# TRACE CHEMISTRIES OF FIRE REVISITED

Warren B. Crummett
Research Fellow Retired
Dow Chemical Company
Midland, Michigan, USA

Ten years ago we said ". . . . chlorinated-p-dioxins are ubiquitous. Their ubiquity is due to the existence of a natural phenomenon, trace chemistries of fire." We said that the hypothesis simply recognized the fact that many different chemical events occur in a fire. We said "the chemistry is such that low concentrations of either inorganic or organic chlorides in the fuel can be expected to produce traces of chlorinated dibenzo-p-dioxins."

Subsequent excellent investigations have shown that fly ash from municipal incinerators always contains PCDDs (2, 3, 4, 5, 6, 7, 8). Soot from wood combustion contains measurable quantities of PCDDs (9,10). PCDDs are in emissions from the combustion of light hydrocarbons (11, 12, 13). About half of the samples of fly ash taken from coal-fired powerhouses had measurable quantities of PCDDs (14, 15). Many more precursors have been identified (16, 17). Thus, the formation of miniscule amounts of PCDDs is one of the numerous chemical events which occur in a fire.

Much more difficult to prove was whether PCDDs are formed by *de novo* synthesis in a fire. However, this has now been shown conclusively (18, 19, 20, 21, 22, 21). The various experimental designs and the elegant analytical chemistry required are examples of measurements made of the highest possible quality.

Another determination requiring the highest quality isomer specific analytical work, as well as an understanding of theoretical chemistry, was that of thermal mechanisms for the *trace chemistry of PCDDs* in combustion. This has now been worked out and clearly shows that at least two mechanisms pertain. Chlorine donors and ring donors react in at least two different ways, and the dioxin products thus produced reach equilibrium resulting in predictable isomer ratios (24.)

Data sufficient to determine if PCDD ubiquity is solely due to 'trace chemistries of fire' are not available. Some investigators apparently believe that the production of PCDDs in paper mills (25), petroleum refineries, and other chemical processes are large contributors to ubiquity. However, any data on their introduction and dispersal in the environment are not readily available. So any comments are purely speculative and not scientific.

Nevertheless, it is reasonable to assume that the 6 part per trillion concentration of 2,3,7,8-TCDD in *average human adipose tissues from industrialized societies* (26) can be assigned as follows: less than 1 part per trillion from *de novo* synthesis in fires, about 3 parts from other syntheses in fires, and the rest from other sources.

Such speculation makes it obvious that archaeological investigation (27) cannot determine if dioxin synthesis was occurring in ancient camp fires since such synthesis was necessarily *de novo* in nature, and the analytical methodology is simply not sensitive enough.

Thanks to the extraordinary work of many scientists, the "trace chemistries of fire" hypothesis may now be called a theory. Even the most difficult part of the hypothesis, *de novo* synthesis, has been established.

In the Rome workshop on incineration, it was concluded that: "Rather than attempting to avoid certain items in incineration, it may be more important to optimize combustion conditions." This requires quantitative information which describes improved operating conditions for the incineration of waste. Unfortunately, we are just now starting to systematically address that very important subject (28).

Most analytical facilities capable of determining PCDDs at subpart per trillion levels are now so tied up assuring compliance with regulations that very little basic research is possible. By plunging abruptly into regulation, we have missed the opportunity to understand basic chemistry at trace levels; and worse still, we have ignored other trace products of fire. A new approach is needed.

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