

## THE DOW CHEMICAL ROLE IN ADVANCING THE TRACE CHEMISTRIES OF FIRE HYPOTHESIS

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### ABSTRACT

The foundations for the initial hypothesis that trace chemical reactions could be an unexpected by-product of common combustion can be found in the published work of Olie, Vermeulen and Hutzinger. In their 1977 publication entitled: "Chlorodibenzo-p-dioxins and Chlorodibenzofurans Are Trace Components of Fly Ash and Flue Gas of Some Municipal Incinerators in the Netherlands," these scientists set the stage for environmental studies which would span more than a decade and would lead to controversy regarding the source of CDD/CDF pollutants in the environment.<sup>1</sup> It would be less than a year from the time of this publication before The Dow Chemical Company Michigan Division plant site would become the target of intense scrutiny regarding the source of CDDs that were discovered in fish collected from the Tittabawassee River which flows adjacent to this industrial facility. Historical Dow involvement in the production of chlorinated phenolics and chlorinated phenoxy herbicides at the Midland facility appeared to be the obvious source of the CDD pollution to the river, however, analytical findings did not support this conclusion and ultimately led to our involvement in furthering the TCOF hypothesis.

CDDs at the Midland plant site were ultimately traced to fly ash emissions from an industrial hazardous waste incinerator rather than the obvious "leak" from one of the chlorophenolics production facilities. Because this finding was contrary to the current beliefs of many within the scientific community at that time, Dow set about to collect additional data to test the TCOF hypothesis. Included in these studies were examinations of fly ash from a variety of incineration devices, soils collected from various rural and urban locations, volcanic ash samples from the early eruptions of Mt. St. Helens in Washington, dried municipal sewage sludge (modern and preserved retainers predating use of chlorophenolics), and laboratory studies involving potential "de novo" synthetic routes which could lead to the trace level generation of CDDs/CDFs during combustion.

### INTRODUCTION

Beginning in 1977, information was becoming available that CDDs/CDFs were produced in municipal incinerators during the combustion of ordinary household refuse. Olie *et al.* detected these compounds in particulates emitted from Dutch municipal waste incinerators,<sup>2</sup> and Buser *et al.* reported similar findings in fly ash from a Swiss municipal incinerator and an industrial heating facility.<sup>2,3</sup> In each of these papers, the authors concluded that the likely source of CDDs/CDFs was a combination of dechlorination and condensation of chlorophenols present in the waste fuel, however, Olie also surmised that their synthesis from non-phenolic precursors (*de novo* synthesis) was possible. Employing the work of these scientists as a foundation, workers from The Dow Chemical Company published the results of a study which not only supported previous findings, but also expanded the scope of potential sources to include virtually all combustion situations.<sup>4</sup>

The findings of the Dow study led to the formulation of an hypothesis called "*Trace Chemistries of Fire*" (TCOF). Although this hypothesis has been interpreted in many different manners, the original work set forth a very simple statement which has been summarized by Crummett and Townsend:<sup>5</sup>

"...the TCOF hypothesis states that numerous chemical reactions occur during combustion. These reactions produce numerous products, some of which are at very low concentration (parts per million or less) and are emitted in smoke or are retained in the ash. Among such trace products are the well known polynuclear aromatic hydrocarbons, as reported by the National Academy of Sciences.<sup>6</sup> The trace chemistries of fire hypothesis includes chlorinated aromatic compounds among such products—particularly chlorinated dibenzodioxins, chlorinated dibenzofurans, and polychlorinated bi- and terphenyls."

Perhaps due to frequent misinterpretation of the basic TCOF hypothesis or the motivations of its founders, this theory has been the subject of controversy for more than a decade. Today however, the amassed research of literally hundreds of scientists appears to confirm its basic premise. Some of these subsequent findings have involved the continued efforts of Dow Chemical researchers, and several of these topics will be described herein.

#### DISCUSSION

The discovery of TCDD in catfish, taken from the Tittabawassee River which flows through the Michigan Division plant site, was the event which occurred in 1977 that resulted in the involvement of Dow Chemical in studies leading to the evolution of the TCOF hypothesis. At the time of this finding, it was the consensus opinion of the scientific community that current and historical production of chlorinated phenolics at the site were the reason behind contamination of the river. However, diligent work by a team of Dow scientists failed to confirm this opinion; no leak could be found which emanated from a chlorophenolic production facility. At that time, while the bulk of the Dow team labored over interpretation of these findings, the analytical chemists devoted themselves to finding the source of an annoying reagent blank problem that had continually plagued their work. In the course of this quality assurance program it was discovered that atmospheric dust in the laboratory was the primary culprit relative to the reagent blank problem. Interestingly, it was this simple finding that changed the course of the entire Dow investigation. Instead of searching for a waterborne leak to the river, we turned our attention to airborne sources which ultimately led to the discovery that the Dow hazardous waste incinerator was the major source of TCDD to the local river. To the amazement of all involved, the TCDD was transported into the water via a particulate carrier, namely fly ash.<sup>7</sup>

Although the Dow scientific team was aware of the recent findings of Olie *et al.* and Buser *et al.*, and understood that their identification of the incinerator as the source of TCDD to the river was not a *first*, they were uncertain as to how such information would be interpreted by government regulatory agencies and the general public. Because the findings of the Dow study did not support the consensus opinion of the scientific community at that time, it was imperative that Dow institute additional studies to attempt to confirm the connection between combustion and CDDs pollution of the environment. Such studies were undertaken immediately and by late 1978 when the TCOF report was published, evidence had been collected which indicated that coal-fired powerhouse fly ash, municipal incinerator fly ash, chemical waste incinerator fly ash, internal combustion engine emissions, residential wood combustion unit fly ash, cigarette smoke, and charcoal broiled meat were all sources of CDDs/CDFs to the environment.<sup>7</sup> Despite such data, controversy enveloped the TCOF hypothesis from the very day of its release and to some minor extent, still persists even today.

Throughout the TCOF study, Dow scientists realized the need for improved CDD/CDF isomer specificity if analytical findings were to be useful for determining the source of these compounds in the environment. The concept of using the isomeric distributions of CDDs/CDFs to *fingerprint* sources appeared reasonable if such

analyses could be accomplished routinely in a reliable manner. By the latter part of 1979 new methodology had evolved which met these demands. Via a procedure that employed packed column gas chromatography-low resolution mass spectrometry (LRGC-LRMS), the Dow scientists could examine a multitude of environmental matrices for isomer specific tetra- (22 isomers), hexa- (10 isomers), hepta- (2 isomers) and octachlorodibenzo-p-dioxins. This methodology included preparation of individual isomer standards for each analyte, purchase and synthesis of several [<sup>13</sup>C,<sup>12</sup>J]-labeled CDD internal standards for quality assurance, and the necessary validations of the procedures.<sup>8-10</sup>

From an historical perspective, the initial application of isomer specific CDDs methodology to various soil samples indicated a potential for identifying combustion sources in the environment via their isomeric and congener group distributions.<sup>10</sup> However, the eruption of Mount Saint Helens in May of 1980 offered an opportunity to diverge from the trend of distinguishing man-made combustion sources and allowed us to pursue mother nature herself. While the goal for the study was to discover that volcanic eruptions generate trace amounts of combustion by-products (e.g., PNAs = polynuclear aromatics, PCBs = polychlorinated biphenyls, and CDDs/CDFs), the actual findings returned us to our original course. Interestingly, examination of many ground fall volcanic ash samples indicated that the ash as emitted naturally is virtually free of contamination with the designated contaminants. However, after exposure to various local environmental conditions (e.g. blast zone, rural, near interstate highways, and urban) it was discovered that the ash became contaminated with all of the specified analytes.<sup>7</sup>

During 1981 and 1982 another attempt to test the TCOF hypothesis involved an investigation of particulate material collected from the chimneys of residential wood combustion units.<sup>11</sup> Its purpose was to determine whether, under normal operating conditions, CDDs were produced during the combustion of wood in a variety of home heating units. From the findings, if positive, it was anticipated that we might be able to conclude that the natural combustion of wood (e.g., forest fires) could be a significant source of CDDs input to the environment. To reduce the chances for external bias, the sampling protocol required collection of samples from three different rural regions of the USA and all samples were obtained from units used exclusively for wood combustion where it was the major source of heating for the residence. Eighteen individual samples were examined using analytical methodology developed specifically for these extremely difficult matrices. The results indicated that specific CDD isomers could be detected in every sample at concentrations exceeding 1 part per trillion with total CDDs content as high as ~40 parts per billion in the native chimney ash. Although convincing to us at the time of the work, a significant fraction of the scientific community assessed the study as being flawed because we did not examine samples of the atmosphere supporting combustion, nor did we exclude the potential that man-made materials were burned in the units at some time prior to the sample collection period. For nearly a year the work stood alone with respect to demonstrating the potential that wood combustion represented a sizeable source of CDDs (and also CDFs) to the environment, however, it has since been corroborated by a number of other researchers.<sup>12-14</sup>

The statement in the TCOF report that says CDDs may have existed since the *advent of fire* was intended to illustrate that their presence in the environment is not exclusively due to the manufacture and use of chlorophenolics. Unfortunately, this single premise sustained much of the original controversy surrounding the hypothesis. Many researchers concluded that historical samples of environmental material should therefore be useful to prove or disprove the concept. Such reasoning is not necessarily correct from the perspective of negative findings, but Dow also became involved in analogous studies hoping to provide positive evidence. Mentioned among the samples in the original TCOF was the examination of Milorganite. It is a dried municipal sewage sludge produced commercially by the City of Milwaukee, Wisconsin. In the original TCOF work it was discovered that such dried sewage contains part per trillion to part per billion concentrations of various CDDs. Subsequent discussions with employees of the Milwaukee Metropolitan Sewerage District led to a more detailed examination of current (i.e., 1981 and 1982) production samples of the material as well as an historical sample of the sludge that had originally been displayed at the 1933 Chicago World's Fair.<sup>15</sup> Comparison of the resulting data for the modern and historical Milorganite samples

indicated that with the exception of four particular TCDD isomers (2378-, 1378-, 1237- and 1238-TCDDs) the samples were essentially identical with respect to CDDs content. The fact that 2378-TCDD was present in the historical sample was concluded to be significant since neither 2,4,5-trichlorophenol nor 2,4,5-T were commercially produced at that time.

Throughout the period between 1979 and 1986, Dow Chemical scientists have undertaken considerable work involving the chemistry behind the TCOF hypothesis. Initially this work centered on aspects of producing CDD and CDF isomers in a purified state for use as reference standards in analytical procedures. In doing so, they discovered that the condensation of chlorophenolic salts to produce CDDs was significantly enhanced when conducted on a siliceous surface. Later studies indicated that the chlorination of CDD/CDF isomers via reaction with gaseous chlorine was also facilitated by supporting the precursors on a siliceous surface as opposed to conducting the reaction in a conventional liquid phase media. A procedural need for ~5 microgram quantities of [<sup>14</sup>C]<sub>12</sub>-labeled bromodibenzo-p-dioxin isomers provided the incentive to further improve trace halogenation reactions of aromatic precursors present on siliceous supports. In this case Dow workers discovered that such trace level reactions could be efficiently conducted by exposing the precursors to ferric halide salts at the relatively low temperature of ~150°C. This discovery led to further work which demonstrated that trace levels of CDDs/CDFs can be produced by exposing benzene vapors to iron supported on silica gel in an atmosphere of nitrogen or air that contains hydrogen chloride. The significance of this latter system is that it is believed to mimic the conditions which exist during typical combustion reactions, thereby providing a measure of proof supporting Olie's original contention that CDDs/CDFs might well be synthesized via a *de novo* route during combustion.<sup>7,16</sup>

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