DE NOVO FORMATION OF "DIOXINS": 13 YEARS OF SENSE AND NONSENSE

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The term DE NOVO formation was first applied to the thermal synthesis of PCDD/PCDF in the paper originally describing their presence in flue gas and fly ash from municipal waste incinerators. G. Lunde from Norway had previously observed the formation of chlorobenzenes from polyethylene and inorganic chlorine donors.

Until about 1980 it has generally been assumed that the source of polychlorinated dibenzodioxin (PCDD) and dibenzofuran (PCDF) contamination in the environment is their release with chemicals and wastes. Examples would be the manufacture of polychlorophenol-derived herbicides as well as the incineration of chemical wastes containing known PCDD/PCDF precursors such as polychlorophenols, -benzenes and -diphenyl ethers.

In 1978 DOW scientists reported that in addition to municipal waste incinerators PCDD and PCDF were found among others in an oil-fired power plant, city dust, in commercial sludge fertilizer, residues from car and truck mufflers, as well as in soot from home fireplaces and cigarette smoke. Such findings inferred that dioxins could also form from many kinds of combustion processes not necessarily related to the production or incineration of industrial chemicals. These and other findings led to the so-called "Trace Chemistries of Fire" hypothesis which stated that numerous products, such as PCDDs, PCDFs and other chlorinated aromatics form in trace amounts, whenever carbon compounds and chlorine are combusted at high temperatures. This hypothesis thus suggest de novo formation of dioxins, i.e. dioxin formation from the pyrolysis of a variety of chemically unrelated precursors including naturally occurring precursors together with a chlorine donor. Consequently, dioxins can form by combustion not only of man-made, chlorinated organic chemicals such as pentachlorophenol and PCB but they can also result from the burning of natural materials.

The discussion and controversy about Trace Chemistries Of Fire (TRACOF) or De Novo Formation (DENOFO) hypothesis has shifted considerably. Initially the main emphasis and strength of TRACOF was the realization that for PCDD/PCDF in the environment other sources than production of chlorine chemicals exist. In the last few years proponents and opponents of the TRACOF hypothesis have come closer.

DEVELOPMENT OF TRACOF

TRACOF

Original position:

- there are other, thermal sources of PCDD/PCDF unrelated to chlorinated phenol production
- whenever C, and Cl containing materials are burned PCDD/PCDF are formed by a complex mechanism
- dioxin background is at least partially due to natural processes.

OPPONENTS

Original position:

- organic (aromatic!) chlorine chemistry is sole cause (source) of PCDD/PCDF in the environment
- one molecule of TCDD in the environment is one molecule too much
- dioxins can easily be avoided by shutting down Cl-phenol and related productions.

Present general agreement:

TRACOF has theoretical basis but most PCDD/PCDF in the environment probably come from "Civilisatory Activity" related to combustion of a wide variety of substances including chlorinated compounds but not first order to chlorine chemistry production.

Evidence for de novo formation can come from: 1) Theoretical considerations, 2) experimental evidence, 3) analysis of historical (preindustrial) samples.

1. With the exception of approaches by Shaub and Townsend little theoretical information is available

2. Considerable information has become available from small scale laboratory experiments. PCDD/PCDF have been detected from thermal reactions of a variety of precursors and the following list ranks some systems which yielded "Dioxins" from the most likely to the least likely:

2,4,5-Trichlorophenol	→	D
Halogenated aliphatics	→	I
Benzene + $AlCl_3$	→	O
Short chain alkanes + HCl	→	X
Carbon + Catalyst	→	I
CO_2 + Catalyst	→	N

3. Historical samples can be devided into sediment samples and archaeological human samples. Sediment samples clearly show a dramatic increase of PCDD/PCDF content beginning with 1940 sediment layers. However, several reports show the presence of low level dioxin content of sediment layers dated much earlier.

Human adipose samples have been analyzed from frozen and desiccated samples. Since human body burden, even today, essentially comes from contaminated food and not inhalation only extremely low levels are expected because the environment and thus food sources was likely not contaminated in pre-industrial times.