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REVIEW AND DEVELOPMENT OF CHLORINATED
DIOXINS AND FURANS EMISSIONS DATA

March 1983

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CORPORATION

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DIOXINS AND FURANS EMISSIONS DATA

March 1983

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PREFACE

The U.S. Environmental Protection Agency (EPA) is interested in chlorinated dioxins and furans because of their potential toxicities to humans and because several industrial operations have been demonstrated to emit low concentrations of these compounds into the ambient air. Many of the determinations of industrial chlorinated dioxin and furan sources have only recently been made possible due to advancements in sampling and analytical techniques. To expand its knowledge on industrial sources of chlorinated dioxins and furans, EPA's Office of Air Quality Planning and Standards (OAQPS) requested the development of a specific technical data base relating to chlorinated dioxin and furan air emissions. The results of the data base development effort are summarized in this report.

In developing the chlorinated dioxin and furan air emissions data base, the following four topics or questions were deemed as key.

- What source categories might emit chlorinated dioxins and furans?
- How many individual sources are in each source category and where are they located?
- What is the availability of emissions and emission factor data pertaining to chlorinated dioxins and furans?
- Have chlorinated dioxins and furans been measured in the ambient air?

The answers to these questions will help EPA decide whether more extensive and detailed efforts are needed to investigate possible regulation development for certain dioxin and furan sources.

EXECUTIVE SUMMARY

Chlorinated dibenzo-p-dioxins (chlorinated dioxins) and chlorinated dibenzofurans (chlorinated furans) are families of organic compounds theoretically containing 75 and 135 different structural isomers, respectively. The toxicity to humans of all these isomers has not been determined because not all have been isolated and analyzed. Of the isomers studied, the 2,3,7,8-isomers of the chlorinated dioxin and furan groups have been determined to exhibit the highest toxicity levels.

This report provides information on chlorinated dioxin and furan source categories, individual sources, emissions, and ambient exposure levels. The information gathered was abstracted from an extensive literature search and data base development study. Source categories of chlorinated dioxin and furan air emissions, that have been confirmed by testing, include municipal, hazardous, and chemical waste incinerators, wire reclamation incinerators, industrial boilers, wood stoves, fireplaces, residential furnaces, and internal combustion engines. Although there are numerous individual sources within each of these source categories, only seven individual sources were specifically identified and discussed in the literature. Potential sources of chlorinated dioxin and furan air emissions have also been indicated by laboratory research. The types of laboratory experiments which have produced chlorinated dioxin and/or furan emissions are the combustion of wood, grass, and paper treated with a formulation of 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), the combustion of wood treated with a trichlorophenolate and tetrachlorophenolate formulation, the pyrolysis of commercial polychlorinated biphenyls (PCBs) and PCB isomers, the pyrolysis of tri-, tetra-, and pentachlorobenzene, the high temperature oxidation and chlorination of coal, and the combustion of birch leaves and wood wool treated with chlorophenates.

Chlorinated dioxin and furan emissions have been measured in relatively low concentrations in both particulate and gaseous exhaust streams; however, most emission tests have only analyzed particulate emissions for these compounds. The majority of available emissions data for chlorinated dioxins and furans is in the form of emission concentrations and emission factors. Because the identification and measurement of chlorinated furans has only recently become important, more emissions data are available for chlorinated dioxins than for furans. For the source category in which the most data exist, municipal waste incinerators, total chlorinated dioxin levels in the exhaust fly ash have been measured to range from 23.3 ppb to 2966 ppb. Total chlorinated furan levels from the same source range from 13.4 ppb to 2036 ppb. Emission factors developed for municipal waste incinerators on the basis of the amount of waste burned, have been found to range from 0.23 to 16.3 $\mu\text{g}/\text{kg}$ for total chlorinated dioxins and from 2.3 to 17.4 $\mu\text{g}/\text{kg}$ for total chlorinated furans.

Virtually no data are available which estimate chlorinated dioxin and furan source category emissions on an annualized mass emission basis. One reference, however, has estimated that nationwide, tetrachlorinated dibenzo-p-dioxin (TCDD) emissions from residential wood stoves and fireplaces are 0.27 kg (0.6 lb)/yr, TCDD emissions from commercial wood burning are 0.54 kg (1.2 lb)/yr, estimated TCDD emissions from controlled wood burning are 0.32 kg (0.7 lb)/yr, and estimated TCDD emissions from forest fires are 3.1 kg (6.9 lb)/yr.

No data on the levels of chlorinated dioxins and furans in the ambient air were reported in the identified published literature. There was only one reported indication that actual ambient measurements had ever been attempted. In this case it was only qualitatively determined that chlorinated furans were present in a sample taken downwind of a hazardous waste incinerator. Other studies have been conducted to estimate ambient chlorinated dioxin and furan levels by using actual emission test data and atmospheric dispersion models. The results of such modelling and exposure analyses at five sources of TCDD compounds has led EPA to conclude that municipal waste incinerators do not present a public health hazard in regard to their TCDD emissions.

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CHAPTER 1

SUMMARY OF THE CHLORINATED DIOXIN AND FURAN PROJECT

1.1 PROJECT SUMMARY

The U.S. Environmental Protection Agency (EPA) is interested in chlorinated dioxins and furans because of their potential toxicities to humans and because several industrial operations have been demonstrated to emit relatively low concentrations of these compounds into the ambient air. Many of the determinations of industrial chlorinated dioxin and furan sources have only recently been made possible due to advancements in sampling and analytical techniques. To expand its knowledge on industrial sources of chlorinated dioxins and furans, EPA's Office of Air Quality Planning and Standards (OAQPS) requested the development of a specific technical data base relating to chlorinated dioxin and furan air emissions. The results of the data base development effort are summarized in this report.

In developing the chlorinated dioxin and furan air emissions data base, the following four topics or questions were deemed as key.

- What source categories might emit chlorinated dioxins and furans?
- How many individual sources are in each source category and where are they located?
- What is the availability of emissions and emission factor data pertaining to chlorinated dioxins and furans?
- Have chlorinated dioxins and furans been measured in the ambient air?

The technical literature search was extensive and identified 462 possibly applicable references pertaining to chlorinated dioxin and furan

air emissions. After a thorough review of these references only 87 were determined to be germane to one or more of the key air emission topics given above. The list of references developed from the literature search pertaining to chlorinated dioxin and furan air emissions is given in Appendix A, Table A-1. The numbers assigned to the references in Table A-1 are used throughout this report when citing a particular reference. No reference sections are used at the end of each individual chapter. For example, Reference number 5 can be used to document material in Chapters 2, 3, and 4, but it always refers to Reference 5 of Table A-1. The details of the literature search effort that generated the 87 references are given in Appendix B.

In the remaining chapters to this report, each of the important topic areas is discussed individually. Chapter 2 discusses the chemical nature of chlorinated dioxins and furans, Chapter 3 covers source categories and individual sources of chlorinated dioxin and furan emissions, Chapter 4 presents chlorinated dioxin and furan emissions and emission factor data, and Chapter 5 presents available data on ambient levels of chlorinated dioxins and furans. Only information that was determined from the 87 references given in Table A-1 is presented in Chapters 2 through 5. It is the purpose of these chapters to only report technical and scientific results that have been given in the published literature. No theories or conclusions regarding chlorinated dioxin and furan source categories, individual sources, emission levels, and ambient exposure levels are given. Whenever the terms literature or published literature are used in Chapters 2 through 5, they refer solely to the contents of the references in Table A-1.

1.2 SUMMARY OF CHLORINATED DIOXIN AND FURAN SOURCE CATEGORIES AND EMISSIONS

Source categories of chlorinated dioxin and furan air emissions, that have been confirmed by testing, include municipal, hazardous, and chemical waste incinerators, wire reclamation incinerators, industrial boilers, wood stoves, fireplaces, residential furnaces, and internal combustion engines.

Although there are numerous individual sources within each of these source categories, only seven individual sources were specifically identified and discussed in the literature. Potential sources of chlorinated dioxin and furan air emissions have also been indicated by laboratory research. The types of laboratory experiments which have produced chlorinated dioxin and/or furan emissions are the combustion of wood, grass, and paper treated with a formulation of 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), the combustion of wood treated with a trichlorophenolate and tetrachlorophenolate formulation, the pyrolysis of commercial polychlorinated biphenyls (PCBs) and PCB isomers, the pyrolysis of tri-, tetra-, and pentachlorobenzene, the high temperature oxidation and chlorination of coal, and the combustion of birch leaves and wood wool treated with chlorophenates.

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1.3 RECOMMENDATIONS FOR FURTHER STUDY OF CHLORINATED DIOXIN AND FURAN AIR EMISSIONS

From the review of the references in Table A-1, several observations or conclusions have been made concerning areas of the chlorinated dioxin and

uran problem where more study appears to be needed. The first area of the chlorinated dioxin and furan air emissions situation requiring more examination concerns the great variability of the emission test data that have been reported for several similar sources. There needs to be more concentrated study on why chlorinated dioxins and furans were found in the emissions of one municipal waste incinerator and not others burning wastes of a similar composition. On this subject, more work needs to be done on analyzing the composition of the materials being burned to find out if they contain chlorinated dioxins and furans or dioxin and furan precursors. Other questions also persist such as why have dioxin and furan compounds not been detected in the emissions of utility boilers, while they have been found in industrial boiler and incinerator emissions. Some limited theories have been expressed to explain this occurrence, but more work is required to scientifically validate these theories. Related to studies of this type would be additional examinations of the formation and destruction characteristics of chlorinated dioxins and furans. If chlorinated dioxin and furan emissions from a source are potentially deemed to be significant, technically effective and economically reasonable control measures need to be determined.

The second area requiring more study, as shown by the literature search, involves determining what are the ambient air levels of chlorinated dioxins and furans. Basically no data are available because measurements have not been made. Limitations of currently available analytical techniques to detect these compounds in the environment may be responsible for the absence of ambient measurements. The extent of the limitations caused by analytical techniques needs to be further investigated. If currently available analytical techniques are capable of detecting chlorinated dioxins and furans in ambient air samples, an ambient testing program focused on confirmed dioxin and furan sources, such as incinerators and boilers, needs to be initiated.

CHAPTER 2

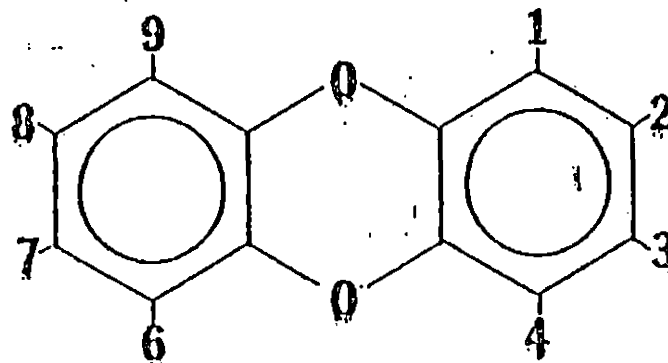
CHEMICAL BACKGROUND ON CHLORINATED DIOXINS AND FURANS

The purposes of this chapter are to describe the general chemical composition of dioxins and furans and to describe the specific chemical characteristics of chlorinated dioxins and furans. Brief discussions regarding chlorinated dioxin and furan formation mechanisms are given, however, the reader is urged to consult the references provided for a complete and detailed treatment of these topics.

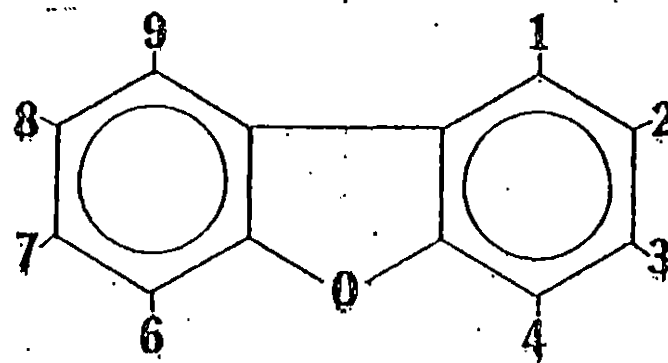
2.1 CHEMICAL DESCRIPTION OF DIOXINS

A dioxin is any member of a family of organic compounds known chemically as dibenzo-p-dioxins. The common aspect of all dioxin compounds is that they contain a triple-ring nucleus structure consisting of two benzene rings interconnected to each other through a pair of oxygen atoms. The structural formula of the dioxin nucleus and the convention used in numbering its substituent positions are shown in Figure 2-1. Each of the substituent positions shown in Figure 2-1, numbered 1 through 4 and 6 through 9, can hold a chlorine or other halogen atom, an organic radical, or a hydrogen atom (provided no other substituent is indicated in the formula or chemical name). The only differences between individual members of the dioxin group are in the nature and position of substituents.⁵⁸

From an environmental standpoint, chlorinated dioxins have received the greatest amount of attention.³² In chlorinated dioxins, chlorine atoms occur at various substituent positions within the nucleus structure. Theoretically, one to eight chlorine atoms can occur at dioxin substituent positions such that 75 different chlorinated dioxin isomers are possible. Each isomer has its own physical and chemical properties, and differs from



a. Dioxin configuration.



b. Furan configuration.

Figure 2-1. Dioxin and furan configurations showing the dioxin and furan nuclei and conventional substituent numbering system.⁵⁸

others in the number and relative position of its chlorine atoms. The schedule of potential chlorinated dioxin isomers is given in Table 2-1. The abbreviations given in Table 2-1 for classes of chlorinated dioxin isomers are used throughout this report.

The chlorinated dioxin isomer receiving the most attention is 2,3,7,8-TCDD. Unfortunately in the published literature chemical nomenclature has often been rather loosely applied and 2,3,7,8-TCDD has been reported as TCDD or simply as dioxin. It is incorrect to use the terms TCDD or dioxin when referring to a specific positional isomer such as 2,3,7,8-TCDD because there are 22 different TCDD isomers and eight different isomer classes of chlorinated dioxins. This nomenclature problem has led to confusion when trying to assess reported results of 2,3,7,8-TCDD detection. In this report the term chlorinated dioxin is used as a substitute for chlorinated dibenzo-p-dioxin and refers to any organic compound with the basic dioxin structure given in Figure 2-1a and the term TCDD (or other isomer abbreviation) is used to refer to the specific group of tetrachlorinated dioxin isomers (or other isomer group). When specific positional isomers such as 2,3,7,8-TCDD are indicated or discussed, they are specifically delineated by chlorine substituent numbers.

2.2 CHEMICAL DESCRIPTION OF FURANS

Furans are a group of organic compounds known chemically as dibenzofurans. They have a similar structure to the dibenzo-p-dioxins, except that the two benzene rings in the nucleus are interconnected with only one oxygen atom and a single carbon bond (c-c).³⁶ The structural formula of the furan nucleus and the convention used in numbering its substituent positions are shown in Figure 2-1. As with the dioxin nucleus, furan substituent positions are numbered 1 through 4 and 6 through 9, and the positions can be occupied by a chlorine or other halogen atom, an organic radical, or a hydrogen atom provided no other substituent is indicated in the formula or chemical name. The positioning and number of substituents determines the

TABLE 2-1. SCHEDULE OF THEORETICAL CHLORINATED DIOXIN ISOMERS⁵⁸

Chlorinated Dioxin Compound	Number of Isomers
Monochlorodibenzo-p-dioxin (MCDD)	2
Dichlorodibenzo-p-dioxin (DCDD)	10
Trichlorodibenzo-p-dioxin (T ₃ CDD)	14
Tetrachlorodibenzo-p-dioxin (TCDD)	22
Pentachlorodibenzo-p-dioxin (PCDD)	14
Hexachlorodibenzo-p-dioxin (HCDD)	10
Heptachlorodibenzo-p-dioxin (H ₇ CDD)	2
Octachlorodibenzo-p-dioxin (OCDD)	1
TOTAL	<u>75</u>

physical and chemical properties of the furan.⁷⁰ A detailed discussion of the properties of dibenzofurans is given in Reference 70.

The chlorinated furans, like the chlorinated dioxins, have been the subject of most of the furan research. Theoretically, the chlorinated furan group can contain up to 135 different structural isomers, each with varying physical and chemical properties. The schedule of potential chlorinated furan isomers is given in Table 2-2. The abbreviations given in Table 2-2 for classes of chlorinated furan isomers are used throughout this report. The nomenclature explained in Section 2.1 for references to dioxins in this report, is also used for furans. The term chlorinated furan is used as a substitute for chlorinated dibenzofuran and refers to any organic compound with the basic structure given in Figure 2-1b. Classes of furan isomers are indicated by the appropriate abbreviations (e.g., TCDF, OCDF) and specific furan isomers are delineated by positional substituent numbers.

2.3 OCCURRENCE AND FORMATION OF CHLORINATED DIOXINS AND FURANS

Chlorinated dioxins and furans are not intentionally manufactured, except in small quantities for chemical and toxicological research purposes. However, chlorinated dioxins and furans occur in several commercial organic chemicals as unavoidable synthesis contaminants, and as such potentially can be released to the atmosphere during normal operations or upon use of the chemical. The mechanisms by which chlorinated dioxins and furans are formed, during the synthesis of various organic chemicals, are complex and have been intensively studied by researchers. In this report, the objective is to briefly discuss and familiarize the reader with the types of chemicals known to contain, or with a propensity to form, chlorinated dioxins and furans. Extensive and detailed discussions and analyses of chlorinated dioxin and furan formation mechanisms and organic chemicals associated with these mechanisms can be found in References 13, 70, and 77.

TABLE 2-2. SCHEDULE OF THEORETICAL CHLORINATED FURAN ISOMERS⁷⁰

Chlorinated Furan Compound	Number of Isomers
Monochlorodibenzofuran (MCDF)	4
Dichlorodibenzofuran (DCDF)	16
Trichlorodibenzofuran (T ₃ CDF)	28
Tetrachlorodibenzofuran (TCDF)	38
Pentachlorodibenzofuran (PCDF)	28
Hexachlorodibenzofuran (HCDF)	16
Heptachlorodibenzofuran (H ₇ CDF)	4
Octachlorodibenzofuran (OCDF)	1
TOTAL	<u>135</u>

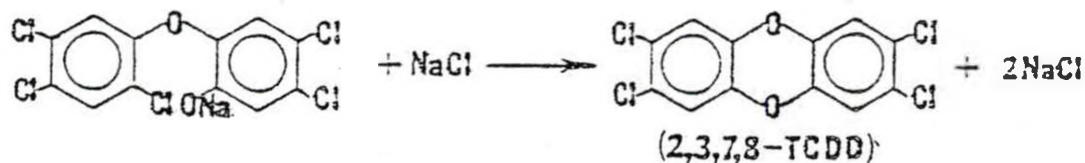
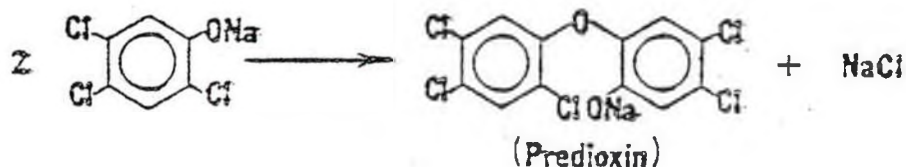
One route of chlorinated dioxin formation that has been demonstrated is generalized below:¹⁸



The reaction shown above indicates that for a compound to be a dioxin precursor it must meet the following conditions:

- the precursor compound must be an ortho-substituted benzene ring in which one of the substituents includes an oxygen atom directly attached to the ring
- it must be possible for two of the substituents, excluding the oxygen atom, to react with each other to form an independent compound.

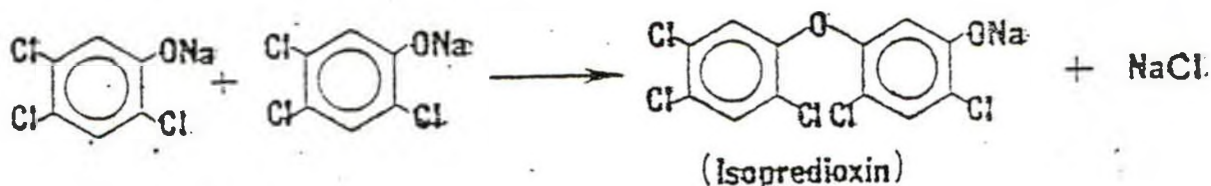
An example of this concept involving 2,4,5-trichlorophenol is shown below:



Many organic compounds meet the dioxin precursor conditions specified above. The more prominent compounds in which chlorinated dioxins have been

found are given in Table 2-3. The 2,3,7,8-TCDD isomer has been determined in 2,4,5-T, 2,4,5-TCF, and hexachlorophene.^{1,57,80} In PCPs the major chlorinated dioxins found have been HCDD, H₇CDD, and OCDD.^{1,57} Because of their chemical structure and composition, several more synthetic organic compounds than are given in Table 2-3 have the potential to contain chlorinated dioxins.

During the manufacture of an organic chemical, chlorinated furans may be formed as a result of reactions competing with chlorinated dioxin-forming reactions. With some precursor compounds, condensation of a chlorine atom in the ortho position to a hydroxyl group may not occur and a chlorinated dioxin is not formed. This situation is demonstrated by the following reaction:¹⁸



The end product of the above reaction has been termed an isopredioxin. The isopredioxin can polymerize into long chains, or it can lose chlorine which leads to the creation of a chlorinated furan, as illustrated below:¹⁸

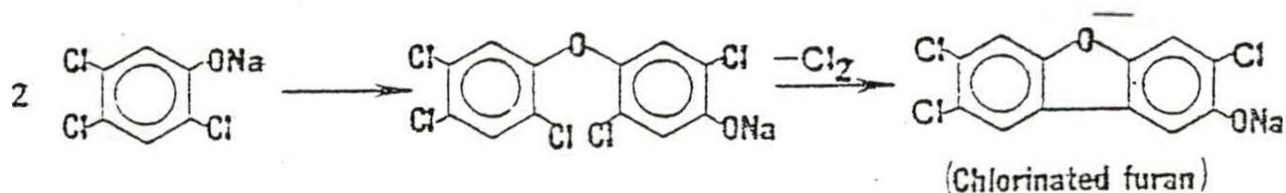


TABLE 2-3. TYPES OF COMPOUNDS THAT HAVE BEEN IDENTIFIED
TO CONTAIN CHLORINATED DIOXINS^{1,18,57,80}

Compounds Confirmed to Contain Chlorinated Dioxin Contaminants^a

Chlorinated Phenols

- Pentachlorophenol (PCP)
- 2,4,5-trichlorophenol (2,4,5-TCP)
- 2,4,6-trichlorophenol
- 2,3,4,6-tetrachlorophenol

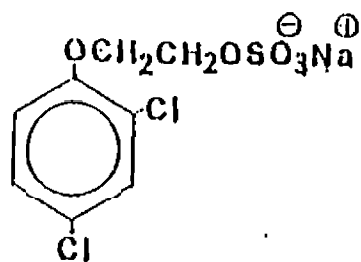
Phenoxy Acids and Their Esters and Salts

- 2,4,5-trichlorophenoxy acetic acid (2,4,5-T)
- 2,4-dichlorophenoxy acetic acid (2,4-D)
- 2-(2,4,5-trichlorophenoxy) propionic acid (Silvex)
- 2,2-dichloropropanoic acid 2-(2,4,5-trichlorophenoxy)
ethyl ester (Erbon)
- 2,4-dichlorophenoxyethyl sulfate (Sesone)
- Phosphorothioic acid (Roumal)

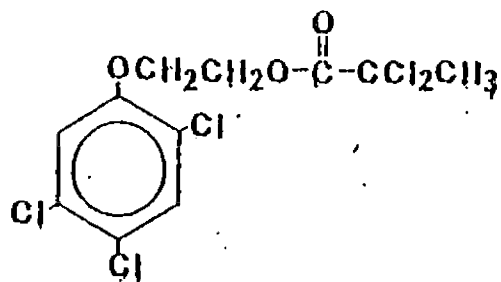
Hexachlorophene

- 2,2'-methylene bis (3,4,6-trichlorophenol)
-

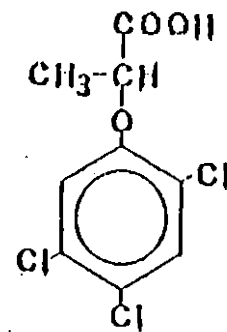
^aMolecular diagrams of the compounds given above are shown in Figure 2-2.



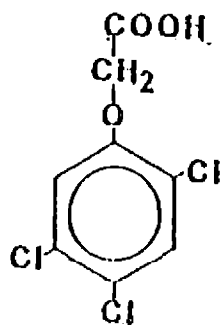
Sosono



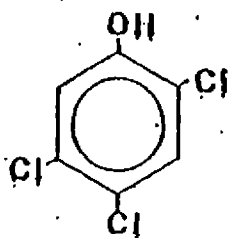
Erbon



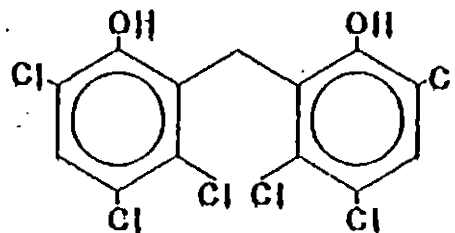
Silvex



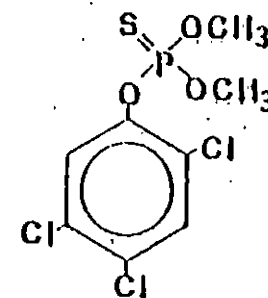
2,4,5-Trichlorophenoxy acetic acid



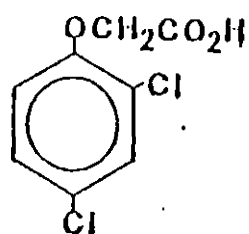
2,4,5-Trichlorophenol



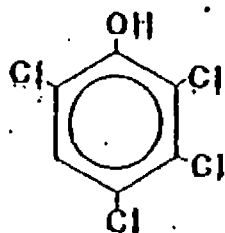
Hexachlorophene



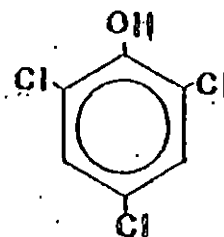
Ronnel



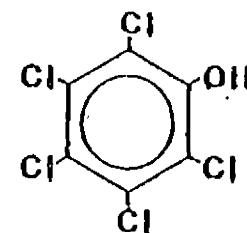
2,4-Dichlorophenoxy acetic acid



2,3,4,6-Tetrachlorophenol



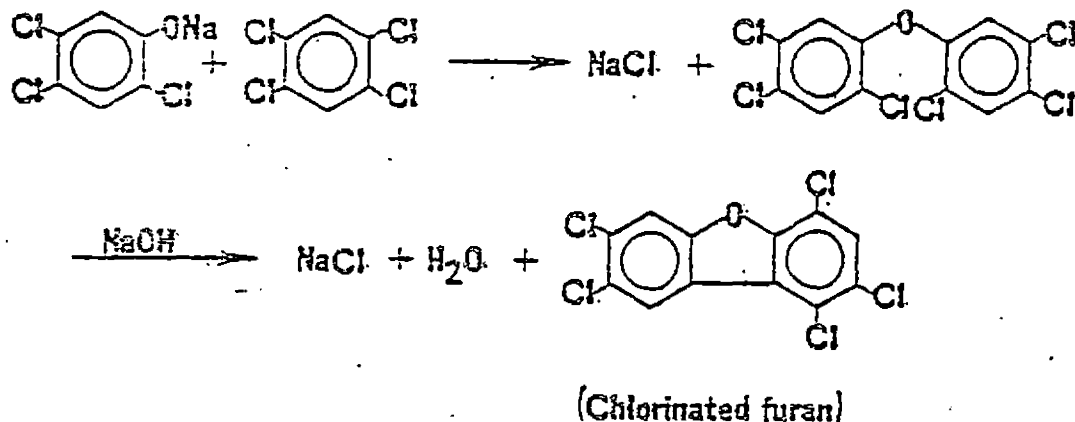
2,4,6-Trichlorophenol



Pentachlorophenol

Figure 2-2. Molecular diagrams of compounds identified to contain chlorinated dioxins.¹⁸

It is also believed that chlorinated furans can be formed by a reaction between a chlorophenol and a polychlorobenzene through an intermediate creation of a diphenyl ether. An example of this reaction is given below:



As expected, many of the compounds that have been found to contain chlorinated dioxins also contain chlorinated furans. The major sources of chlorinated furans are phenoxy acids (and their esters and salts) including 2,4,5-T and 2,4-D, chlorinated phenols including PCP, hexachlorobenzene, and polychlorinated biphenyls (PCBs).^{52,57,70} In PCPs and hexachlorobenzene the predominant furans found have been 2,3,7,8-TCDF and OCDF isomers, although TCDF, PCDF, and HCDF isomers have also been determined. In some samples of PCBs, the furan isomers 2,3,7,8-TCDF and 2,3,4,7,8-PCDF have been found to be the most prevalent chlorinated furans present.^{57,70}

As a result of the concern raised over suspected health risks of dioxin- and furan-containing chemicals, certain uses of several of these substances such as 2,4,5-T and Silvex have been suspended or greatly reduced by State and Federal authorities.^{1,14} Consequently, the need to produce such chemicals for present or future use has diminished to the point where only one or two companies make several of the chemicals, and in some cases (e.g., 2,4,5-TCP and 2,4,5-T) production has ceased. The current producers of major chemicals confirmed to contain chlorinated dioxins and/or furans are listed in Table 2-4.

TABLE 2-4. PRODUCTION SOURCES OF MAJOR CHLORINATED
DIOXIN AND FURAN CONTAINING CHEMICALS^a

Chemical	Producer - Location
Pentachlorophenol	Reichhold Chemicals - Tacoma, WA Vulcan Materials, Vulcan Chemical Division - Wichita, KS
2,4,6-Trichlorophenol	Dow Chemical - Midland, MI Rhône-Poulenc, Agrochemical Division - Portland, OR
2,3,4,6-Tetrachlorophenol	Dow Chemical - Midland, MI
Silvex	Riverdale Chemical - Chicago Heights, IL Dow Chemical - Midland, MI
2,4-D	Amvac Chemical - Los Angeles, CA Diamond Shamrock - Tuscaloosa, AL Dow Chemical - Midland, MI Guth Corp. - Hillside, IL Rhône-Poulenc, Agrochemical Division - Portland, OR Riverdale Chemical - Chicago Heights, IL Vertac Chemical - Jacksonville, AR
Hexachlorophene	Givaudan Corp., Chemical Division - Clifton, NJ

^aSource: 1982 Directory of Chemical Producers, Stanford Research
Institute, Menlo Park, CA, 1982.

Several non-chemical, industrial sources such as power plants, incinerators, and boilers have been identified as potential sources of chlorinated dioxin and furan environmental emissions. These sources are extensively discussed in Chapter 3.

CHAPTER 3

SOURCE CATEGORIES OF CHLORINATED DIOXIN AND FURAN AIR EMISSIONS

In this chapter confirmed and potential source categories of chlorinated dioxin and furan air emissions are identified. Two broad types of emission source categories are discussed. The first type includes industrial, commercial, and residential emission source categories that have been determined by testing. The second type involves potential emission source categories that have been extrapolated from laboratory experiments. Quantification of the chlorinated dioxin and furan air emissions from the source categories identified in this chapter are presented in Chapter 4.

3.1 INTRODUCTION

In 1973 Dow Chemical Company issued a report which stated that "chlorinated dioxins are ubiquitous." Dow concluded that "their presence is due to the existence of a natural phenomenon, trace chemistries of fire." In its study Dow investigated many combustion sources and determined that all were sources of chlorinated dioxin air emissions. Included in Dow's list of chlorinated dioxin sources are:^{6,11,51}

- hazardous waste incinerators,
- municipal refuse incinerators,
- industrial boilers,
- internal combustion engines,
- home heating furnaces,
- fireplaces, and
- charcoal grills.

The Dow work centered solely on determining the existence of chlorinated dioxins. None of the obtained samples were analyzed for the presence of chlorinated furans.

The Dow study and its "trace chemistries of fire" hypothesis aroused the interest of many researchers in the field. Spurred by the Dow results, and similar but more qualitative results from European research, a considerable amount of work was begun to address the question of chlorinated dioxin ubiquity and the relationship to combustion chemistry. As a result of the increased interest and research in chlorinated dioxins, the existence and prevalence of similar and related chlorinated furan compounds became more important and more well-known. Research into the formation mechanisms of both families of organic compounds indicated that chlorinated furans also may be connected with combustion chemistry. Following the 1978 Dow report, many researchers in the United States and Europe began examining combustion sources and other potential formation mechanisms of chlorinated dioxins and furans. Much of the work focused on possible sources of chlorinated dioxin and furan air emissions. The results and conclusions of these studies on source categories of chlorinated dioxin and furan air emissions are summarized in this chapter.

3.2 CONFIRMED SOURCE CATEGORIES OF CHLORINATED DIOXIN AND FURAN AIR EMISSIONS

The discussion of confirmed chlorinated dioxin and furan air emission sources is divided into four major classes or types of source categories. These major classes are incinerators, boilers, residential stoves, fireplaces, and furnaces, and internal combustion engines. Distinct emission source categories within each class are identified.

3.2.1 Incineration Source Categories

In the list of references given in Table A-1 of Appendix A, 34 different and distinct references are given on the occurrence of chlorinated dioxin

and furan air emissions from over 50 incinerators. Tables 3-1 and 3-2 present a summary of the chlorinated dioxin and furan air emission information from these 34 references. Included in the information of Tables 3-1 and 3-2 are the types of incinerators where dioxin and furan emissions have been determined, the classes of chlorinated dioxin and furan isomers that have been found, and the types of samples in which the dioxins and furans were measured. Chlorinated dioxins and furans have been discovered in the air emissions of incinerators burning municipal refuse, chemical wastes, hazardous wastes, and scrap wire. These incinerators are located in the United States, Canada, Japan, Italy, France, Germany, Sweden, Switzerland, and the Netherlands. An analysis to determine the presence of both chlorinated dioxins and furans has not been performed on all incinerator air emission samples. However, in the cases where both groups of organic compounds were analyzed for, both have been found to be present. From all reports to date, it appears that whenever incinerator sources have been specifically examined for chlorinated dioxin or furan air emissions, these emissions have been found.

The spectrum of testing that has been conducted on incinerator sources varies from single sample tests of one incinerator to multi-sample tests of up to 25 incinerators.^{32,40,59} Tests have been conducted over as long a period as 9 months in order to monitor the variability of chlorinated dioxin and furan emissions with varying input loads, load characteristics, and incinerator operating conditions.^{68,83}

In attempting to detect chlorinated dioxin and furan emissions from incinerator sources, researchers have primarily examined fly ash emissions collected by incinerator control devices such as electrostatic precipitators (ESPs). There are cases, however, where samples have been taken of fly ash emissions from an ESP stack, fly ash emissions from an incinerator stack, and fly ash and gaseous emissions from an incinerator stack. Sampling of ESP fly ash catches predominates primarily because it is a much less difficult procedure than extractive sampling of particulate and gaseous

Table 3-1. SUMMARY OF CHLORINATED DIOXIN AIR EMISSION SOURCE CATEGORIES

Type of Source	Type of Sample	HCDD, DCDH TCDD	2,3,7,8-TCDF	TCDD Total	PCDD	HCDD	H ₇ CDH	OCDD	Comments	Reference
HWI	FG	0.065 µg/kg of TCDD	0.002 µg/kg	0.032 µg/kg	ND	0.082 µg/kg	0.030 µg/kg	0.013 µg/kg	All dioxin and furan species measured in gas-phase phase, none found in fly ash.	1
HWI	FA from ESP, FG	NA NA	NA NA	93 ppb 37 µg/m ³	134 ppb 344 µg/m ³	604 ppb 440 µg/m ³	760 ppb 347 µg/m ³	343 ppb 432 µg/m ³	Average results of tests on 9 incinerators in the Netherlands, each test had 14 samples taken. Data are reported for fly ash and flue gas results.	39
HWI	FA from ESP, stack	NA	NA	2.4-12 ppb	2.8-4.2 ppb	3.4-124 ppb	7.2-11.2 ppb	7.6-15.9 ppb	The range of results found in tests of 2 Japanese, 2 Canadian, and one Dutch incinerator are given. The furan values were derived and are only semi-quantitative.	26
HWI	FA from ESP, stack	NA	NA	NA	NA	NA	NA	NA	Total chlorinated dioxins equal 0.2 ppm, total chlorinated furans equal 0.4 ppm. 2,3,7,8-TCDD is a minor component of the emissions. 2,3,7,8-TCDF is a major component of the emissions.	23, 34
HWI (waste oil boiler)	FA from ESP, stack	NA	NA	NA	NA	NA	NA	NA	Total chlorinated dioxins equal 0.6 ppm, total chlorinated furans equal 0.3 ppm. 2,3,7,8-TCDD is a minor component of the emissions. 2,3,7,8-TCDF is a major component of the emissions.	23, 34
HWI	FA from stack	NA	NA	ND	NG	1-20 ppb	27-160 ppb	190-440 ppb	System is a liquid tar incinerator. Supplemental natural gas fuel is used.	2, 6, 11, 31
HWI	FA from stack	NA	ND-110 ppb	3300-12000 ppb	NA	1300-1600 ppb	3000-37000 ppb	3000-59000 ppb	Motory bit chemical waste incinerator with no supplemental firing fuel.	2, 6, 11, 31

Table 3-1. (Continued) SUMMARY OF CHLORINATED DIOXIN AIR EMISSION SOURCE CATEGORIES

Type of Source	Type of Sample	PCDD, PCDF Total	2,3,7,8-TCDF	TCDF Total	PCDD	PCDF	H ₂ PCDD	PCDF	Comments	Reference
IMI	FA from stack	NA	<2 ppb	<2-4 ppb	NR	<0.5-5 ppb	4-110 ppb	9-350 ppb	Rotary kiln chemical waste incinerator with supplemental firing fuel.	2, 6, 11, 51
IMI	FA from ESP	NA	0.4 ppb	2.7 ppb	NR	14 ppb	28 ppb	30 ppb		2, 6, 11, 51
IMI	FA from stack	NA	NR	410 ppt	NA	NA	NA	NA	2,3,7,8-isomers were not specifically analyzed for.	67
IMI	FA from ESP	NA	<130 ppt	7.3 ppb	NR	14 ppb	28 ppb	30 ppb		37, 40
IMI	FA from ESP	NA	2.3 ppb	67.5 ppb	NR	550 ppb	1040 ppb	650 ppb		37, 40
IMI	FA from boiler	NA	ND	ND	ND	ND	ND	6 ppb	Boiler and stack samples taken simultaneously.	32, 40
IMI	FA from stack	NA	NR	12 ppb	8 ppb	30 ppb	60 ppb	120 ppb		32, 40
IMI	FA from ESP	ND	0.29 ppb	6.1 ppb	NR	NR	NR	150 ppb	Only results for TCDF, PCDD, and 2,3,7,8-TCDF reported.	4
IMI	FA from ESP	ND	0.065 ppb	1.12 ppb	NR	NR	NR	35.3 ppb		4
IMI	FA from ESP	ND	0.14 ppb	2.74 ppb	NR	NR	NR	0.6 ppb		4
IMI	FA from ESP	ND	NR	0.7 ppb	NR	NR	NR	166 ppb		4
IMI	FA from ESP	NA	NR	NR	NR	NR	NR	NR		22
IMI	FA from ESP	NA	NR	NR	NR	NR	NR	NR		22
IMI	FA, FG	NA	NR	NR	NR	NR	NR	NR	NR (FA) indicates found only in fly ash	22
IMI	FA from ESP	NA	NR	8.6 ppb	15 ppb	13 ppb	3.2 ppb	0.4 ppb	Averages from combined samples of two Canadian incinerators.	22
IMI	FA from ESP, stack	NA	NR	40 ppb	114 ppb	540 ppb	900 ppb	200 ppb		69

Table 3-1. (Continued) SUMMARY OF CHLORINATED DIOXIN AIR EMISSION SOURCE CATEGORIES

Type of Source	Type of Sample	HCB, DCCB, TCDD	2,3,7,8-TCDF	TCDF Total	PCDF	HCB	H, CDF	DCCB	Comments	Reference
IMI	FA, FG	NA	NKS	NKS	NKS	NKS	NKS	IMH	3 Station Incinerators were tested and total amounts of dioxins and furans were reported as one sum. Values ranged from 1200-1530 ppb.	55
IMI	FA from ESR	NA	0.1 ppb	NP	NP	NA	NA	NA	Single test of a municipal waste pyrolysis system in Sweden.	56
IMI	FA, FO from stack	NA	NKS	120 $\mu\text{g}/\text{m}^3$	NA	366 $\mu\text{g}/\text{m}^3$	286 $\mu\text{g}/\text{m}^3$	126 $\mu\text{g}/\text{m}^3$	17 samples taken from an Italian Incinerator over a 9 month period. Results are the average of all tests. Total chlorinated dioxin emission factor is 14,767 $\mu\text{g}/\text{ton}$ of waste burned. Total chlorinated furan emission factor is 15,825 $\mu\text{g}/\text{ton}$ of waste burned.	60, 63
IMI	FA from ESR	NA	NKS	13.3 ppb	23.2 ppb	23.8 ppb	14.9 ppb	6.3 ppb	Results represent the average of eight samples.	63
IMI	FA from ESR	NA	ND	ND	7.0 ppb	21.8 ppb	12.4 ppb	106 ppb		67
IMI	FA, FG	NA	0.015 $\mu\text{g}/\text{kg}$	0.013 $\mu\text{g}/\text{kg}$	NA	NA	NA	NA	4 samples were only analyzed for tetrachlorinated dioxins and furans. Average values are shown.	17
IMI	FA, FG	NA	0.021 $\mu\text{g}/\text{kg}$	0.043 $\mu\text{g}/\text{kg}$	NA	NA	NA	NA	Incinerator burns refuse and waste oils. 3 samples were only analyzed for tetrachlorinated dioxins and furans. Average values are shown.	17
IB (coal-fired)	FA, FG	NA	0.20 $\mu\text{g}/\text{kg}$	0.69 $\mu\text{g}/\text{kg}$	NA	NA	NA	NA	Sample was only analyzed for tetrachlorinated dioxins and furans.	17
IB (refuse-fired)	FA, FG	NA	0.11 $\mu\text{g}/\text{kg}$	0.36 $\mu\text{g}/\text{kg}$	NA	NA	NA	NA	Sample was only analyzed for tetrachlorinated dioxins and furans.	17
IMI	FA from stack	NA	NKS	100 ppb	160 ppb	180 ppb	130 ppb	140 ppb		22, 40

Table 3-1. (Continued) SUMMARY OF CHLORINATED DIOXIN AIR EMISSION SOURCE CATEGORIES

Type of Source	Type of Sample	HCDD, DCCDD, 1,3,4,6-TCDD	2,3,7,8-TCDD	TCDD Total	PCDD	HCDD	1,2,3,7,8-PeCDD	OCDD	Comments	Reference
IND	FA from ESP	NA	NRS	5-110 ppb	31-488 ppb	80-1200 ppb	190-902 ppb	106-266 ppb	Range of values found from 80 analyses of 25 incinerators.	32, 40
IND	FG	NA	NRS	<1.2-360 ppt	NA	NA	NA	NA	Tests conducted onboard the H/T Vulcanus during combustion of Agent Orange. Results are the range of values from 21 tests.	40, 84
IS	FA from stack	NA	ND	38 ppb	NR	2 ppb	4 ppb	24 ppb	Boiler is fired with coal and fuel oil. Detection limit for 2,3,7,8-TCDD was only 10 ppb.	6, 11 51
KMS	FA	NA	90-100 ppt	1041-4923 ppt	NA	1800-4300 ppt	2800-4100 ppt	2000-3300 ppt	Chimney particulate samples were taken. Tested after were in New Hampshire.	15
KMS	FA	NA	ND-13 ppt	ND-374 ppt	NA	2.2-2000 ppt	8.9-9000 ppt	14-12400 ppt	Chimney particulate samples were taken. Tested after were in Minnesota and Michigan.	15
KMS	FA	NA	6-11 ppt	124-137 ppt	NA	850-2600 ppt	1700-4000 ppt	1700-4000 ppt	Chimney particulate samples were taken. Tested after were in Oregon.	15
KIP	FA	NA	ND-0.1 ppb	ND-0.4 ppb	NA	0.2-3 ppb	0.2-16 ppb	0.9-25 ppb	Chimney particulate samples taken from two residential fireplaces.	6, 11 51
KIP	FA	NA	0.6 ppb	1 ppb	NA	34 ppb	430 ppb	1300 ppb	Particulate samples collected from the ESP plates of a natural gas-fired home heating furnace.	6, 11 51
ICE (gasoline)	FA from mufflers	NA	ND-0.004 ppb	ND-0.008 ppb	NA	ND	0.003-0.01 ppb	0.02-0.07 ppb	Loaded and unloaded fuels were used in the tested automobiles.	6, 11 51
ICE (diesel)	FA from mufflers	NA	0.003 ppb	0.023	NA	0.02 ppb	0.10 ppb	0.26 ppb		6, 11 51
IND	FA, FG from stack	NA	NRS	ND-6.9 ppb	NA	NA	NA	NA	Incinerator burns PCB-contaminated wastes.	8

Table 3-1. (Continued) SUMMARY OF CHLORINATED DIOXIN AIR EMISSION SOURCE CATEGORIES

Type of Source	Type of Sample	HCBH, BCBH T ₃ CDD	2,3,7,8-TCDF	TCDF Total	PCDF	HCBP	H ₇ CDF	PCDF	Comments	Reference
DM1	FA, IG from stack	NA	NKS	ND=0.48 ppb	NA	NA	NA	NA	Incinerator burns PCB-contaminated wastes.	8
IR	FA from fabric filter	NR	NR	NR	NR	NR	NR	NR	Boiler in firing wood waste and a PCP/cresolite waste-water mixture.	3
UB	FA, IG from ESP	NA	NA	NA	NA	NA	NA	NA	Chlorinated furans qualitatively determined to be present in ESP fly ash and stack gas emissions.	7b

*Legend:

DM1 - Municipal Waste Incinerator
 CM1 - Chemical Waste Incinerator
 HM1 - Hazardous Waste Incinerator
 WR1 - Waste Recclamation Incinerator
 IM1 - Industrial Waste Incinerator
 RUS - Residential Wood Stove
 RFP - Residential Fireplace
 RHF - Residential Heating Furnace
 ICE - Internal Combustion Engine
 IHP - Industrial Heating Plant
 IB - Industrial Boiler
 UB - Utility Boiler

FA - Fly Ash
 IG - Flue Gas
 ESP - Electrostatic Precipitator
 NA - Not Analyzed
 ND - Not Detected
 NR - Species determined to be present but quantification not reported
 NKS - Not Reported Separately
 ppm - Parts Per Million
 ppb - Parts Per Billion
 ppt - Parts Per Trillion

^b Data for References 7 and 17 are in terms of emissions per unit of waste burned.

^c Companion chlorinated furan data points for each of the tests in this table are given in Table 3-2.

Table 3-2. SUMMARY OF CHLORINATED FURAN AIR EMISSION SOURCE CATEGORIES

Type of Source	Type of Sample	HCDF, HCDF T ₃ CDP	2,3,7,8-TCDF	TCDF Total	PCDF	HCBP	H ₂ CDP	HCDF	Comments	Reference
IMI	FO	1.5 ug/kg of T ₃ CDP	NR	0.45 ug/kg	NR	0.31 ug/kg	0.035 ug/kg	0.003 ug/kg	All dioxin and furan species measured in gaseous phase, none found in fly ash.	7
IMI	FA from ESP FO	NA	NRS	171 ppb	312 ppb	459 ppb	314 ppb	51 ppb	Average results of tests on 9 incubators in the Hethers- lands, each test had 14 samples taken. Data are reported for fly ash and flue gas samples.	59
		NA	NRS	161 ug/m ³	277 ug/m ³	520 ug/m ³	293 ug/m ³	68 ug/m ³		
IMI	FA from ESP, stack	NR	NRS	1.4-6.3 ppb	3.8-11 ppb	1.9-2.7 ppb	4.3-5 ppb	2-4.6 ppb	The range of results found in tests of 2 Japanese, 2 Canadian, and one Dutch incubator are given. The furan values were derived and are only semi-quantitative.	76
IMI	FA from ESP, stack	NR	NR	NR	NR	NR	NR	NR	Total chlorinated dioxins equal 0.2 ppm, total chlorinated furans equal 0.1 ppm. 2,3,7,8-TCDF is a minor component of the emissions. 2,3,7,8-TCDF is a major component of the emissions.	23, 34
IMF (waste oil boiler)	FA from ESP, stack	NR	NR	NR	NR	NR	NR	NR	Total chlorinated dioxins equal 0.6 ppm, total chlorinated furans equal 0.3 ppm. 2,3,7,8-TCDF is a minor component of the emissions. 2,3,7,8-TCDF is a major component of the emissions.	23, 34
IMI	FA from stack	NA	NA	NA	NA	NA	NA	NA	System is a liquid tar in- cinerator. Supplemental natural gas fuel is used.	2, 6, 11, 51
IMI	FA from stack	NA	NA	NA	NA	NA	NA	NA	Rotary kiln chemical waste incinerator with no supple- mental firing fuel.	2, 6, 11, 51

Table 3-2. (Continued) SUMMARY OF CHLORINATED FURAN AIR EMISSION SOURCE CATEGORIES

[illegible]

Table 3-2. (Continued) SUMMARY OF CHLORINATED FURAN AIR EMISSION SOURCE CATEGORIES

Type of Source	Type of Sample	HCDF, DCDP, T ₁ CDP	2,3,7,8-TCDF	TCDF Total	PCDF	BCDF	H ₁ CDP	HCDF	Comments	Reference
IMI	FA, IG	NA	NMS	NMS	NMS	NMS	NMS	NMS	3 Italian incinerators were tested and total amounts of dioxins and furans were reported as one sum. Values ranged from 1200-1570 ppb.	55
IMI	FA from ESP	NA	0.3 ppm	NR	NR	NR	NR	NR	Single test of a municipal waste pyrolysis system in Sweden.	56
IMI	FA, FG from stack	NA	NMS	309 ng/m ³	250 ng/m ³	314 ng/m ³	215 ng/m ³	124 ng/m ³	1) samples taken from an Italian incinerator over a 9 month period. Results are the average of all tests. Total chlorinated dioxin emission factor is 14,167 µg/ton of waste burned. Total chlorinated furan emission factor is 15,825 µg/ton of waste burned.	60, 61
IMI	FA from ESP	NA	NA	NA	NA	NA	NA	NA	Results represent the average of eight samples.	62
IMI	FA from ESP	NA	NA	NA	NA	NA	NA	NA		62
IMI	FA, FG	NA	0.074 µg/kg	0.17 µg/kg	NA	NA	NA	NA	4 samples were only analyzed for tetrachlorinated dioxins and furans. Average values are shown.	17
IMI	FA, FG	NA	0.13 µg/kg	0.26 µg/kg	NA	NA	NA	NA	Incinerator burn refuse and waste oils. 3 samples were only analyzed for tetrachlorinated dioxins and furans. Average values are shown.	17
ID (coal-fired)	FA, IG	NA	2.0 µg/kg	5.8 µg/kg	NA	NA	NA	NA	Sample was only analyzed for tetrachlorinated dioxins and furans.	17
IS (refuse-fired)	FA, FG	NA	1.3 µg/kg	3.7 µg/kg	NA	NA	NA	NA	Sample was only analyzed for tetrachlorinated dioxins and furans.	17
IMI	FA from stack	NR	NMS	100 ppb	100 ppb	70 ppb	50 ppb	NR		32, 40

Table 3-2. (Continued) SUMMARY OF CHLORINATED FURAN AIR EMISSION SOURCE CATEGORIES

Type of Source	Type of Sample	HCBF, OCBF TCDF	2,3,7,8-TCDF	TCDF Total	PCDF	HCBF	H ₂ CBF	OCDF	Comments	Refer- ences
IND	FA from ESP	NR	NRB	13-223 ppb	42-510 ppb	109-870 ppb	89-407 ppb	18-76 ppb	Range of values found from 80 analyses of 25 incinerators.	32, 40
IND	GC	NA	NA	NA	NA	NA	NA	NA	Tests conducted onboard the H/T Vulcanus during combustion of Agent Orange. Results are the range of values from 21 tests.	40, 84
IB	FA from stack	NA	NA	NA	NA	NA	NA	NA	Boiler (a fired with coal and fuel oil). Detection limit for 2,3,7,8-TCDF was only 10 ppb.	6, 11 51
RUS	FA	NA	NA	NA	NA	NA	NA	NA	Chimney particulate samples were taken. Tested sites were in New Hampshire.	13
RWB	FA	NA	NA	NA	NA	NA	NA	NA	Chimney particulate samples were taken. Tested sites were in Minnesota and Michigan.	13
RWS	FA	NA	NA	NA	NA	NA	NA	NA	Chimney particulate samples were taken. Tested sites were in Oregon.	13
RYP	FA	NA	NA	NA	NA	NA	NA	NA	Chimney particulate samples taken from two residential fireplaces.	6, 11 51
RIY	FA	NA	NA	NA	NA	NA	NA	NA	Particulate samples collected from the ESP plates of a natural gas-fired home heating furnace.	6, 11 51
ICK (gasoline)	FA from mufflers	NA	NA	NA	NA	NA	NA	NA	Loaded and unloaded fuels were used in the tested automobiles.	6, 11 51
ICE (diesel)	FA from mufflers	NA	NA	NA	NA	NA	NA	NA		6, 11 51
IND	FA, FC from stack	NA	1.7-2.5 ppb	2-22 ppb	NA	NA	NA	NA	Incinerator burns PCB-contaminated wastes.	8

Table 3-2. (Continued) SUMMARY OF CHLORINATED FURAN AIR EMISSION SOURCE CATEGORIES

Type of Source	Type of Sample	HCBF, PCBF T ₁ CBF	TCDF 2,3,7,8-TCDF	TCDF Total	PCDF	HCBF	H ₂ CBF	HCDF	Comments	Refer- ence
IMI	FA, FG from stack	NA	ND-1.5 ppb	ND-4 ppb	NA	NA	NA	NA	Incinerator burns PCB- contaminated wastes.	8
IR	FA from fabric filter	NR	NR	NR	NR	NR	NR	NR	Bullets in firing wood waste and a PCP/cinnamate waste- water mixture.	1
UB	FA, FG from ESP	NR	NR	NR	NR	NR	NR	NR	Chlorinated furans quali- tatively determined to be present in ESP fly ash and stack gas emissions.	14

* Legend:

IMI - Municipal Waste Incinerator	FA - Fly Ash
IMI - Chemical Waste Incinerator	FG - Flue Gas
IMI - Hazardous Waste Incinerator	ESP - Electrostatic Precipitator
WRI - Wire Reclamation Incinerator	NA - Not Analyzed
IMI - Industrial Waste Incinerator	ND - Not Detected
RVS - Residential Wood Stove	NR - Species determined to be present but quantification not reported
RFP - Residential Fireplace	NRS - Not Reported Separately
RHF - Residential Heating Furnace	ppm - Parts Per Million
ICE - Internal Combustion Engine	ppb - Parts Per Billion
IRP - Industrial Heating Plant	ppt - Parts Per Trillion
IB - Industrial Boiler	
UB - Utility Boiler	

^b Data for References 1 and 14 are in terms of emissions per unit of waste burned.

^c Companion chlorinated dibenz data points for each of the tests in this table are given in Table 3-1.

components in a flue gas stream. In the cases where only collected fly ash is analyzed for chlorinated dioxins and furans, the evaluation to determine potential air emissions can be incorrect due to the enrichment of organics on sub-micron size particles. A device such as an ESP is very effective at removing relatively large fly ash particles, however, its efficiency drops off considerably in the fine particle size range less than 1 micron. Available data indicate that chlorinated dioxins and furans preferentially adsorb onto the fine particles which are escaping collection by the ESP. Data from one municipal incinerator in Germany illustrate this point.² The concentration of TCDD in ESP collected fly ash was 0.025 µg/g, while the TCDD concentration in the exhausted fine particulate was 300 µg/g.²

The results of several incinerator tests have also pointed out the need to obtain and analyze both fly ash and gaseous samples for chlorinated dioxins and furans. Both chlorinated dioxins and furans have been measured in the gaseous emission streams of incinerators and other sources.^{7,17,59,68,83} In several incinerator tests the levels of chlorinated dioxins and furans in the gaseous phase were greater than those measured on the fly ash. In the case of one municipal incinerator, no chlorinated dioxins or furans were found on the fly ash, while practically all isomer classes of chlorinated dioxins and furans were found in the gaseous emissions.⁷ These results demonstrate that to conclusively prove or disprove the existence of chlorinated dioxin and furan air emissions, a source's fly ash and gaseous emissions must be sampled and analyzed.

3.2.1.1 Municipal Waste Incinerators—

As an examination of Tables 3-1 and 3-2 shows, the incinerator type which has been tested the most and found to contain chlorinated dioxin and furan air emissions is the municipal refuse or municipal waste incinerator (MWI). In source tests of MWIs all classes of chlorinated dioxin and furan isomers given in Tables 2-1 and 2-2 have been identified. The isomer class suspected to be the most toxic, TCDD, has been shown to consistently be a minor component of measured chlorinated dioxin emissions. The isomer

2,3,7,8-TCDD is generally either a very minor part of the TCDD load or it is not present at all.^{2,4,7,11,23,40} Generally, the higher chlorinated dioxin compounds predominate in the samples that have been analyzed. As a contrast, the chlorinated furan isomer class TCDF is often a major component of total chlorinated furan emissions. The 2,3,7,8-TCDF isomer has been shown in several MWI tests to be a major constituent of total TCDF emissions and of total chlorinated furan emissions. References 7, 17, 23, 26, 34, 68, and 83 are just a few of the instances in which these types of furan results are reported.

Three hypotheses have been put forth in the literature to explain the existence of chlorinated dioxins and furans in MWI air emissions.^{2,32} The first hypothesis states that chlorinated dioxins and furans occur in MWI air emissions because these same compounds are present in the materials to be incinerated. The heat of incineration releases the chlorinated dioxins and furans which adsorb onto fly ash or homogeneously condense into fine particles. The second hypothesis predicts that chlorinated dioxin and furan emissions from MWIs occur as a result of chlorinated organic precursors such as chlorophenols and chlorobenzenes being a component of the wastes to be burned. The temperatures of incineration initiate chemical transformations of these precursors to form chlorinated dioxins and furans. This transformation process by heating has been demonstrated by several researchers (see Section 3.3). The third hypothesis, for which there is very little direct evidence, predicts de novo chlorinated dioxin and furan formation can result from high temperature reactions between non-chlorinated organics and inorganic chlorine/chloride present in the wastes.

3.2.1.2 Hazardous and Chemical Waste Incinerators—

The literature in Table A-1 contained information on seven different hazardous and chemical waste incinerators (HWIs and CWIs) that have been shown to be emitting chlorinated dioxins and furans. The substances burned by these incinerators include waste chemical tars, PCBs, waste oils, and the herbicide Agent Orange. The source burning Agent Orange is the hazardous waste disposal ship M/T Vulcanus.

In only three of the seven HWI and CWI tests were both chlorinated dioxins and furans analyzed for. In two of these three tests involving PCB incinerators, only TCDD, TCDF, and their 2,3,7,8-isomers were the subject of analysis.⁸ The pattern discussed in Section 3.2.1.1 concerning the occurrence of TCDD and TCDF was evident in these PCB incinerator tests. Levels of TCDF were 1 to 12 times greater than TCDD. In the third test of a CWI for which chlorinated dioxins and furans were analyzed, TCDD, PCDD, HCDD, H₇CDD, OCDD, TCDF, PCDF, HCDF, and H₇CDF were found. Equal quantities of TCDD and TCDF were measured.

In the remaining four HWI tests, samples were only analyzed for chlorinated dioxin compounds. These incinerators were burning waste tars, pesticide chemical wastes, and the herbicide Agent Orange. Chlorinated dioxin isomer groups TCDD, PCDD, HCDD, H₇CDD, and OCDD were found. The toxic 2,3,7,8-TCDD isomer was identified separately in two of the four tests. In the incineration of Agent Orange, 2,3,7,8-TCDD levels were not reported separately from total TCDD, and in the incineration of chemical tars no TCDD of any type was detected.^{6,11,84}

3.2.1.3 Wire Reclamation Incinerator—

Wire reclamation incinerators (WRIs) are used to burn off the casings of scrap wire for the purpose of recovering the metal value of the wire. Several types of casings have been shown to contain organic and chlorinated organic materials that may be chlorinated dioxin and furan precursors. Reference 67 reports the findings of one source test conducted to determine the existence and amount of TCDD and TCDF in a WRI's air emissions. Both isomer groups were identified in the incinerator's emissions and TCDF levels were 30 times higher than TCDD levels. Only fly ash samples were analyzed for TCDD and TCDF. Speciation for individual TCDD and TCDF isomers was not performed in this test.

3.2.2 Boiler Source Categories

The air emissions of utility and industrial boilers have been analyzed for the presence of chlorinated dioxins and furans. Boilers burning a variety of fuels including coal, fuel oil, wood, refuse-derived-fuel (RDF), waste oils, and waste wood treatment solutions have been tested. The results of the analyses to determine chlorinated dioxin and furan emissions from these sources are discussed in the following sections.

3.2.2.1 Utility Boilers--

Air emission samples from ten utility or electric power boilers have been analyzed for the presence of TCDD and/or its 2,3,7,8-isomer. No other chlorinated dioxin isomer groups or individual isomers have been analyzed for in the samples taken to date. In the ten tests, TCDD and 2,3,7,8-TCDD levels have been below the particular detection limits used. In only one of the ten tests was gaseous phase sampling and analysis for chlorinated dioxins and furans conducted.

In one test of a 750 MW power plant burning low sulfur, high ash western coal, no TCDD was detected in fly ash samples at a lower detection limit of 1.2 parts per trillion (ppt). The analyzed fly ash sample was collected from the stack downstream of the plant's ESP control device.¹⁰ In another case, fly ash samples from seven coal-fired utility boilers were analyzed for the presence of TCDD and 2,3,7,8-TCDD. Lower limits of detection ranged from 1.0-2.8 ppt with the average detection limit being 1.8 ppt. No TCDD or 2,3,7,8-TCDD was detected in any of the seven samples.⁴⁰ Other tests have been conducted on a coal-fired utility boiler to determine the presence of TCDD in fly ash emissions at a lower detection limit of 1.5 ppt. No TCDD was detected on the fly ash.⁴⁵

No TCDD or 2,3,7,8-TCDD was detected in tests of a 35 MW utility boiler burning a combination of coal and RDF. Fly ash and gaseous emissions samples taken downstream of the ESP control device were analyzed for these

compounds. The lower detection limits for fly ash and gaseous samples were 0.1 parts per billion (ppb) and 0.0005 ng/liter, respectively.³⁰ The authors of Reference 30 state that TCDD was not found because more complete combustion occurs in the utility boiler (as opposed to an incinerator), thereby destroying the TCDD compounds. More complete combustion occurs because firebox temperatures are maintained at higher levels and firebox residence times are longer. It should be noted, however, that in separate tests of the JS ~~W~~ boiler, chlorinated furan compounds were qualitatively identified in both fly ash and vapor samples.⁷⁸

In similar work reported in Reference 7, a boiler burning coal and RDF was tested and found not to be emitting chlorinated dioxins or furans as either fly ash or gaseous emissions. The detection limit reported for measuring TCDD and TCDF in the vapor samples was 0.00025 ng/liter.

3.2.2.2 Industrial Boilers—

An industrial boiler burning waste oils was found to be emitting chlorinated dioxins and furans on fly ash particles.^{23,34} Fly ash from the boiler stack and the ESP catch was analyzed. Chlorinated furan isomer groups T₃CDF, TCDF, PCDF, ECDF, E₇CDF, and OCDF were identified in the emissions. The 2,3,7,8-TCDF isomer was a major component of the TCDF group. Chlorinated dioxin isomer groups TCDD, PCDD, ECDD, E₇CDD, and OCDD were also identified. The 2,3,7,8-TCDD isomer was found to be a minor component of the TCDD group.^{23,34}

Two separate tests were conducted on another industrial boiler burning coal only and RDF only to determine the presence of TCDD, TCDF, and their 2,3,7,8-isomers. In tests with each fuel type, fly ash and gaseous samples were taken from the ESP stack and analyzed. The TCDD, TCDF, 2,3,7,8-TCDD, and 2,3,7,8-TCDF compounds were identified in fly ash and gaseous samples from the combustion of each fuel type.¹⁷ Chlorinated dioxin and furan emissions from burning coal only were slightly higher than those from burning RDF only.

In a test of an industrial boiler fired with coal and fuel oil, only chlorinated dioxins were the subject of analysis.^{6,11,51} Stack fly ash samples were analyzed and found to contain TCDD, ECDD, H₇CDD, and OCDD. No results were reported for levels of PCDD. The combined quantities of TCDD and OCDD accounted for approximately 90 percent of the total chlorinated dioxins found. The 2,3,7,8-TCDD isomer was not detected at a lower detection limit of 10 ppb.^{6,11,51}

Tests of emissions from an industrial boiler in a wood preserving plant indicated a potential for chlorinated dioxin and furan emissions from the combustion of wood preserving wastewaters.³ In the plant tested, the boiler was burning wood waste and a PCP/creosote wastewater mixture. Chlorinated dioxins and furans were not detected in the fly ash air emissions from the boiler's fabric filter control device; however, chlorinated dioxins and furans were found in the boiler bottom ash and in the fly ash collected by the fabric filter. Chlorinated dioxins were detected primarily in the bottom ash, while chlorinated furans predominated in the collected fly ash. Mono- through octachlorinated isomers of dioxins and furans were found in the fly ash and bottom ash samples.³ Although its detection is not explained, Reference 3 reports that 2,3,7,8-TCDD appears (emphasis added) to be present in the collected fly ash.

3.2.3 Residential Stoves, Fireplaces, and Furnaces

From the literature cited in Table A-1, chlorinated dioxins have been identified in the fly ash emissions of six residential wood stoves, two residential fireplaces, and one residential heating furnace. These sources are identified as chlorinated dioxin emitters because chlorinated dioxin compounds have been measured in chimney particulates from each source. Stack gas fly ash samples have not, however, been taken and analyzed. None of the chimney particulate samples from these sources have been analyzed for the presence of chlorinated furan compounds. Characteristics of each source's chlorinated dioxin emissions are discussed in the following sections.

3.2.3.1 Residential Wood Stoves—

Chlorinated dioxin emissions were identified in the chimney particulates of wood stoves located in the eastern (New Hampshire), central (Michigan and Minnesota), and western (Oregon) parts of the United States.¹⁵ In choosing stoves to test, researchers attempted to pick stoves burning wood that had not been previously treated with preservatives or herbicides that could act as chlorinated dioxin precursors. In New Hampshire primarily red oak was burned, in Michigan and Minnesota birch was the primary fuel, and in Oregon fir was used. In all four locations chimney particulates were found to contain TCDD, HCDD, H₇CDD, and OCDD. The 2,3,7,8-TCDD isomer was also measured in several samples but was found to be a minor component of total TCDD emissions.¹⁵

3.2.3.2 Residential Fireplaces—

Chlorinated dioxin emissions were detected in the chimney particulates of two residential fireplaces burning wood that had not been treated with preservatives or herbicides. The chlorinated dioxin isomer groups identified in the fireplace emissions included TCDD, HCDD, H₇CDD, and OCDD. The 2,3,7,8-TCDD isomer was identified in the particulates of one fireplace, while in the other none was found at a lower detection limit of 0.04 ppb.^{6,11,51}

3.2.3.3 Residential Heating Furnace—

Particulate matter removed from the plates of an ESP installed on a natural gas-fired, residential heating furnace was found to contain chlorinated dioxin compounds. The chlorinated dioxin isomer groups measured were TCDD, HCDD, H₇CDD, and OCDD. Levels of TCDD were less than 0.6 percent of the total chlorinated dioxins found, however, the isomer 2,3,7,8-TCDD represented approximately 60 percent of the TCDD measured.^{6,11,51}

3.2.4 Internal Combustion Engines

The authors of References 6, 11 and 51 have extrapolated that internal combustion engines burning gasoline and diesel fuel are sources of chlor-

inated dioxin air emissions. These extrapolations have been made on the basis of researchers measuring chlorinated dioxin compounds in particulate matter scraped from the inside of mufflers installed on gasoline- and diesel fuel-burning cars and trucks.

The muffler scrapings were only analyzed for chlorinated dioxins. Five mufflers were sampled from cars burning leaded and unleaded gasoline and all were found to contain chlorinated dioxin particulates. The specific isomer groups detected were TCDD, H₇CDD, and OCDD. The toxic 2,3,7,8-TCDD isomer was detected in one of the five gasoline-burning samples.^{6,11,51}

Muffler samples from two trucks burning diesel fuel were also found to contain chlorinated dioxin particulates. The isomer groups detected were TCDD, HCDD, H₇CDD, and OCDD. The 2,3,7,8-TCDD isomer was detected in one of the muffler samples from a diesel fuel-burning truck.

3.3 POTENTIAL SOURCES OF CHLORINATED DIOXIN AND FURAN AIR EMISSIONS FROM LABORATORY EXPERIMENTS

In this section potential sources of chlorinated dioxin and furan air emissions that have been identified by laboratory experiments are discussed. The majority of these experiments involve heating or burning confirmed and suspected precursors of chlorinated dioxin and furan compounds, and then analyzing offgases or residual material for the presence of chlorinated dioxins and furans. All experimental data of this type found in the references of Table A-1 are summarized in Tables 3-3 and 3-4. Each experiment given in Tables 3-3 and 3-4 is discussed below.

3.3.1 Combustion of Wood, Grass, and Paper Treated with a Formulation of 2,4,5-T

In the first experiment, wood chips were treated with a commercial herbicide containing 2-butoxyethyl, 2,4,5-trichlorophenoxyacetate (2,4,5-T)

Table 3-3. LABORATORY RESEARCH EXPERIMENTS THAT HAVE IDENTIFIED SOURCES OF CHLORINATED DIOXINS

Experimental Procedure	HCDD, DCDD, TCDD	2,3,7,8-TCDD	TCDD Total	PCDD	HCDD	H, I, PB	DCDD	Comments	Reference
Combustion of wood chips treated with a 2,4,5-T formulation	NA	NA	<0.1-3 mg/kg	<0.3-1.2 mg/kg	<0.2-2 mg/kg	<0.2-0.6 mg/kg	<0.05-1.4 mg/kg	Results represent the range of 8 test runs. Results are expressed as emissions per kg of 2,4,5-T burned.	20
Combustion of paper and grass treated with 2,4,5-T formulations	NA	0.12-0.63 µg/g	NR	NA	NA	NA	NA	Results are for paper treated with 2,4,5-T. Results are expressed as emissions per g of 2,4,5-T burned. Results have been corrected for the level of 2,3,7,8-TCDD originally in the 2,4,5-T formulation.	20
	NA	1.6 and 1.3 µg/g	NR	NA	NA	NR	NA	Results are for grass treated with 2,4,5-T and have been corrected for the level of 2,3,7,8-TCDD originally in the 2,4,5-T formulation. The values given represent emissions directly after treatment and one week after treatment, respectively.	20
Combustion of wood chips treated with a trichlorophenolate formulation	DCDD: 0.4-3 µg T, CDD: 0.2-33 µg/g	NR	1.0-230 µg/g	1.7-81 µg/g	0.2-9 µg/g	<0.05-8 µg/g	<0.04-6 µg/g	Results are expressed as emissions per g of formulation used and they reflect the range of five test samples.	56
Combustion of wood chips treated with a tetrachlorophenolate formulation	DCDD: 0.4 µg/g T, CDD: 3-42 µg/g	NR	10-140 µg/g	14-240 µg/g	17-360 µg/g	10-93 µg/g	<2-5 µg/g	Results are expressed as emissions per g of formulation used and they reflect the range of five test samples.	56
Pyrolysis of commercial PCBs	NA	NA	NA	NA	NA	NA	NA	Laboratory-generated and commercial PCB formulations were tested.	43

Table 3-3. LABORATORY RESEARCH EXPERIMENTS THAT HAVE IDENTIFIED SOURCES OF CHLORINATED DIOXINS

Experimental Procedure	HCDD, HCDD T ₃ CD	TCDD 2,3,7,8-TCDD	Total	PCDD	PCDD	H ₇ CD	PCDD	Comments	Refer- ence
Burning birch leaves and wood wool treated with commercial chlorophenates	NA	NR	26-210 ug/g	39-352 ug/g	37-342 ug/g	0-65 ug/g	0.2-2.2 ug/g	Results are expressed as calculations per g of chlorophenate used. Higher values were obtained from the wood wool tests.	21
Burning of birch leaves treated with purified chlorophenates	NA	NR	3.2-2100 ug/g	3-14 ug/g	1-56 ug/g	3-172 ug/g	6-110 ug/g	Results were expressed as calculations per g of chlorophenate used.	21
Pyrolysis of commercial TCDD	NA	NA	NA	NA	NA	NA	NA	The highly toxic 2,3,7,8-TCDD was one of the major isomers produced.	34
Pyrolysis of PCB isomers	NA	NA	NA	NA	NA	NA	NA	Eighteen different PCB isomers were tested. The PCB isomers were tetra- to octachlorinated.	36,42
Pyrolysis of trichlorobenzene	NA	NR	2 ug/ug	3.3 ug/ug	2.14 ug/ug	0.25 ug/ug	<0.025 ug/ug	Results for all chloroben- zene pyrolysis tests are expressed as calculations per ug of chlorobenzene used. Though the toxic 2,3,7,8-isomers of TCDD and TCDF were determined in these tests, their presence was very minor compared to other isomers.	25
Pyrolysis of tetrachlorobenzene	NA	NR	<0.01 ug/ug	0.025 ug/ug	0.5 ug/ug	2.25 ug/ug	1 ug/ug		25
Pyrolysis of pentachlorobenzene	NA	NR	<0.01 ug/ug	<0.025 ug/ug	<0.025 ug/ug	0.025 ug/ug	0.15 ug/ug		25
Pyrolysis of combined tri- tetra- and pentachloro- benzene	NA	NR	0.16 ug/ug	1.2 ug/ug	2.2 ug/ug	1.7 ug/ug	0.12 ug/ug		25
High temperature oxidation of coal	NA	ND	ND	NA	ND	0.6 ug/g	1-3 ug/g	Results expressed as calculations per g of coal starting material.	60
High temperature oxidation and chlorination of coal using sodium chloride	NA	ND	ND	NA	ND	0.5 ug/g	2-7 ug/g	Results expressed as calculations per g of coal starting material.	60
High temperature oxidation and chlorination of coal using hydrochloric acid	NA	NR	1.4 ug/g	NA	0.4 ug/g	25 ug/g	64 ug/g	Results expressed as calculations per g of coal starting material.	60
High temperature oxidation and chlorination of coal using chlorine gas	NA	NR	1.2 ug/g	NA	29 ug/g	91 ug/g	290 ug/g	Results expressed as calculations per g of coal starting material.	60

*NA - Not analyzed.

NR - Species determined to be present but quantification not reported.

ND - Not detected.

NRS - Not reported separately.

^b Companion chlorinated furan data points for each of the tests in this table are given in Table 3-4.

Table 3-4. LABORATORY RESEARCH EXPERIMENTS THAT HAVE IDENTIFIED SOURCES OF CHLORINATED FURANS

Experimental Procedure	HCBF, HCBF, T ₃ CBF	2,3,7,8-TCDF	TCDF Total	PCDF	HCBF	H ₂ CBF	HCBF	Comments	Reference
Combustion of wood chips treated with a 2,4,5-T formulation	NA	NR	<0.2-8 pg/kg	<0.3-7.1 pg/kg	<0.2-4.9 pg/kg	<0.2-7.4 pg/kg	<0.1-0.2 pg/kg	Results represent the range of 8 test runs. Results are expressed as emissions per kg of 2,4,5-T burned.	28
Combustion of paper and grass treated with 2,4,5-T formulations	NA	NA	NA	NA	NA	NA	NA	Results are for paper treated with 2,4,5-T. Results are expressed as emissions per g of 2,4,5-T burned. Results have been corrected for the level of 2,3,7,8-TCDF originally in the 2,4,5-T formulation.	29
	NA	NA	NA	NA	NA	NA	NA	Results are for grass treated with 2,4,5-T and have been corrected for the level of 2,3,7,8-TCDF originally in the 2,4,5-T formulation. The values given represent emissions directly after treatment and one week after treatment, respectively.	29
Combustion of wood chips treated with a trichlorophenolate formulation	NA	NA	NA	NA	NA	NA	NA	Results are expressed as emissions per g of formulation used and they reflect the range of five test samples.	36
Combustion of wood chips treated with a tetrachlorophenolate formulation	NA	NA	NA	NA	NA	NA	NA	Results are expressed as emissions per g of formulation used and they reflect the range of five test samples.	36
Pyrolysis of commercial TCDF	NR	NR	NR	NR	NR	NR	NR	Laboratory-generated and commercial PCDF formulations were tested.	41

Table 3-4. LABORATORY RESEARCH EXPERIMENTS THAT HAVE IDENTIFIED SOURCES OF CHLORINATED FURANS

Experimental Procedure	HCDF, DCDF, TCDF	2,3,7,8-TCDF	TCDF Total	PCDF	HCDF	H ₂ CDP	HCDF	Comments	Reference
Burning birch leaves and wood wool treated with commercial chlorophenates	NA	NRS	1 pg/g	NR	NR	NR	NR	Results are expressed as 21	
								calculated per g of chlorophenates used. Higher values were obtained from the wood wool tests.	
Burning of birch leaves treated with purified chlorophenates	NA	ND	ND	ND	ND	ND	ND	Results were expressed as 21	
								calculated per g of chlorophenates used.	
Pyrolysis of commercial PCBs	NR	NR	NR	NR	NR	NR	NR	The highly toxic 2,3,7,8-TCDF was one of the major isomers produced.	14
Pyrolysis of PCB isomers	NR	NR	NR	NR	NR	NR	NR	Eighteen different PCB isomers were tested. The PCB isomers were tetra- to octachlorinated.	16,43
Pyrolysis of trichlorobenzene	NA	NRS	0.13 ng/μg	0.1 ng/μg	<0.025 ng/μg	<0.025 ng/μg	<0.025 ng/μg	Results for all chloroben- 25	
								zene pyrolysis tests are expressed as calculated per μg of chlorobenzene 25	
Pyrolysis of tetrachlorobenzene	NA	NRS	<0.01 ng/μg	0.025 ng/μg	0.7 ng/μg	0.0 ng/μg	0.15 ng/μg	used. Through the toxic 2,3,7,8-isomers of TCDF and TCDF were determined 25	
Pyrolysis of pentachlorobenzene	NA	NRS	<0.01 ng/μg	<0.01 ng/μg	<0.025 ng/μg	0.025 ng/μg	0.025 ng/μg	In these tests, their presence was very minor compared to other isomers. 25	
Pyrolysis of combined tri- tetra- and pentachlorobenzene	NA	NRS	0.1 ng/μg	0.44 ng/μg	0.44 ng/μg	0.14 ng/μg	0.01 ng/μg		
High temperature oxidation of coal	NA	NA	NA	NA	NA	NA	NA	Results expressed as 60	
								calculated per g of coal starting material.	
High temperature oxidation and chlorination of coal using sodium chloride	NA	NA	NA	NA	NA	NA	NA	Results expressed as 60	
								calculated per g of coal starting material.	
High temperature oxidation and chlorination of coal using hydrochloric acid	NA	NA	NA	NA	NA	NA	NA	Results expressed as 60	
								calculated per g of coal starting material.	
High temperature oxidation and chlorination of coal using chlorine gas.	NA	NA	NA	NA	NA	NA	NA	Results expressed as 60	
								calculated per g of coal starting material.	

NA - Not analyzed.
 NR - Specimen determined to be present but quantification not reported.
 ND - Not detected.
 NRS - Not reported separately.

and burned in a laboratory oven.²⁸ Eight test burns were made and the offgases of burning were sampled and analyzed for chlorinated dioxin and furan compounds. Tetra-, penta-, hexa-, hepta-, and octachlorinated isomer groups of both chlorinated dioxins and furans were detected. As shown in Tables 3-3 and 3-4, the higher chlorinated dioxin isomer groups (ECDD, H₇CDD, OCDD) predominated for that family of compounds, while the lower chlorinated furan isomer groups (TCDF, PCDF) were more abundant among the total chlorinated furan population.²⁸ From this experiment the authors of Reference 23 attempted to show qualitative and quantitative impacts associated with burning forests (e.g., by forest fire) treated with 2,4,5-T.

In a second group of experiments involving 2,4,5-T, other researchers separately treated paper and grass with a 2,4,5-T ester formulation known as Esteron 245²⁰ (a registered Dow Chemical formulation) and burned the materials in the laboratory.²⁰ The objectives of the experiments were to determine the quantity of highly toxic 2,3,7,8-TCDD produced by burning materials treated with the 2,4,5-T herbicide and to estimate if the quantity produced could have significant impacts to natural environmental systems, i.e., forest fires in 2,4,5-T treated forests. There was 2,3,7,8-TCDD produced from the paper and grass burnings additional to that already contained in the applied 2,4,5-T formulation.²⁰ Though they state that their experiments are not inclusive of every possible burning condition, the authors of Reference 20 conclude that the data "strongly suggest that only a very small fraction of 2,4,5-T (or other 2,4,5-trichlorophenoxy species) is converted to TCDD."

3.3.2 Combustion of Wood Treated with a Trichlorophenolate and Tetrachlorophenolate Formulation

To determine the quality and quantity of chlorinated dioxin and furan emissions resulting from burning wood treated with preservatives, researchers in Sweden burned wood chips treated first with a trichlorophenolate preservative formulation and then with a tetrachlorophenolate

preservative formulation.⁵⁶ The fly ash and gaseous emissions generated by each experiment were analyzed only for chlorinated dioxin compounds. Compounds in the chlorinated dioxin isomer groups DCDD, T₃CDD, TCDD, PCDD, ECDD, H₇CDD, and OCDD were detected from burning both chlorophenolate formulations.⁵⁶ Chlorinated dioxins were also identified in the emissions from the combustion of wood chips treated with a PCP wood preservative formulation. Dioxin emission levels were much less from PCP combustion than from tri- or tetrachlorophenolate combustion except when PCP combustion was carried out with insufficient oxygen. Quantitative results of PCP combustion were not reported in Reference 56. The researchers did not attempt to extrapolate any of the laboratory results to natural or other combustion situations.

3.3.3 Pyrolysis of Commercial PCBs and PCB Isomers

Two experiments involving the pyrolysis of commercial PCBs are reported in the references given in Table A-1.^{34,43} The results of these experiments are summarized in Tables 3-3 and 3-4. In each experiment commercially available PCB formulations were heated in quartz ampoules to temperatures ranging from 550-850°C (1023-1563°F) for about 60 seconds. Residual ash from the pyrolysis procedure was analyzed only for chlorinated furan compounds. In the first of these experiments (Reference 43), MCDF, DCDF, T₃CDF, TCDF, and PCDF isomer groups were detected. In the second experiment (Reference 34), MCDF, DCDF, T₃CDF, TCDF, PCDF, ECDF, H₇CDF, and OCDF isomer groups were detected, and the toxic 2,3,7,8-TCDF isomer was found to be a major component of the TCDF group. References 34 and 43 contain conclusions that hazardous waste incinerators used to destroy PCB wastes may be sources of chlorinated furan compounds.

Researchers have also pyrolyzed 18 individual, laboratory-prepared PCB isomers to determine if they are capable of producing chlorinated furans. A list of the PCB isomers pyrolyzed is given in Table 3-5.^{36,43} Again, the PCB samples were heated in quartz ampoules to temperatures of 550-850°C

TABLE 3-5. LIST OF PCB ISOMERS THAT WERE PYROLYZED TO
DETERMINE POTENTIAL CHLORINATED FURAN EMISSIONS³⁶

Isomer Class	Individual Isomers
Tetrachlorobiphenyl	2,3,4,5- 2,3,5,6- 2,6,2',6'-
Pentachlorobiphenyl	2,3,4,5,6- 2,4,5,2',5'- 2,4,5,3',4'- 2,4,6,2',4'- 2,3,6,2',5'-
Hexachlorobiphenyl	2,4,5,2',4',5'- 2,4,6,2',4',6'- 2,4,5,2',4',6'- 2,3,4,2',3',4'- 2,3,5,2',3',5'- 2,3,6,2',3',6'- 3,4,5,3',4',5'-
Heptachlorobiphenyl	2,3,4,5,2',3',4'- 2,3,4,5,2',4',5'-
Octachlorobiphenyl	2,3,4,5,2',3',4',5'-

(1023-1563°F) for 60 seconds. An analysis of the pyrolysis residues from all 18 PCB isomers showed the presence of chlorinated furan compounds. However, not all chlorinated furan isomer groups were produced by each PCB isomer. For example, the pyrolysis of tetrachlorobiphenyls yielded DCDF, T₃CDF, and TCDF, the pyrolysis of pentachlorobiphenyls yielded T₃CDF, TCDF, and PCDF, hexachlorobiphenyls yielded TCDF, PCDF, and ECDD, and so on.³⁶ The researchers who conducted the PCB isomer experiments made the following two conclusions based on their results.³⁶

- Most of the major chlorinated furan isomers found in fly ash samples are the same as those formed from the pyrolysis of PCB samples, thereby giving strong support that chlorinated furans originate from the uncontrolled burning of PCBs.
- The uncontrolled burning of PCBs in waste incinerators is forming toxic chlorinated furan compounds that are being emitted to the environment.

3.3.4 Pyrolysis of Trichlorobenzene, Tetrachlorobenzene, and Pentachlorobenzene

Pyrolysis experiments involving polychlorobenzenes were conducted in a similar manner to those conducted and previously described for PCBs. Technical grade formulations of trichlorobenzene, tetrachlorobenzene, and pentachlorobenzene were put into separate quartz ampoules and pyrolyzed at 620°C (1148°F) for 60 seconds in the presence of air.²⁵ In addition, a combined sample of equal amounts of tri-, tetra-, and pentachlorobenzene was also pyrolyzed under these same conditions. In all cases, residual material from pyrolysis was analyzed for chlorinated dioxin and furan compounds. Tetra through octa isomer groups of both chlorinated dioxins and furans were detected from the pyrolysis samples of trichlorobenzenes, tetrachlorobenzenes, pentachlorobenzenes, and the combination mixture of tri-, tetra-, and pentachlorobenzene. The 2,3,7,8-TCDF and 2,3,7,8-TCDD isomers were detected in all samples, however, they were found to be minor components

relative to other isomers within the TCDF and TCDD groups and other isomer groups.²⁵

3.3.5 High Temperature Oxidation and Chlorination of Coal

The series of laboratory experiments described here were undertaken to show whether chlorinated dioxins could be formed from a naturally occurring organic material such as coal.⁸⁰ The four primary tests to determine whether chlorinated dioxins could be produced from coal were:

- the reaction of coal with air at high temperatures,
- the reaction of coal with air and sodium chloride at high temperatures,
- the reaction of coal with air and hydrochloric acid at high temperatures, and
- the reaction of coal with air and chlorine gas at high temperatures.

All reactions were carried out in a quartz tube suspended in a furnace with a maximum reaction temperature of 600°C (1112°F). Coal residue in the quartz tube and reaction offgases were analyzed for TCDD, HCDD, H₇CDD, and OCDD.

As shown in Table 3-3, the high temperature oxidation of coal yielded only isomer groups H₇CDD and OCDD, the majority of which were detected in the reaction offgases. High temperature oxidation and chlorination of coal by sodium chloride produced similar results to that achieved by simple oxidation. Only H₇CDD and OCDD were detected, however, the split between tube residue and offgases was about equal. When hydrochloric acid and chlorine gas were used as chlorination agents, the formation of chlorinated dioxins increased about 30 and 130 times, respectively, over that produced with sodium chloride.⁶⁰ The chlorinated dioxin isomer groups TCDD, HCDD, H₇CDD, and OCDD were detected when hydrochloric acid and chlorine gas

chlorinators were used. In the case of chlorination by hydrochloric acid, 89 percent of the detected chlorinated dioxins were found in the tube residue. However, when chlorine gas was the chlorination agent, 79 percent of the detected chlorinated dioxins were found in the reaction offgases.⁶⁰ The levels of TCDD detected in the coal reaction samples using hydrochloric acid and chlorine gas chlorinators were, on the average, less than 1 percent of the total chlorinated dioxins measured.

3.3.6 Burning of Birch Leaves and Wood Wool Treated with Chlorophenates

Wood treatment plants often burn chlorophenate-treated wood wastes for their fuel value. Researchers have been interested in determining if this practice produced chlorinated dioxin and furan air emissions; therefore, an experiment to burn chlorophenate-treated birch leaves and wood wool was conducted.²¹ In the first part of this experiment, birch leaves and wood wool were treated with commercial grade chlorophenate wood preservatives and burned. The offgases and ash produced by burning were analyzed for chlorinated dioxin and furan compounds.²¹

Chlorinated dioxin isomer groups TCDD, PCDD, HCDD, H₇CDD, and OCDD were detected in samples from both birch leaf and wood wool burning. For all chlorinated dioxin isomer groups, emissions were greater from the burning of wood wool than from burning birch leaves.²¹ In addition to chlorinated dioxins, chlorinated furan isomer groups TCDF, PCDF, HCDF, H₇CDF, and OCDF were also found in the samples of the burned birch leaves and wood wool. The TCDF isomer group constituted a major part of total chlorinated furan compounds detected. Levels of TCDF found in the burned sample offgases and ash were 100 times greater than that contained in the treated birch leaf and wood wool samples prior to burning.²¹

In the second part of this experiment, birch leaves treated with purified chlorophenate preservatives were burned and the resulting emissions

analyzed for chlorinated dioxin and furan compounds. The purified chlorophenates used were 2,4,6-trichlorophenate and pentachlorophenate. Chlorinated dioxin emissions were detected in the case of both purified chlorophenates with the isomer groups TCDD, PCDD, ECDD, H₇CDD being found. In the burning of 2,4,6-trichlorophenate-treated birch leaves, TCDD constituted 99 percent of the chlorinated dioxins found. In the burning of pentachlorophenate-treated birch leaves, the higher chlorinated isomer groups H₇CDD and OCDD constituted 92 percent of total chlorinated dioxins. With both purified chlorophenate-treated samples, levels of chlorinated dioxins found after burning were greatly increased over what they were prior to burning.²¹

No chlorinated furans were detected in the samples obtained from burning birch leaves treated with 2,4,6-trichlorophenate and pentachlorophenate. The authors of Reference 21 state that chlorinated furans were not detected because the impurities which cause them to be formed are not present in the purified chlorophenates. The impurities are present, however, in the commercial chlorophenates, therefore, chlorinated furans were detected in burnings of those samples.²¹

As a summary to the experiments conducted with chlorophenates, the authors of Reference 21 conclude that, "the burning of chlorophenates or material like wood shavings, plywood, or waste oil containing chlorophenates seems to be a more important source to environmental pollution by polychlorinated dibenzo-p-dioxins including 2,3,7,8-TCDD than the accidental burning of 2,4,5-T derivatives or vegetation treated with 2,4,5-T derivatives."

CHAPTER 4

CHLORINATED DIOXIN AND FURAN EMISSIONS DATA

The purpose of this chapter is to present available chlorinated dioxin and furan emissions data found in the literature. The majority of data in the literature is in the form of chlorinated dioxin and furan emission concentrations and emission factors. Very few data are available on an annualized mass emission basis (i.e., lb/yr) for either source categories or individual sources. Summaries of the available literature data on chlorinated dioxin and furan emissions from source categories and individual sources have been presented in Tables 3-1 and 3-2 of Chapter 3. It is not the purpose of this chapter to repeat every data point given in this table. Instead, when sufficient data are available, emission averages for particular source categories are discussed to show variability in the emissions of similar sources. Annualized emissions data for individual sources or source categories are given where available.

4.1 CHLORINATED DIOXIN AND FURAN EMISSIONS FROM INCINERATION SOURCES

No annualized chlorinated dioxin or furan mass emissions data were available in the literature for incineration sources. The majority of data that were available for all incinerator types were in the form of chlorinated dioxin and furan concentrations in the fly ash. For MWIs, total chlorinated dioxin levels in fly ash emissions ranged from 23.3 ppb to 2966 ppb, with an average value of 863 ppb being calculated. Total chlorinated furan levels from MWI emissions ranged from 13.4 ppb to 2036 ppb, with the average being 624 ppb. For HWIs and CWIs fewer data were available on which to base emission ranges and averages. Based on only three data points total chlorinated dioxin levels in the emissions of HWIs/CWIs ranged from 15.5 ppb to 164,000 ppb. Data were insufficient to

establish a range for total chlorinated furan emissions from MWIs/CWIs because in the majority of the MWT/CWT tests only chlorinated dioxins, and specifically TCDD and 2,3,7,8-TCDD, were analyzed for.

Table 4-1 presents a breakdown on the range of concentrations of chlorinated dioxin and furan isomer groups measured in the emissions of MWIs and MWIs/CWIs. The lowest reported detection of each chlorinated dioxin and furan compound is given in Table 4-1. However, if during any test of one of these incinerator types a particular compound was not detected, it is noted in the table. An interesting contrast shown by Table 4-1 involves the level of 2,3,7,8-TCDD in incinerator emissions. Table 4-1 shows that levels as high as 110 ppb have been measured; however, in the SAI report on dioxin, "Human Exposure to Atmospheric Concentrations of Selected Chemicals," 2,3,7,8-TCDD levels in incinerator emissions (and other combustion sources) were assumed to be 2 ppb. A potential difference of this magnitude has a significant impact on the national 2,3,7,8-TCDD emissions estimates made in the SAI document.

In several of the MWT tests reported in the literature, chlorinated dioxin and furan emission factors were developed based on the quantity of waste burned in the facility. The identified factors for total chlorinated dioxins and furans, TCDD, 2,3,7,8-TCDD, TCDF, and 2,3,7,8-TCDF are summarized in Table 4-2. The 0.23 and 2.3 $\mu\text{g}/\text{kg}$ values reported in Table 4-2 for total chlorinated dioxins and furans were determined from tests on incinerators in the United States. The high values in the ranges, 16.3 and 17.4 $\mu\text{g}/\text{kg}$, have been determined for MWIs in Europe. The emission factors for TCDD, 2,3,7,8-TCDD, TCDF, and 2,3,7,8-TCDF were all developed from tests on domestic MWIs. In the tests from which all of the emission factors in Table 4-2 were developed, both gaseous and fly ash emissions were analyzed for the presence chlorinated dioxin and furan compounds.

TABLE 4-1. CONCENTRATION RANGES OF CHLORINATED DIOXIN AND FURAN COMPOUNDS FOUND IN THE EMISSIONS OF INCINERATORS^d

Chlorinated Dioxin or Furan Compound	MWIs	HWIs/CWIs
2,3,7,8-TCDD	<0.13 - 100 ppb ^{a, a}	2 - 110 ppb ^{a, a}
TCDD	0.7 - 110 ppb	0.48 - 12,000 ppb ^a
PCDD	2.9 - 488 ppb ^a	c
ECDD	3.4 - 1200 ppb ^a	0.5 - 5600 ppb
H ₇ CCD	3.2 - 1040 ppb ^a	4 - 37,000 ppb
OCDD	0.4 - 900 ppb	9 - 59,000 ppb
2,3,7,8-TCDF	ND - 300 ppb ^a	ND - 2.5 ppb ^a
TCDF	13 - 223 ppb ^a	2 - 100 ppb ^a
PCDF	3.8 - 510 ppb ^a	c
ECDF	1.9 - 870 ppb ^a	c
H ₇ CDF	4.3 - 407 ppb ^a	c
OCDF	0.12 - 166 ppb ^a	c

^aCompound was not detected in one or more tests.

^bND = Not detected.

^cInsufficient data to characterize the emissions of this compound.

^dAll data in the table was taken from Tables 3-1 and 3-2 of Chapter 3.

^eIn the SAI dioxin report (Systems Applications, Inc., Human Exposure to Atmospheric Concentrations of Selected Chemicals. EPA Contract 68-02-3066. February 1982.) 2,3,7,8-TCDD levels in incinerator emissions and fossil fuel combustion source emissions were assumed to be 2 ppb. All national emission estimates in the SAI document were based on the 2 ppb value.

TABLE 4-2. CHLORINATED DIOXIN AND FURAN EMISSION FACTORS
FOR MUNICIPAL WASTE INCINERATORS^{7,17,68,83}

Chlorinated Dioxin or Furan Compound	Emission Factors, µg/kg of waste burned
Total chlorinated dioxins	0.23 - 16.3
Total chlorinated furans	2.3 - 17.4
TCDD	0.032 - 0.045
TCDF	0.17 - 0.45
2,3,7,8-TCDD	0.002 - 0.021
2,3,7,8-TCDF	ND - 0.13

^aND = Not detected.

4.2 CHLORINATED DIOXIN AND FURAN EMISSIONS FROM BOILER SOURCES

No annualized chlorinated dioxin or furan mass emissions data were available in the literature for boiler sources. As shown in Tables 3-1 and 3-2, very few data are available for boiler sources on any basis. The concentration of total chlorinated dioxin emissions from two industrial boilers in the U.S. and Europe have been measured to be 68 ppb and 600 ppb, respectively.^{6,11,23,34} Both of these concentrations were detected in fly ash from an ESP. In the test of the U.S. boiler with 68 ppb total chlorinated dioxins, 38 ppb were determined to be TCDD. None of the 2,3,7,8-TCDD isomer was detected at a lower limit of 10 ppb. [In contrast, the SAI dioxin report (see Table 4-1) assumed that the 2,3,7,8-TCDD level in fossil fuel combustion source emissions was 2 ppb.] The European boiler with the total chlorinated dioxin emissions concentration of 600 ppb was also determined to have a total chlorinated furan concentration in ESP fly ash of 300 ppb.^{23,34} No other chlorinated furan emissions concentration data were available in the literature for boiler sources.

The only other data available for boiler sources were in the form of chlorinated dioxin and furan emission factors. In two different tests of the same industrial boiler burning coal and RDF, TCDD, TCDF, 2,3,7,8-TCDD, and 2,3,7,8-TCDF emissions were determined on the basis of the amount of fuel burned.¹⁷ The results of these tests are shown below:

	Emissions (µg/kg) from Burning:	
	<u>Coal</u>	<u>RDF</u>
TCDD	0.69	0.36
TCDF	5.3	3.7
2,3,7,8-TCDD	0.20	0.11
2,3,7,8-TCDF	2.0	1.3

These results indicate that when coal and RDF are burned in an industrial boiler, chlorinated dioxin and furan emissions are greater from burning coal. These tests also indicate that regardless of whether coal or RDF is burned, chlorinated furan compound emissions are greater than chlorinated dioxin compound emissions.

4.3 CHLORINATED DIOXIN AND FURAN EMISSIONS FROM RESIDENTIAL WOOD STOVES AND FIREPLACES

The concentration of chlorinated dioxins in the fly ash emissions of wood stoves located in three sections of the United States has been determined by testing. The results of these tests are summarized in Table 4-3.¹⁵ For all tests total chlorinated dioxin emissions ranged from 25.6 ppt to 23,737 ppt. The concentration of TCDD in the emissions of the tested stoves ranged from none detected to 4925 ppt, with concentrations of toxic 2,3,7,8-TCDD ranging from none detected to 100 ppt.¹⁵

A source category similar to wood stoves, residential fireplaces, has been shown to have chlorinated dioxin emissions comparable to those given in Table 4-3. In one test of a residential fireplace, total chlorinated dioxin emissions ranged from 1800 ppt to 44,400 ppt. Emissions of the TCDD isomer group ranged from none detected to 400 ppt, with levels of 2,3,7,8-TCDD ranging from none detected to 100 ppt.

Based on the results of the wood stove and fireplace tests, nationwide emissions of TCDD from wood burning in residential stoves and fireplaces have been estimated to be 0.27 kg (0.6 lb)/yr.⁸⁷ It is also estimated in Reference 87 that commercial wood burning contributes 0.54 kg (1.2 lb)/yr of TCDD to the air, controlled wood burning emits 0.32 kg (0.7 lb)/yr of TCDD to the air, and forest fires are responsible for emitting 3.1 kg (6.9 lb)/yr of TCDD into the air.⁸⁷

4.4 CHLORINATED DIOXIN AND FURAN EMISSIONS FROM INTERNAL COMBUSTION ENGINES

Chlorinated dioxin emissions from automobile and truck internal combustion engines burning gasoline and diesel fuel are summarized in Table 3-1. Total chlorinated dioxin levels ranged from 0.023 ppb to 0.092 ppb. Levels of the TCDD isomer group ranged from none detected to

TABLE 4-3 CHLORINATED DIOXIN EMISSIONS FROM RESIDENTIAL WOOD STOVES¹⁵

Chlorinated Dioxin Compound	Dioxin Emission Concentrations in Various Sections of The U.S.		
	Eastern U.S. Stoves	Central U.S. Stoves	Western U.S. Stoves
MCDD	NA	NA	NA
DCDD	NA	NA	NA
T ₃ CDD	NA	NA	NA
TCDD	1041-4925 ppt	ND-374 ppt	124-137 ppt
2,3,7,8-TCDD	90-100 ppt	ND-13 ppt	6-11 ppt
PCDD	NA	NA	NA
ECDD	1800-4300 ppt	2.7-2000 ppt	850-2600 ppt
H ₇ CDD	2800-4100 ppt	8.9-9000 ppt	1700-4000 ppt
OCDD	2000-5300 ppt	14-12,400 ppt	1700-4000 ppt
Total Chlorinated Dioxins	7641-18,625 ppt	25.6-23,774 ppt	4374-10,737 ppt

0.008 ppb, with detections of toxic 2,3,7,8-TCDD ranging from none detected to 0.004 ppb.⁶

Levels of chlorinated dioxin emissions from diesel fuel internal combustion engines were determined to be greater than the emissions from gasoline engines. As shown in Table 3-1, total chlorinated dioxin levels from diesel fuel engines were found to be about 0.40 ppb. The TCDD isomer group and its most toxic isomer, 2,3,7,8-TCDD, were measured at levels of 0.023 ppb and 0.003 ppb, respectively.⁶

4.5 SOURCE EMISSIONS OF CHLORINATED DIOXINS AND FURANS DETERMINED FROM LABORATORY EXPERIMENTS

Laboratory-generated data concerning potential chlorinated dioxin and furan emissions have been presented in Tables 3-3 and 3-4. In only two of the experiments (References 20 and 28) reported in Tables 3-3 and 3-4 were the emission results used to extrapolate chlorinated dioxin or furan emissions on a source category or individual source basis. Both extrapolations involved chlorinated dioxin emissions, specifically 2,3,7,8-TCDD and TCDD from the combustion of materials treated with 2,4,5-T.

In Reference 20 experiments were conducted to find out the level of 2,3,7,8-TCDD generated from the combustion of grasses and paper treated with a 2,4,5-T formulation. The researchers attempted to apply their results to the real world situation of forest fires in a forest previously sprayed with a 2,4,5-T herbicide. Based on the level of 2,3,7,8-TCDD generated by their experiments the researchers concluded that "the TCDD burden added to the environment by the combustion of natural materials treated with 2,4,5-trichlorophenoxy species is no larger than 1 ppt of TCDD per ppm of 2,4,5-T residue burned." In Reference 20 TCDD is used to abbreviate 2,3,7,8-TCDD.

In Reference 23 experiments were conducted to determine the level of TCDD and other chlorinated dioxins emitted from the combustion of wood chips treated with a 2,4,5-T herbicide. From their experimental results, researchers have extrapolated that the uncontrolled burning (forest fire) of 1 square meter of forest, directly after treatment with 2,4,5-T, will yield 1 ug of TCDD.²³ In these experiments the exact 2,4,5-T formulation used was 2-butoxyethyl 2,4,5-trichlorophenoxyacetate.

CHAPTER 5

DATA ON PUBLIC EXPOSURE TO CHLORINATED DIOXINS AND FURANS

No quantitative measurements of ambient air levels of chlorinated dioxin and furan compounds are reported in the references given in Appendix A, Table A-1. There is only one indication in the literature where an attempt was even made to sample and analyze ambient air for the presence of chlorinated dioxins or furans. In Reference 8 one instance of qualitative ambient air sampling for chlorinated furan compounds is briefly reported. The source of the chlorinated furans in this case was the ENSCO PCB incinerator in El Dorado, Arkansas. The U.S. EPA obtained ambient air samples downwind of this incinerator and analyzed them by high resolution gas chromatography/mass spectroscopy (HR GC/MS) for the presence of chlorinated furans. The results of the analysis "suggested" the presence of TCDF in the samples. As a result of these findings, a source test was initiated at the ENSCO incinerator to measure TCDF and 2,3,7,8-TCDF emissions.⁸

The only other reported work in the area of ambient air chlorinated dioxin and furan exposures has involved calculating potential ambient exposures to these compounds based on the results of atmospheric dispersion modelling. Source tests at MWIs and HWIs have furnished input data for these modelling studies. References 5, 8, 12, 13, 17, and 82 present the results of five studies in which potential human exposures to TCDD, TCDF, 2,3,7,8-TCDD, and 2,3,7,8-TCDF have been estimated by the U.S. EPA based on dispersion modelling results.

To conduct exposure assessments involving chlorinated dioxin and furan compounds, the U.S. EPA uses its PTMAX dispersion model and an approach known as the "upper limit of risk estimate (ULORE)." The ULORE approach

incorporates several worst case assumptions which ensure that the exposure estimates determined are an upper bound to what could potentially occur. These assumptions are given below.¹²

- The carcinogenic properties and reproductive effects of all TCDDs and TCDFs are the same as that of 2,3,7,8-TCDD.
- All of the emissions from a stack are respirable and are retained in the body.
- All of the TCDDs and TCDFs that are respired are biologically available to the organism, even though some fraction is tenaciously bound in or on the emission particles.
- The composition of the emission products found in the stack is identical to the composition (but not the concentration) found at the ground level.
- The air dispersion modelling is representative of what happens in the natural environment.
- The exposed population is subjected to the maximum average annual concentration found at the point of highest concentration.
- The maximum annual average concentration is equal to 1/40 of the maximum hourly concentration.
- The population is exposed to this maximum average annual concentration from the source for 24 hours a day throughout a 70 year lifetime.
- The linearized multi-stage model and other assumptions of the cancer unit risk assessment used by EPA's Cancer Assessment Group (CAG) are utilized and represent an upper limit of risk at the 95 percent confidence level.

Using the ULORE approach, the following range of annual maximum average ground level concentrations of TCDD isomers was determined for the five incineration sites analyzed.^{12,82}

<u>Compound</u>	<u>Range (ng/m³)^a</u>
Total TCDDs	up to 9.2×10^{-5}
2,3,7,8-TCDD ^b	up to 3.8×10^{-5}

^aThe lower end of the range is related to the non-detected amount of TCDDs found at the sites.

^bIn some cases the analytical method used could not distinguish 2,3,7,8-TCDD from several of the other TCDD isomers. It is recognized that some other TCDD isomers may be co-eluting with the 2,3,7,8-TCDD isomer; therefore, this value could be an overestimate of 2,3,7,8-TCDD exposures.

APPENDIX A

LIST OF REFERENCES OBTAINED FROM THE CHLORINATED DIOXIN AND FURAN LITERATURE SEARCH THAT PERTAIN TO AIR EMISSIONS

Table A-1 presents the list of references obtained from the literature search that discuss some aspect of chlorinated dioxin and furan air emissions. The 87 chlorinated dioxin and furan references given in Table A-1 were reviewed to specifically determine data on source categories of emissions, individual sources of emissions, emission levels, and ambient exposure levels. The specific topics of chlorinated dioxin and furan air emissions contained in the references are summarized in Appendix A, Table A-2. As shown in Table A-2, there is considerable information on source categories of emissions, a moderate amount of data on emission levels, and very little data on individual sources of emissions and ambient exposure levels.

TABLE A-1. LIST OF REFERENCES PERTAINING TO CHLORINATED
DIOXIN AND FURAN AIR EMISSIONS

1. Kriebel, D. Dioxins: Toxic and Still Troublesome. Environment. Volume 23, Number 1. January/February 1981. pp. 6-13.
2. Study on State-of-the-Art of Dioxin from Combustion Sources. (Prepared by Arthur D. Little, Inc.) Issued by the American Society of Mechanical Engineers. 1981.
3. DaRos, E., et al. (Acurtex Corporation) Measured Multimedia Emissions from the Wood Preserving Industry. (Prepared for U.S. Environmental Protection Agency, Cincinnati, Ohio) Contract No. 68-03-2567, Task 4028. March 1981.
4. Cavallaro, A., et al. Sampling, Occurrence, and Evaluation of PCDDs and PCDFs from Incinerated Solid Urban Waste. Chemosphere. Volume 9, 1980. pp. 611-621.
5. Incineration of PCBs: Summary of Approval Actions for Rollins Environmental Services in Deer Park, Texas. Air and Hazardous Materials Division, Region VI, U.S. Environmental Protection Agency, Dallas, Texas. February 6, 1981.
6. Bumb, R. R., et al. (Dow Chemical) Trace Chemistries of Fire: A Source of Chlorinated Dioxins. Science. Volume 210. October 1980. pp. 383-391.
7. Redford, D. P., et al. Emissions of PCDDs and PCDFs from Combustion Sources. Presented at the International Symposium on Chlorinated Dioxins and Related Compounds, Arlington, VA, October 25-29, 1981.
8. Agenda and minutes of the Dioxin Sources Subgroup of the Chlorinated Dioxins Work Group. March 6, 1981. Meeting No. 10.
9. Memo from Homolya, J. B., U.S. EPA to Spatola, J., U.S. EPA. April 7, 1980. Organic Analyses and TCDD Determination in Extracts of Samples Collected from the Hempstead Resources Recovery System Incinerator.
10. Kimble, B. J. and M. L. Gross. Tetrachlorodibenzo-p-dioxin Quantitation in Stack-Collected Coal Fly Ash. Science. Volume 207. January 1980. pp. 59-61.
11. 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 of Dow Chemical U.S.A. 1978.

TABLE A-1. LIST OF REFERENCES PERTAINING TO CHLORINATED
DIOXIN AND FURAN AIR EMISSIONS (CONTINUED)

12. Upper Limit of Risk Estimate (ULORE) for Tetrachlorinated Dioxin Emissions from Municipal Waste Combustion. Unauthored paper. August 12, 1981. Property of SASD files.
13. Interim Evaluation of Health Risks Associated with Emissions of Tetrachlorinated Dioxins from Municipal Waste Resource Recovery Facilities. Unauthored paper. November 1981. Property of SASD files.
14. Duckett, E. J. Dioxins in Perspective: Knowns, Unknowns, Resolving the Issues. Solid Wastes Management. May 1981. pp. 56-57, 88-89.
15. Nestrick, T. J., et al. Methodology and Preliminary Results for the Isomer-Specific Determination of TCDDs and Higher Chlorinated Dibenzop-dioxins in Chimney Particulates from Wood-Fueled Domestic Furnaces Located in Eastern Central, and Western Regions of the United States. Presented at the International Symposium on Chlorinated Dioxins and Related Compounds, Arlington, VA, October 25-29, 1981.
16. Dellinger, B., et al. (Northrop Services). Results of Source Emissions Characterization at the Hempstead, NY Refuse Energy Recovery System. (Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC). EPA Contract 68-02-2566. April 1980.
17. Higgins, G. H. (Systech Corporation) An Evaluation of Trace Organic Emissions from Refuse Thermal Processing Facilities. (Prepared for U.S. Environmental Protection Agency, Washington, D.C.) Contract No. 68-01-6071. July 1982.
18. Esposito, M. P., et al. Dioxins. EPA-600/2-80-197. (Prepared for U.S. Environmental Protection Agency, Cincinnati, Ohio) November 1980.
19. Rawls, R. L. Dow Finds Support, Doubt for Dioxin Ideas. Chemical and Engineering News. February 12, 1979. pp. 23-29.
20. Stahl, R. E., and L. L. Lamparski. Combustion of Several 2,4,5-Trichlorophenoxy Compounds: Formation of 2,3,7,8-TCDD. Science. Volume 197. September 1977. pp. 1008-1009.
21. Rappe, C., et al. Formation of Polychlorinated Dibenzop-dioxins (PCDDs) and Dibenzofurans (PCDF) by Burning or Heating Chlorophenates. Chemosphere. Volume 7, 1978. pp. 269-281.
22. Olie, K., et al. Chlorodibenzo-p-dioxins and Chlorodibenzo-furans are Trace Components of Fly Ash and Flue Gas of Some Municipal Incinerators in the Netherlands. Chemosphere. Volume 6, 1977. pp. 455-459.

TABLE A-1. LIST OF REFERENCES PERTAINING TO CHLORINATED
DIOXIN AND FURAN AIR EMISSIONS (CONTINUED)

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TABLE A-1. LIST OF REFERENCES PERTAINING TO CHLORINATED
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TABLE A-2. INDEX TO THE CATEGORIES OF INFORMATION CONTAINED IN
THE DIOXIN/FURAN REFERENCES OF TABLE A-1

Master Reference List Number Given in Table A-1	Literature Search Information Categories ^a			
	Source Category Data	Individual Sources Data	Emissions Data	Public Exposure Data
1	+,D			
2	+,D		+	
3	+,D/F		+	
4	+,D		+	
5	+,D/F	+		+
6	+,D/F	+	+	
7	+,D/F		+	
8	+,D/F	+	+	+
9	+,D		+	
10	+,D			
11	+,D		+	
12	+,D		+	+
13	+,D		+	+
14	+,D	+	+	
15	+,D		+	
16	+,D		+	
17	+,D/F		+	+
18	+,D/F		+	
19	+,D		+	
20	+,D		+	
21	+,D/F		+	
22	+,D/F			
23	+,D		+	
24	+,D			
25	+,D/F		+	
26	+,D/F			
27	+,D			
28	+,D/F		+	
29	+,D/F		+	
30	+,D		+	
31	+,D			
32	+,D/F		+	

TABLE A-2. INDEX TO THE CATEGORIES OF INFORMATION CONTAINED IN
THE DIOXIN/FURAN REFERENCES OF TABLE A-1

Master Reference List Number Given In Table A-1	Literature Search Information Categories ^a			
	Source Category Data	Individual Sources Data	Emissions Data	Public Exposure Data
33	+,D			
34	+,F			
35	+,D		+	
36	+,F			
37	+,D	+	+	
38	+,D/F			
39	+,D/F		+	
40	+,D/F		+	
41	+,D			
42	+,D			
43	+,F		+	
44	+,D			
45	+,D			
46	+,D			
47	+,D/F			
48	+,D		+	
49	+,D		+	
50	+,D		+	
51	+,D		+	
52	+,F		+	
53	+,D/F			
54	+,D/F		+	
55	+,D/F		+	
56	+,D/F		+	
57	+,D/F			
58	+,D	+	+	
59	+,D/F		+	
60	+,D		+	
61	+,D/F			
62	+,D		+	
63	+,D		+	
64	+,D/F			

TABLE A-2. INDEX TO THE CATEGORIES OF INFORMATION CONTAINED IN
THE DIOXIN/FURAN REFERENCES OF TABLE A-1

Master Reference List Number Given In Table A-1	Literature Search Information Categories ^a			
	Source Category Data	Individual Sources Data	Emissions Data	Public Exposure Data
65	+,D			
66	+,D			
67	+,D/F	+	+	
68	+,D/F		+	
69	+,D/F			
70	+,F		+	
71	+,D/F			
72	+,D			
73	+,D			
74	+,D/F			
75	+,D			
76	+,D		+	
77	+,D			
78	+,F			
79	+,D		+	+
80	+,D			
81	+,D/F	+	+	
82	+,D		+	+
83	+,D/F		+	
84	+,D	+	+	
85	+,D/F			
86	+,D/F			
87	+,D	+	+	

D = dioxin data; F = furan data.