Chemosphere, Vol.13, No.7, pp 777 - 788, 1984
Printed in Great Britain

0045-6535/84 $3.00 + .00

see p. 778

THE TRACE CHEMISTRIES OF FIRE HYPOTHESIS REVIEW AND UPDATE

Warren B Crummett and Donald L Townsend

Michigan Applied Science and Technology Laboratory
574 Building
Dow Chemical U.S.A.
Midland, MI 48640

Chlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) were first discovered by Olie et al[65] to be on fly ash from municipal incinerators in The Netherlands. Shortly thereafter, Buser et al[10,11] reported that these compounds were also present on particulate matter from a municipal incinerator and an industrial heating facility in Switzerland.

By the end of 1978, scientists from a Dow Chemical Company Chlorinated Dioxin Task Force[79] announced that chlorodibenzodioxins were present in all particulate matter taken inside or close to combustion facilities. The dioxins were found to be present in fly ash from municipal and industrial incinerators and an oil-fired powerhouse; dust from the cities of Midland, Detroit, Lansing, Chicago, and St. Louis; soil from Midland, Detroit, Lansing, Chicago, and Gaylord, Michigan; commercial sludge fertilizer from Milwaukee, particulate deposits from inside automobile and truck mufflers, both diesel and gasoline; soot from home fireplaces; and smoke from cigarettes. These findings together with those earlier reported by Olie[65] and Buser[10] lead to the formulation of an hypothesis called "trace chemistries of fire". This hypothesis was described in the original report, and in more recent papers by Bumb[4,5], Crummett[17], and the National Research Council Canada[59].

The trace chemistries of fire hypothesis simply says 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[16] The trace chemistries of fire hypothesis[5,17,79] includes chlorinated aromatic compounds among such products - particularly chlorinated dibenzodioxins, chlorinated dibenzofurans, and polychlorinated bi- and terphenyls The concentration of the trace products is expected to vary with the (1) molecular structure of fuel, (2) chlorine content of fuel, (3) presence of precursors and contaminants in fuel, (4) reaction temperature within the combustion zone and post combustion zone, (5) residence time of reactants and intermediate products in the high temperature zone, (6)

mixing efficiency of air with fuel, (7) air-fuel ratio, and (8) fuel feed size according to Shih et al[76]. The nature and concentration of the products can also be affected by the metals in the fly ash acting as catalysts.

The hypothesis as originally presented was based on the following facts:

(1) Combustion processes are seldom more than 99.9 percent efficient in converting the carbon content of fuel to carbon dioxide[20].

(2) The remaining 0.1 percent of the carbon in the fuel is converted to a large number of trace organic compounds including chlorinated hydrocarbons, only a few of which have been identified[21,45,48,68]. Only a tiny fraction of this remainder need be converted to dioxins to account for the trace quantities of dioxins observed in combustion.

(3) Refuse and fossil fuels are extremely complex mixtures of many chemicals and compounds, some of which are present at low concentrations.

(4) The natural chlorine content of fuels ranges from one to five thousand parts per million[58]. This is much more chlorine than necessary to create chlorinated dioxins observed in combustion products.

(5) Particles emitted from oil-fired heating and power plants contain vanadium and nickel[49]. Those emitted from coal-fired boilers contain vanadium, nickel, iron, and manganese[43]. These transition metals together with silicon and unoxidized carbon can serve as catalysts in the combustion process.

(6) Chemical reactions which are known to occur in flames include pyrolysis, oxidation, reduction, and acidolysis. Ions, electrons, free radicals, and free atoms interact in a continuously changing environment.

(7) In the Bumb study[5,17], chlorinated dibenzo-p-dioxins were found in all particulate matter taken from areas close to combustion processes.

(8) Precursors for the formation of chlorinated dibenzo-p-dioxins have been convincingly demonstrated to include chlorinated phenols[69] and chlorobenzenes[6].

Since polyvinyl chloride produces chlorobenzenes[35,67] during pyrolysis, its role as a precursor is also suspect.

Since the trace chemistries of the dibenzo-p-dioxins was presented, many studies have been made which test the hypothesis. These may be placed in several categories as follows:

(1) Studies of the combustion products of incinerators. Eustenhouwer et al[55] reviewed the literature and reported that PCDDs and PCDFs were found in fly ash from all thirty-five municipal incinerators examined by all investigators. These include data on nine incinerators in The Netherlands as reported by Olie et al[66]. Cavallaro et al[12,13] found similar distributions of PCDDs and PCDFs in fly ash from each of six Italian municipal incinerators examined; Eiceman et al[26] reported finding a variety of chlorinated organic compounds including PCDDs, and PCDFs, in fly ash from municipal incinerators in Canada, Japan, and The Netherlands. Also in Canada, Wang et al[86] and Chiu et al[14] reported PCDDs and PCDFs were present in the effluent from two municipal incinerators. Samuelson and Lindskog[74] and Eklund and Stromberg[22] found PCDDs and PCDFs in fly ash from Swedish municipal incinerators. Rappe[71] and Buser[8,9] found PCDDs and PCDFs in fly ash samples from municipal incinerators in Switzerland. Janssens et al[36] found them in Belgium. In Italy these compounds were found in emissions from urban incinerators by Liberti et al[50,51] in Milan, Bologna, Florence, and Rome and by Marselli et al[57] in Bologna. Gizza et al[29] studied the variability in PCDD and PCDF content of emissions from an Italian urban incinerator. Karasek et al[27,40] reported on a municipal incinerator in France and compared it with one in Ontario, Canada. In the United States Redford et al[72] and Tiernan et al[81] found PCDDs in municipal incinerator effluent. Tiernan[81] also found PCDDs in extracts of effluents from a Hempstead, New York incinerator. In Germany Ballschmitter et al[2] used OCDD as a PCDD indicator and found it in five of six municipal incinerators. These compounds were also found by Buser et al[7,9] in fly ash from an industrial incinerator and Hrybarczuk et al[33] found the tetra isomers in fly ash from a wire reclamation incinerator. The fact that PCDDs have been found in all municipal incinerators thus far examined, supports the conclusion that this is a general phenomenon.

(2) Studies on the combustion products of wood. Ahling and Lindskog[1] reported that pyrolysis of wood or paper mill liquors, containing little or no organic chlorine, form the recognized dioxin precursors, polychlorobenzenes and polychlorophenols. Tiernan[80] qualitatively confirmed that PCDDs are present in soot in fireplaces. Nestrick and Lamparski[59,60,61] found PCDDs in soot from the top of all chimneys examined that were connected to wood-burning stoves in Oregon, Minnesota, New Hampshire, and the Upper Peninsula of Michigan. Olie et al analyzed fly ash from the combustion of painted wood over 60 years old and new wood treated with pentachlorophenol and found the PCDD and PCDF content of the fly ash from the two woods to be virtually the same. Wang et al[86] also found PCDDs in woodstove effluents but only "components with high chlorine numbers". The body of data strongly suggest that the production of PCDDs from the combustion of natural wood is a general phenomenon.

(3) Studies on the combustion products of coal Kimble and Gross[42] were unable to find TCDD in fly ash from a powerhouse fired with low-sulfur, high-slag coal Likewise, Harless and Lewis[31] were unable to find TCDD in seven ash samples Furthermore, DeRoos and Bjorseth[19] did not detect TCDD in fly ash from a coal-fired power plant The latter two studies had a limit of detection of about 2 parts per trillion In yet another study Junk and Richard[37] were unable to detect TCDD at a level of 10 parts per trillion in effluent from coal/refuse combustion. The negative results were attributed to the temperature of ~1200°C at which the unit operated Also, Redford et al[72] failed to find PCDDs and PCDFs in a facility which burned coal and refuse derived fuel.

On the other hand, Eklund and Stromberg[22] detected PCDDs and PCDFs in two coal-fired combustors in Sweden. Chu et al[14] found measurable amounts of PCDDs and PCDFs in a sample from one coal-fired power plant in Canada but not from a coal-powered central heating plant Czuczwa and Hites[18] found PCDDs in fly ash from coal combustion In addition to PCDDs and PCDFs, Eklund and Stromberg[22] also reported finding chlorinated benzenes, biphenyls, and polynuclear aromatics in flue gas from coal combustion

A laboratory study by Mahle and Whiting[56] of the combustion of bituminous coal in air showed that PCDDs are found either with coal alone or in combination with various chlorine donors Thus available data on coal-fired powerhouses taken collectively are not sufficient for extrapolation to a reasonable conclusion at this time.

(4) Studies on the combustion products of light hydrocarbons. Krishnan and Hites[44] used methane and a methane/dichloromethane mixture as a fuel in a burner They found chlorinated aromatic organic compounds in the effluent from the mixture but not from the methane alone However, their analytical methodology was not sensitive or specific enough to detect PCDDs, if present. Also, others[78] have reported the formation of dioxin precursors when hydrogen chloride was added to the flame of a Bunsen burner. The possibility that PCDDs may be formed from gasoline in an automobile or truck motor has not been reported. Tiernan[80] did not detect PCDDs in scrapings from the tail pipe of a few old cars However, his methodology was not as sensitive as that of Bumb[5]. Sensitivity of analytical methodology will be the key to further study With respect to this body of data nothing can be concluded at this time.

(5) Theoretical studies related to the "trace chemistries of fire" hypothesis. Choudhry et al[15] examined a range of potential PCDD formation mechanisms and formulated a mechanism from published data and their own work which makes a good case for the production of PCDDs from simple organic carbon and non-organic chlorine molecules Shih et al[76] did a thermochemical equilibrium analysis to determine the potential for PCDD and PCDF formation in combustion systems over the temperature range of 533-1093°C Although thermodynamic quantities were not available for the PCDDs and PCDFs, they were able to show that the formation of the polychlorobenzene precursors are favored. Shaub and Tsang[75] have constructed a kinetic model from

which they conclude that homogeneous gas phase formation of PCDDs in incinerators is unlikely but surface reactions and/or reactions inside solids (such as fly ash and other materials) seem to be strong candidates as potential sources for PCDD and PCDF formation. Theoretical studies thus far reported tend to support the hypothesis.

(6) Studies to identify precursors and elucidate reaction mechanisms. Lindahl et al[53] have shown that PCDFs and PCDDs are formed from the pyrolysis of polychlorinated diphenyl ethers. Liberti et al[3,50] describe "the basis of PCDD and PCDF formation through a thermal synthesis between two families of precursors one supplying the phenol as polyphenolic structure and the other acting as a chlorine donor." Polyvinyl chloride (PVC) was given as a typical example of a chlorine donor. Later Liberti et al[52] showed that pyrolyzed PVC indeed produced trace quantities of PCDDs and PCDFs. The quantity produced was not sufficient, however, to measureably increase the quantity of PCDDs and PCDFs produced by an incinerator operating at equilibrium as shown by Karasek[41].

Eiceman and Rghei[25,73] demonstrated the production of chlorinated aromatic compounds in flame chemistry through chlorination of fly ash and raised the possibility of a second mechanism of production, namely, gas-phase particulate reactions. They[73] also showed that 1,2,3,4-TCDD dehydrochlorinates to T_3CDD on fly ash in helium atmosphere between 250 and 300°C. Olie et al[54] added hexachlorobenzene to wastes burned in a municipal incinerator and found no clear increase in either PCDDs or PCDFs.

Rappe and Marklund[70] studied both baghouse ash and bottom ash from an industrial boiler burning pentachlorophenol containing waste and sludge. The baghouse ash contained both PCDDs and PCDFs but the bottom ash had only PCDDs. This observation "could possibly be interpreted in terms of a de novo formation of PCDFs" in the flames. More than 90 percent of the PCDDs in the baghouse ash were those containing less than eight chlorines, providing further evidence for dehydrochlorination.

Junk and Ford[34] have listed the reported identified organic emissions from selected combustion processes. They found 331 different components in total, 109 from the combustion of coal, 235 from the incineration of wastes, and 69 from coal/refuse combustion processes. The precursors of most of these compounds have not been established although Ballschmiter[2] discusses this to some extent. Also not established is which of these are precursors for the formation of PCDDs and PCDFs. More precursors for the formation of PCDDs and PCDFs are continually being identified. The list is no longer limited to chlorinated phenols and their derivatives.

(7) Studies on the detection of PCDDs and PCDFs in environmental samples. The "trace chemistries of fire" hypothesis pointed out that PCDDs and PCDFs found in soil and dusts appeared to be related to combustion sources. Isomer group ratios related to dehydrochlorination chemistry were used by Townsend[82,83,84,85]

to establish this relationship and identify thermochemical sources Moreover, the concentration of PCDD isomers remaining in environmental samples after subjection to various natural processes should relate directly to the intensity of combustion in the vicinity of sampling as well as the nature of the destruction process Eiceman and Rhee[24] have produced data which support this theory By heating 1,2,3,4-TCDD adsorbed on fly ash in the presence of hydrogen chloride and air, higher chlorinated PCDDs were produced

Although the concentration of 2,3,7,8-TCDD found in fish appears to vary with the intensity of combustion on the banks of the rivers from which the fish were taken as suggested by Crummett[17] and confirmed by Kaczinar et al[38], the contribution from combustion relative to that from industrial sources remains undetermined Considerable fish data are now available as reported by Harless et al[30], O'Keefe et al[63], and Stalling et al[77] However, these data have only been collected from areas suspected of being contaminated by industrial activity. Collectively these data imply ubiquity which is the conclusion of Norstrom[62] in his study of gull eggs Support for this position relative to other chlorinated dioxins is also given in a study of human milk[54].

Czuczwa and Hites[18] examined lacustrine sediments from Lake Michigan, Lake Huron, Lake Siskiwit, and Lake Zurich. They concluded that the "input of dioxins and furans to the sedimentary environment is due to the combustion of chlorinated organic products present in various wastes". The total isomer distribution from all these various lakes was remarkably similar and corresponded to that of the general background obtained by theoretical projections.

Particulate matter from the eruption of Mount Saint Helens was examined by Lamparski et al[46]. The amount of PCDD found varied with the sample collection zone urban>interstate highways>rural>blast area. This suggests that PCDDs were adsorbed on volcanic ash as it moved into areas where combustion was occurring

Analysis of a sample of dried municipal sewage sludge sealed in glass and displayed at the Chicago World's Fair in 1933 revealed a dioxin pattern almost identical to 1981 and 1982 samples of dried sludge from the same source. Lamparski et al[47] showed that the concentration of OCDD, H_7CDD, and H_6CDDs were identical in the three samples and the isomer ratios were constant The tetra isomers were in the same ratios but the concentrations were less in the 1933 sample. Since chlorinated phenols were not being produced commercially in 1933, the source of these dioxins is worthy of further study

(8) Studies consisting of reviews, conclusions, and recommendations Two studies reviewed the literature on PCDDs from combustion with considerable variation in their conclusions and recommendations One of these[32], commissioned by The American Society of Mechanical Engineers, concludes that "PCDDs are present at low levels in the emissions from many types of combustion sources" and defined the "most obvious need" to be the establishment of "the quantitative relationship between effects levels and emission levels" thus establishing "criteria for tolerable PCDD emission levels". The report recom-

mended studies on: "exposure and risk assessment, advances in measurement methodology, improvements in the toxicological effects data base, and improvements in the emissions data base"

The second review[76], sponsored by the U S. Environmental Protection Agency, concludes that the data indicates "that emissions of PCDDs and PCDFs are general phenomena related to all combustion processes". A research strategy is suggested which emphasizes the study of combustion process characteristics of specific combustion systems with the goal of minimizing the formation of PCDDs and PCDFs. The review supplies a "ranked priority list of combustion systems for source testing". This research position is similar to that taken by the Incineration Workship at The Rome, Italy, Conference[34], which concluded, in part, "Rather than attempting to avoid certain items in incineration, it may be more important to optimize combustion conditions".

It is not yet possible to quantify the relative amounts of dioxins created during chemical manufacture, incineration, and other types of combustion. However, consideration of all the data on the formation of PCDDs and PCDFs leads to a conclusion similar to that of Gilbertson[28] who wrote· "The apparently disparate pieces of evidence from the late 1978 presentation by Dow now form a connected body. It is difficult, therefore, not to believe that chlorodioxins are entering the environment in trace quantities from very many sources."

REFERENCES

1. Ahling, B. and A. Lindskog, "Emission of Organic Substances From Combustion." "Chlorinated Dioxins and Related Compounds", O. Hutzinger, R. W. Frei, E. Merian, and F Pocchiari, editors Pergamon Press, Oxford, 1982, p. 215.

2. Ballschmiter, K., W. Zaller, C. Scholz, and A. Nollrodt, "Occurence and Absence of Polychloro-dibenzofurane and Polychloro-dibenzodioxins in Fly Ash from Municipal Incinerators." Chemosphere 12, 585 (1983)

3. Brocco, D , A. Cecinato, and A. Liberti, "Polychlorodibenzodioxins in the Environment." Chemosphere, 7, 199 (1978)

4. Bumb, R.R., "Direct Testimony of Dr. Robert R. Bumb." Before the Environmental Protection Agency of The United States of America." In Re: The Dow Chemical Company, et al. Docket Nos. 415, et al. Exhibit No. 806.

5. Bumb, R.R., W. B. Crummett, S. S. Cutie, J. R. Gledhill, R. H. Hummel, R. O. Kagel, L. L. Lamparski, E. V. Luoma, D. L Miller, T J Nestrick, L. A. Shadoff, R. H. Stehl, and J S. Woods, "Trace Chemistries of Fire: A Source of Chlorinated Dioxins." Science 210, 385 (1980).

6 Buser, H. R., "Formation of Polychlorinated Dibenzofurans (PCDFs) and Dibenzo-p-dioxins (PCDDs) From The Pyrolysis of Chlorobenzenes " Chemosphere, 8, 415 (1979).

7 Buser, H. R. and Bosshardt, H. P , "Polychlorierte Dibenzo-p-dioxine, Dibenzofurane, and Benzole in der Asche kommunaler and industrieller Verbrennungsinlagen." Mitt. Gebiete Lebensm. Hyg. 69, 191, (1978).

8 Buser, H. R. and C. Rappe, "High Resolution Gas Chromatography of the 22 Tetrachlorodibenzo-p-dioxin Isomers " Anal. Chem. 52, 2262 (1980).

9 Buser, H R and C Rappe, Identification of Substitution Patterns in Polychlorinated Dibenzo-p-dioxins (PCDDs) by Mass Spectrometry" Chemosphere 7 (1978)

10 Buser, H R , H P Bosshardt, and C Rappe, "Identification of Polychlorinated Dibenzo-p-dioxin Isomers Found in Fly Ash" Chemosphere 2, 165, 1978

11 Buser, H. R , H P. Bosshardt, C Rappe, and R. Lindahl, "Identification of Polychlorinated Dibenzofuran Isomers in Fly Ash and PCB Pyrolysis" Chemosphere 5, 419, 1978

12 Cavallaro, A , G Bandi, G Invernizzi, L. Luciani, E. Mongini, and A. Garni, "Sampling, Occurrence and Evaluation of PCDDs and PCDFs from Incinerated Solid Urban Waste" Chemosphere, 9, 611 (1980).

13. Cavallaro, A., L Luciani, G Ceroni, I Rocchi, G Invernizzi, and A. Garin, "Summary of Results of PCDDs Analyses from Incinerator Effluents." Chemosphere 11, 859 (1982)

14 Chiu, C , P S Thomas, J Lockwood, K Li, R. Halenan, and R. C. C Lao, "Polychlorinated Hydrocarbons from Power Plants, Wood Burning and Municipal Incinerators." Chemosphere 12, 607 (1983)

15. Choudhry, G. G , K. Olie, and O Hutzinger, "Mechanisms in The Thermal Formation of Polychlorinated Dibenzo-p-dioxins and Related Compounds" "Chlorinated Dioxins and Related Compounds," O. Hutzinger, R W. Frei, E Merian, and F. Pocchiari, editors Pergamon Press, Oxford, 1982, p 275.

16. Committee on Biological Effects of Atmospheric Pollutants, "Particulate Polycyclic Organic Matter." National Academy of Sciences, Washington, D C , 1972.

17 Crummett, W. B , "Environmental Chlorinated Dioxins From Combustion - The Trace Chemistries of Fire Hypothesis." "Chlorinated Dioxins and Related Compounds", O. Hutzinger, R. W. Frei, E. Merian, and F Pocchiari, editors. Pergamon Press, Oxford (1982), p 253.

18 Czuczwa, J M. and R. A Hites, Environmental Fate of Combustion - Generated Polychlorinated Dioxin and Furans." Personal communication

19 DeRoos, F L. and A Bjorseth, "TCDD Analysis of Fly Ash Sample." Report prepared by Battelle Columbus Laboratories for The U.S. Environmental Protection Agency. June 15, 1979

20. EPA-600/2-7-086 "At-Sea Incineration of Herbicide Orange Onboard The M/T Vulcanus" (1978).

21. Edwards, J. B., "Combustion The Formation and Emission of Trace Species." Ann Arbor Science, Ann Arbor, MI (1977).

22. Eklund, G and B. Stromberg, "Detection of Polychlorinated Polynuclear Aromatics in Flue Gases from Coal Combustion and Refuse Incinerators." Chemosphere 12, 657 (1983).

23. Eiceman, G. A., A. C Vian, and F. W. Karasek, "Ultrasonic Extraction of Polychlorinated Dibenzo-p-dioxins and Other Organic Compounds From Fly Ash from Municipal Incinerators." Anal Chem., 52, 1494 (1980)

24. Eiceman, G A. and H. O Rghei, "Chlorination Reactions of 1,2,3,4-Tetrachlorodibenzo-p-dioxin on Fly Ash with HCl in Air." Chemosphere. 11, 833 (1982)

25 Eiceman, G A and H O Rghei, Products From Laboratory Chlorination of Fly Ash From A Municipal Incinerator" Environ. Sci. Technol., 16, 53 (1982)

26 Eiceman, G A , R. E. Clement, and F W Karasek, "Analysis of Fly Ash From Municipal Incinerators for Trace Organic Compounds" Anal. Chem , 51, 2243 (1979)

27 Eiceman, G. A., R. E. Clement, and F W Karasek, "Variations in Concentrations of Organic Compounds Including Polychlorinated Dibenzo-p-dioxins and Polynuclear Aromatic Hydrocarbons in Fly Ash from A Municipal Incinerator " Anal. Chem. 53, 955 (1981)

28 Gilbertson, M , "Report of The Meeting on 'The Dow Dioxin Theory'" Contaminants Control Branch - EICD, Government of Canada, March 4, 1980.

29. Gizzi, F , R Reginato, E. Benfenati, and R Fanelli, "Polychlorinated Dibenzo-p-dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF) In Emissions from An Urban Incinerator 1 Average and Peak Values " Chemosphere, 11, 577 (1982).

30. Harless, R L., E. O. Oswald, R. G. Lewis, A, E. Dupuy, J. , D. D, McDaniel, and H. Tai, "Determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Fresh Water Fish." Chemosphere 11, 193 (1982)

31. Harless, R L. and R. G. Lewis, "Quantitative Determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin Residues by Gas Chromatography/Mass Spectrometry."; Paper presented at Workshop - Impact of Chlorinated Dioxins and Related Compounds in The Environment. Instituto Superiore di Sanita, Roma (Italy), October 22-24 (1980).

32. Harris, J. C., R. C. Anderson, B. E. Goodwin, and C E Rechsteiner, "Dioxin Emissions From Combustion Sources: A Review of The Current State of Knowledge", Artbur D. Little, Inc. basic report to Research Committee on Industrial and Municipal Wastes, The American Society of Mechanical Engineers, New York, NY (1981).

33 Hryharczuk, D. W., W. A. Withrow, C. S Hesse, and V R. Beasley, "A Wire Reclamation Incinerator as a Source of Environmental Contamination with Tetrachlorodibenzo-p-dioxins and Tetrachlorodibenzofurans." Arch. Environ. Health, 36, 228 (1981).

34. Hutzinger, O and A Liberti, "Conclusions of Discussion Sessions - Incineration Story." "Chlorinated Dioxins and Related Compounds." O Hutzinger, R W. Frei, E. Merian, and F. Pocchiari, editors, Pergamon Press, 1982, p. 603,

35 Iida, I., M Nakoshima, and R. Goto, "Evolution of Aromatics on Pyrolysis of Poly(vinylchloride) and Its Mechanism." J. Polym. Sci. Chem. Ed., 12, 737, (1964).

36. Janssens, J., L. Van Vaeck, P Schepens, and F Adams, "Qualitative and Quantitative Analysis of Emissions of A Municipal Incineration Installation " Comm. Env Communities, EUR7624, 28 (1982).

37 Junk, G A and J J Richard, "Dioxins Not Detected In Effluents From Coal/Refuse Combustion." Chemosphere 10, 1237 (1981)

38. Kaczinar, S , M. J. Zabik, and F. D'Itri, "The Extent and Geographical Distribution of 2,3,7,8-Tetrachlorodibenzo-p-dioxin Residues in Michigan." Personal communication.

39 Karasek, F. W., "Dioxins from Garbage." Can. Res , 13, 50 (1980).

40. Karasek, F W., R. E. Clement, and A. C. Viau, "Distribution of PCDDs and Other Toxic Compounds Generated on-Fly Ash Particulates in Municipal Incinerators " J. of Chromato., 239, 173 (1982)

41. Karasek, F. W , A. C Viau, G. Guichon, and M. F Gonnard, "Gas-Chromatographic-Mass Spectrometric Study on the Formation of Polychlorinated Dibenzo-p-Dioxins and Polychlorobenzenes from Polyvinyl Chloride In A Municipal Incinerator" J. Chromato , 270, 227 (1983)

42. Kimble, B. J and M L. Gross, "Tetrachlorodibenzo-p-dioxin Quantitation in Stack Collected Fly Ash " Science, 207, 59 (1980).

43 Kobayashi, T and Ikeajawa, Hyogo-Ken Kogai Kenkyusho Kenyu Hokoku 7, 1 (1975)

44. Kirshman, S and R. A. Hites, "Chlorinated Organic Compounds Formed in a Methane - Dichloromethane Flame " Chemosphere 9, 679 (1980)

45. Lahaniatis, H. Parlar, F. Karte, "Uber das Varkommen Chlorieter Kohlenwasserstoffe in Flugaschens von Mullverbrennungsenlagen," Chemosphere 6 (No. 1), 11 (1977)

46 Lamparski, L L., T J Nestrick and S. S Cutie, "The Impact of The Environment on Airborne Particulate Matter from the Eruption of Mount Saint Helens." Chemosphere, in press (1984)

47 Lamparski, L L., T. J Nestrick, and V. A Stenger, "Presence of Chlorodibenzo Dioxins in a Sealed 1933 Sample of Dried Municipal Sewage Sludge." Personal communication.

48 Larson, J W , Ed , "Organic Chemistry of Coal " ACS, Washington, D C 1978.

49. Lasiewicz, K. and D. Logewada, Ochr Porvietrze 10 (No. 5), 127 (1976).

50. Liberti, A. and D. Brocco, "Formation of Polychlorodibenzodioxins and Polychlorodibenzofurans in Urban Incinerators Emissions." "Chlorioated Dioxins and Related Compounds," O. Hutzinger, R. W. Frei, E. Merian, and F. Pocchiari, editors Pergamon Press, Oxford, 1982, p. 245

51. Liberti, A., P. Ciccioli, E. Brancaleoni, and A. Cecinato, "Determination of Polychlorodibenzo-p-dioxins and Polychlorinate-p-dibenzofurans in Environmental Samples by Gas Chromatography-Mass Spectrometry." J. Chromat , 242, 111 (1982).

52. Liberti, A , G. Goretti, and M. V. Russo, "PCDD and PCDF Formation in the Combustion of Vegetable Wastes," Chemosphere 12, 661 (1983).

53. Lindahl, R., C. Rappe, and H. R. Buser, "Formation of Polychlorinated Dibenzofurans (PCDFs) and Polychlorinated Dibenzo-p-dioxins (PCDDs) from the Pyrolysis of Polychlorinated Diphenyl Ethers." Chemosphere 9, 351 (1980).

54. Loomis, T A., L. A. Shadoff, and M. L. Langhorst, "Chlorinated Dibenzodioxins in Human Milk and Their Toxicologic Significance " Submitted to Tox. and Appl. Pharm. (1981).

55 Lustenhouwer, J W. A., K. Olie, and O. Hutzinger, "Chlorinated Dibenzo-p-dioxins and Related Compounds in Incinerator Effluents." Chemosphere 9, 501 (1980).

56 Mahle, N. H. and L F. Whiting, "The Formation of Chlorodibenzo-p-dioxins by Air Oxidation and Chlorination of Bituminous Coal." Chemosphere 9, 693 (1980).

57. Massalli, L., F. Trifiro, and B. Villori, "Analysis of The Effluents of An Urban-Solid Refuse Incinerator: Study of Methods of Extraction and Analysis for The Quantitative Determination of Polychlorodibenzo-p-dioxins." Anal. di Chem., p. 557 (1981).

58. National Academy of Sciences. "Chlorine and Hydrogen Chloride." Washington, D.C., 1976.

59 National Research Council Canada, "Polychlorinated Dibenzo-p-dioxins. Criteria for Their Effects on Man and His Environment " NRCC No 18574, pp. 24-36

60. Nestrick, T. J. and L. L. Lamparski, "Assessment of Chlorinated Dibenzo-p-dioxin Formation and Potential Emission to the Environment from Wood Combustion." Chemosphere 12, 617 (1983).

61. Nestrick, T. J. and L. L. Lamparski, "Isomer-Specific Determination of Chlorinated Dioxins for Assessment of Formation and Potential Environmental Emission from Wood Combustion." Anal. Chem. 54, 2292 (1982).

62. Norstrom, R. J., D. J. Hallett, M Simon, and M. J Mulvihill, "Analysis of Great Lakes Herring Gull Eggs for Tetrachlorodibenzo-p-dioxins." "Chlorinated Dioxins and Related Compounds," O Hutzinger, R W Frei, E. Merian, and F. Pocchiari, editors Pergamon Press, Oxford, 1982, p 173.

63. O Keefe, P. O., C Meyer, D. Hilkes, K. Aldous, S Jelus-Tyror, K Dillon, R. Donnelly, E. Horn, and R. Sloan, "Analysis of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Great Lakes Fish." Chemosphere, 11, 325 (1982)

64. Olie, K., M. v d. Berg, and O Hutzinger, "Formation and Fate of PCDD and PCDF from Combustion Processes." Chemosphere, 12, 627 (1983).

65. Olie, K., P. L. Vermeulen, and O. Hutzinger, "Chlorodibenzo-p-dioxins and Chlorodibenzofurans Are Trace Components of Fly Ash and Flue Gas of Some Municipal Incinerators in The Netherlands." Chemosphere 8, 455, 1977.

66. Olie, K., J. W. A. Lustenhouwer and O. Hutzinger, "Polychlorinated Dibenzo-p-dioxins and Related Compounds in Incinerator Effluents." "Chlorinated Dioxins and Related Compounds," O. Hutzinger, R. W. Frei, E. Merian, and F. Pocchiari, editors. Pergamon Press, Oxford, 1982, p 227.

67. O'Mara, M. M , "High-Temperature Pyrolysis of Poly(vinyl chloride). Gas Chromatographic - Mass Spectrometric Analysis of The Pyrolysis Products from PVC Resin and Plastisols." J Polym. Sci., A1, 8, 1887 (1970).

68. Palmer, H. B and P. J. Seery, "Chemistry of Pollutant Formation in Flames " Annu. Rev. Phys. Chem. 24, 235 (1973).

69. Rappe, C., S. Marklund, H. R. Buser, and H. P. Bosshardt (1978) "Formation of Polychlorinated Dibenzo-p-dioxins (PCDDs) and Dibenzofurans (PCDFs) by Burning or Heating Chlorophenates." Chemosphere, 7, 269-281.

70 Rappe, C. and S. Marklund, "Thermal Degradation of Pesticides and Xenobiotics. Formation of Polychlorinated Dioxins and Dibenzofurans", "Pesticide Chemistry. Human Welfare and the Environment " Vol. 3, J Miyamoto and P. C Kearney, editors, IUPAC. Pergamon Press (1983), p 317.

71. Rappe, C., H. R. Buser, and H. P. Bosshardt. "Polychlorinated Dibenzo-p-dioxins (PCDDs) and Dibenzofurans (PCDFs)· Occurance, Formation, and Analysis of Environmentally Hazardous Compounds." CIPAC Proceedings Symposium Papers, W. R Bontoyan, editor, CIPAC Publications (1979), p 74.

72. Redford, D. P., C. L. Haile, and R. M. Lucas, "Emissions of PCDDs and PCDFs from Combustion Sources " Human and Environmental Risks of Chlorinated Dioxins and Related Compounds", R. E Tucker, A. L. Young, and A. P. Gray, editors. Plenum Press, 1982, p. 143.

73. Rghei, H. O. and G. A. Eiceman, "Adsorption and Thermal Reactions of 1,2,3,4-Tetrachlorodibenzo-p-dioxin On Fly Ash From A Municipal Incinerator." Chemosphere, 11, 569 (1982).

74. Samuelson, U. and A. Lindskog, "Chlorinated Compounds in Emissions From Municipal Incineration." Chemosphere 12, 665 (1983).

75. Shaub, W. M. and W Tsand, "Dioxin Formation in Incinerators", accepted for publication in Environ Sci & Tech

76 Shih, C., D. Ackerman, L. Scinto, and B. Johnson, "Emissions of Polychlorinated Dibenzo-p-dioxins (PCDDs) and Dibenzofurans (PCDFs) From The Combustion of Fossil Fuels, Wood, and Coal-Refuse " Draft, EPA Contract No. 68-02-3138, TRW Environmental Engineering Division, December, 1980.

77 Stalling, D L , L. M Smith, J D Petty, J W Hogan, J L Johnson, C. Rappe, and H R. Buser, "Residues of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Laurentian Great Lakes Fish " "Human and Environmental Risks of Chlorinated Dioxins and Related Compounds." R. E Tucker, A L. Young, and A.P. Gray, editors. Plenum Press, 1982, p. 221.

78 Svec H , private communication.

79 "The Trace Chemistries of Fire - A Source of and Routes For The Entry of Chlorinated Dioxins Into The Environment." The Chlorinated Dioxin Task Force, The Michigan Division, Dow Chemical U S A , 1978

80 Tiernan, T O , "Direct Testimony of Dr. Thomas O. Tiernan. Before the Environmental Protection Agency of The United States of America." In Re The Dow Chemical Company, et al Docket Nos 415, et al Exhibit No. 222

81 Tiernan, T. O., M. L. Taylor, J. H. Garrett, G. F. Van Ness, J. G. Solch, D. A. Deis, and D. J. Wagel, "Chlorodibenzodioxins, Chlorodibenzofurans, and Related Compounds in The Effluents From Combustion Processes." Chemosphere 12, 595 (1983)

82. Townsend, D. I., "Change of Isomer Ratio and Fate of Polychlorinated-p-dioxins in The Environment." Chemosphere, 12, 637 (1983).

83 Townsend, D I., "Changes in Isomer Group Ratios in The Environment: An Update and Extension of the Present Theory." "Human and Environmental Risks of Chlorinated Dioxins and Related Compounds " R. E. Tucker, A. L Young, and A. P. Gray, editors Plenum Press, 1982, p. 153,

84. Townsend, D I., "The Use of Dioxin Isomer Group Ratios to Identify Sources and Define Background Levels of Dioxins in The Environment. A Review, Update and Extension of the Present Theory." "Chlorinated Dioxins and Related Compounds," O. Hutzinger, R. W. Frei, E Merian, and F Pocchiari, editors. Pergamon Press, Oxford, 1982, p. 265.

85 Townsend, D I., "The Use of Dioxin Isomer Group Ratios to Identify Sources and Define Background Levels of Dioxins in The Environment." J. Environ. Sci. Health, B15(5), 571 (1980).

86. Wang, D K. W., D. H Chiu, P. K. Leung, R. S. Thomas and R. C. Lao, "Sampling and Analytical Methodologies for PCDDs and PCDFs in Incinerators and Wood Burning Facilities," "Human and Environmental Risks of Chlorinated Dioxins and Related Compounds." R. E. Tucker, A. L. Young, and A. P. Gray, editors. Plenum Press, 1982, p 113.

(Received in The Netherlands 8 April 1984; accepted 23 May 1984)