

FROM SOURCE TO EXPOSURE: SOME OPEN QUESTIONS

Hutzinger, O. and Fiedler, H.

Chair of Ecological Chemistry and Geochemistry, University of Bayreuth
P.O. Box 10 12 51, W-8580 Bayreuth, Germany

Introduction

As PCDD/PCDF are not industrial products the production of dioxins cannot be regulated by laws such as the Chemical's Law in Germany or TSCA in the United States. Therefore, indirect measures have been taken worldwide to reduce new inputs of PCDD/PCDF. Laws and guidelines have been released to minimize emissions of dioxins, e.g.

- Several countries have set an emission limit of 0.1 ng TEQ/Nm³ for flue gas of waste incinerators (Sweden, the Netherlands, Austria, Germany)
- No sewage sludge will be allowed to be used in agriculture that exceeds a limit value of 100 ng TEQ/kg dry substance; furthermore a restriction of the amount to be applied on fields and grassland (Germany)
- Ban of products that contain high amounts of dioxins: e.g. pentachlorophenol, polychlorinated biphenyls (PCBs)
- Prohibition of halogenated scavengers in leaded gasoline.

Sources

The sources of PCDD/PCDF can be divided into three groups:

- Industrial processes
- Thermal processes
- Secondary sources = reservoirs

Open questions:

All sources indentified and quantifiable?

Formation Mechanism

PCDD/PCDF formation can be minimized by technological means. Understanding of the formation mechanisms is essential, however, to develop strategies for such minimization.

Chemical Processes

Experiments have proven that chemical processes are suspect to generate PCDD/PCDF under the following conditions:

- high temperatures
- alkaline media
- uv-light
- conditions favoring radical reactions.

Furthermore all processes should be checked for the presence of chlorinated solvents, additives, or catalysts (e.g. AlCl_3 , FeCl_3).

Open questions:

Exact mechanism of formation not known.

Thermal Mechanisms

Although there are several gaps in our knowledge, PCDD/PCDF can be formed as thermodynamically stable compounds in combination of the reactions listed below:

- Homogeneous reactions in the gas phase
 - within the combustion zone at 800-1,200 °C and/or
 - in the after-combustion zone at temperatures below 800 °C.
- Heterogeneous reactions on surfaces of particles
 - within the combustion zone
 - in the after-combustion zone = raw gas
 - in the presence of fly ash (fly ash may act as both reagent as well as catalyst)
 - from particulate carbon present in fly ash
 - from aromatic compounds present in raw gas.

Open questions:

Which mechanism is domineering - which parameters are important?

Pathways Significant for the Environment

Although we think that the most important sources have been recognized it should not be forgotten that it is only 5 years ago that PCDD/PCDF have been detected in the effluents of pulp mills and in pulp and paper products. The knowledge about the occurrence of dioxins in the chloroalkali electrolysis is only 2 years old. In Germany the discovery of about 1 million tons of red copper slag with an average concentration of 50,000 ng TEQ/kg equals more than 50 kg TEQ. This material has been marketed and represents a reservoir of more than 1,000 secondary sources in about 250 cities. These examples show that it is almost impossible to a) know all sources, and b) to quantify the amount of dioxins present in the environment.

To estimate human exposure it is important to know the pathways from the different categories of sources to man and/or environment. We would like to rank the known sources into three different categories with respect to its impact:

- 1) Little impact on man and environment
 - Industrial processes: closed circles, intermediates, residues
 - Thermal Processes: solid and liquid residues
 - Reservoirs: Waste dumps (should be immobile)
 - if the presence of PCDD/PCDF is known the dioxin-containing "products" are treated as hazardous waste and dumped according to national regulation

- 2) Impact on the environment
 - Industrial processes: distribution of final products
 - Thermal processes: flue gas, exhaust gases from stationary and diffuse sources
 - once released to the atmosphere PCDD/PCDF can be distributed (undergo long-range transport or dry/wet deposition) and contaminate vegetation, soil, water, structures (roads, roofs, etc.)
 - entrance to food-web
 - Reservoirs: Leaching from dumps, contaminated areas = accident
 - Application of sewage sludge, compost, liquid manure
 - impact on soil and afterwards to terrestrial food-chain
 - to a lesser extent impact on water → sediments → groundwater
 - Vegetation represents one of the largest reservoirs for PCDD/PCDF
 - leaf fall provides contamination of soil.

- 3) Impact on man
 - Industrial processes: distribution of final products
 - presence in the human surrounding (paper, textiles, etc.) via skin contact, inhalation (indoor air)
 - Thermal processes: flue gases and exhaust gases
 - direct pathways: inhalation of ambient air
 - indirect pathway: terrestrial and aquatic food-chain
 - Reservoirs: → food-web starting from soil or water.

Open questions:

Only concept available, only few quantitative aspects known.

Transfer and Transformation

The most important environmental transfer pathways are:

Evaporation: Relatively little is known about evaporation processes of dioxins. Due to low vapour pressure, high adsorption coefficients, high lipophilicity PCDD/PCDF tend to adsorb on particles (with high content of organic carbon). Thus, especially the higher chlorinated - more lipophilic - PCDD/PCDF will be preferentially found on particles than in the gaseous phase. Nevertheless, analysis of ambient air has shown that tetra- and pentachlorinated PCDD/PCDF are present at relatively high concentration in the

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gaseous phase; the ratio between gas phase and solid phase distribution depends on the temperature and the amount of particles present in the air.

Dry and wet deposition: Dioxins released from thermal sources are removed from the atmosphere by dry and/or wet deposition. In general, dry deposition is the dominating process but wet deposition cannot be neglected.

via water: Due to the low water solubility of PCDD/PCDF aquatic transfer mechanisms will play a minor role.

Erosion: Erosion (transport of PCDD/PCDF bound on particles) may be important for certain contaminated areas (such as old dumps from pesticides manufacture, Kieselrot).

Photodegradation: Photodegradation of dioxins in the gas phase via oxidation occurs relatively fast. Until now, the degradation of PCDD/PCDF by tropospheric OH-radicals has not been studied. PCDD/PCDF adsorbed on particles do not undergo photodegradation neither during long-range transport in the atmosphere nor on soil surfaces.

Microbiological degradation: Under environmental conditions microbiological activities (e.g. peroxidases, lactases) do not influence the background level of dioxins. On the other hand studies on the formation of PCDD/PCDF from chlorophenols by the same enzymatic activities are underway.

Open questions:

Almost all information on transfer and transformation comes from controlled (e.g. laboratory) studies. The significance of these processes in the real environment is in most cases not known. Some examples are: Importance of phototransformation, remobilization of PCDD/PCDF from soils, isomer-specific distribution in vapor-particle partitioning, importance of run-off from surfaces, mechanisms of transfer from air to plants, etc.