gas using graphite electrodes.
2. Thermal reactions. Many types of these processes have been identified as important sources of PCDDs and PCDFs though mechanistic details have not been entirely elucidated. It seems that most thermal reactions involving chlorinated organic or inorganic compounds result in the formation of PCDDs and PCDFs. Of special importance is the incineration of various types of wastes (municipal, hospital, hazardous) and the production of iron and steel, both processes will be discussed below.
3. Photochemical reactions, which can result in the formation as well as the degradation of PCDDs and PCDFs. These reactions are of special interest, as most combustion and incineration sources produce emissions directly into the atmosphere and a large portion of these emissions undergo long-range transport.
4. Enzymatic reactions. In addition to the in vitro reactions described during DIOXIN '91 from chlorophenols and peroxidases, recent evidence shows that these reactions appear also to occur under true environmental conditions in sewage sludge.

In a recent EEC document quantitative data from some European countries from 1989/1990 of the annual emissions of PCDDs and PCDFs into the air were collected. (1). The countries were Germany, UK, The Netherlands, and Sweden. Counted as Toxic equivalents (TEQ) the estimates given in the report are:

Germany	1619 - 12419 g TEQ/year
UK	157 - 933 g TEQ/year
The Netherlands	962 g TEQ/year
Sweden	122 - 288 g TEQ/year

These figures are based on limited data and must be considered as very rough estimates. Moreover, most of the countries have reduced their emissions in the past two years.

Municipal solid waste incineration

The above mentioned EEC report discusses this particular source in detail (1). The conclusion is made that technology now exists to significantly reduce the emissions from these incinerators to a level below 0.1 ng TEQ/m^3, which is a guideline in many European countries. The technology to reach this is based on improved combustion and on various types of dry, semi-dry, or wet scrubbing. The earlier, more primitive, technology could result in emissions 100-1000 times higher. Such emissions have resulted in local contamination problems. Levels exceeding 6 pg TEQ/g milk fat have been fond in the milk obtained from cows grazing in the vicinity of such incinerators.

A question receiving much attention concerns the influence by various chlorinated compounds such as PVC in the wastes being incinerated. In the EEC report it is stated that no data are available to prove that elimination of chlorinated compounds like PVC, would reduce the dioxin emissions.

Production of iron and steel

In 1986 we reported that PCDDs and PCDFs could be identified in dust from a steel mill in Sweden at levels of 800 pg TEQ/g dust. At DIOXIN '88 in Umeå we also reported on a study in a pilot plant where scrap metal was melted and recycled. Using a batchwise charging, the collected smoke contained 110 ng TEQ/m . The Swedish EPA considers the production of iron and steel to be the major source of PCDDs and PCDFs in Sweden.

In 1991 it was found that sinter plants in Sweden and in the Netherlands emit up to 3 ng TEQ/m^3 or 2-4 g TEQ/year and plant (1,2). It has also been found that dust from foundries can be contaminated by PCDDs and PCDFs at levels up to 22 700 pg TEQ/g dust (2).

It is interesting to notice that the specific congener patterns found in these samples from the iron and steel industry are very similar to those which constitute the typical incineration pattern, with the exception that the PCDFs are present at much higher levels than the PCDDs, primarily the tetra- and pentaCDFs. In addition a series of chlorinated dibenzothiophenes (PCDTs) have been identified in the sintering plants and the foundries at approximately the same levels as the PCDFs. The PCDTs have the same nominal masses as the PCDDs, but these two groups of pollutants can be effectively distinguished by MS/MS technique.

ENVIRONMENTAL LEVELS

Abiotic samples

Background levels of PCDDs and PCDFs have been reported in a series of abiotic samples including air, water, snow, soil, and sediments. The patterns found in these samples are the

'combustion' patterns, but for profiles some interesting differences can be noted for the profiles. In samples from combustion sources the profiles are generally not dominated by any particular congener group. However, in air, snow, sewage sludge, and sediment samples the profiles are very much dominated by the hepta- and octa CDDs.

Presently this controversial situation is not completely understood. The widespread use of pentachlorophenol during 1940-1985 has been a suggested explanation, however various samples collected prior to the commercial introduction of pentachlorophenol show a similar feature.

The photochemical degradation of PCDDs and PCDFs has found to be faster for the lower chlorinated congeners as compared to the higher chlorinated congeners. However, the aereal deposition seems to be much larger than the identified sources both counted as TEQ values and total PCDDs and PCDFs. Consequently a photochemical formation of hepta- and octa CDD cannot be ruled out.

Within the Swedish dioxin survey high volume air samples have been collected on the island of Gotland in the Baltic Sea. After trajectory analyses samples collected during stable weather conditions were analyzed. The results show that levels and patterns of PCDDs and PCDFs depend on wind direction. The lowest levels were seen in trajectories from N and NE, the highest levels in samples from S and SW (3).

Biota

The 2,3,7,8-substituted Cl_4-Cl_6 PCDDs and PCDFs bioaccumulate and biomagnify like other stable lipophilic 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, in which most congeners are retained. The hepta- and octachlorinated compounds are normally quite low in biological samples due to their low solubility. The levels are normally much higher in aquatic mammals than in terrestrial.

For fish samples the levels of PCDDs and PCDFs vary with species, tissue, age group, body mass, fat content, sex, season and location. The highest levels have been reported in samples from the Baltic Sea, the Great Lakes of North America, and from the Newark Bay, New Jersey, USA. The levels in fish caught well offshore are generally much lower than in those caught in the vicinity of the coast.

Up to now most data have been generated from pooled samples or single individuals, and very little attention has been given to the individual variation. In a feeding study of farmed salmon using a well defined feed spiked with 13C-labelled compounds a tenfold variation of tetra- and penta CDDs and CDFs could be found between individuals from the same tank. In the future greater attention must be given to individual variations before strict conclusions could be drawn concerning the environmental situation.

An extensive program has been devoted to investigate the levels of PCDDs and PCDFs in herring from various locals of the Baltic Sea. In this study primarily pooled samples were analyzed. In general the levels were found to be higher in the less polluted Gulf of Bothnia than in the Baltic Proper, probably due to the larger biomass in the highly eutrified Baltic Proper. In these samples the major contribution to the TEQ-values were found to come from the 2,3,4,7,8-pentaCDF, a congener that has not been associated with the bleaching of pulp using chlorine gas. Production of bleached pulp is the dominating industry around the Gulf of Bothnia. In contrary to a recent statement this particular

congener has also been found to give a major contribution to the TEQ-values found in air samples.

HUMAN TISSUE LEVELS AND DIETARY INTAKE

Analyses of human fat samples is the best way to estimate the human exposure to PCDDs and PCDFs. It is now undisputed that background levels can be identified in the general population. Enhanced levels have been found in occupationally exposed individuals as well as in people with specific life style (e.g. those with a very high fish consumption).

In an effort to quantify this background exposure WHO/EURO has collected and compared the levels of PCDDs and PCDFs in human milk collected from selected comparable mothers from many countries around the world. The mothers chosen represent urban and rural areas in the respecitve countries, although the differences between these two categories were not remarkable. However the observed differences between countries are interesting. The highest levels were found in samples from Belgium, The Netherlands, Germany, and the UK (30-40 pg TEQ/g milk fat). The lowest levels were found in samples from Hungary and Yugoslavia (5-12 pg TEQ/g milk fat). The Scandinavian countries, Poland and Japan were found to be in the middle.

The observation of almost equal levels in Japan and Sweden is remarkable because it has been estimated that the sources in Japan are up to 100 times larger than the identified sources in Sweden. Both countries have approximately the same area, and Japan is 15 fold more densely populated.

In general only 2,3,7,8-substituted congeners are found in human samples. The hepta- and octa CDDs are by far the highest levels in samples from the general population. Interestingly, these congeners are normally quite low in fish and other food items from the aquatic environment. They are present at low levels in dairy products and beef and pork.

Since food is considered to be the major source for human exposure to PCDDs and PCDFs, food surveys should give valuable information about the exposure situation. Such surveys performed in the Netherlands and in Germany show median daily intakes of 1-2 pg TEQ/kg b.w. However recent analyses of feces from Sweden indicate a much higher daily exposure (4). This is remarkable because the human fat levels are normally two times higher in the Netherlands and Germany as compared to Sweden.

The above discussed feces study also indicates that the daily excretion of octaCDD can be in the range of 5000 - 10000 pg/person. This observation can hardly be explained by the known food intakes.

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