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National Dioxin Study Tier 4 — Combustion Sources

Project Plan

By
Air Management Technology Branch

DRAFT

**U.S. ENVIRONMENTAL PROTECTION AGENCY
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This document is an OAQPS staff draft that is being circulated for technical review and comment. It has not been fully reviewed within EPA and does not represent Agency policy.

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Section 1

Introduction And Summary Of Tier 4 Work Plan

1.1 Introduction

This report presents the U. S. Environmental Protection Agency's (EPA's) plans for identifying likely sources and assessing the magnitude of dioxin* emissions from combustion sources under Tier 4 of the National Dioxin Strategy. The report describes the information EPA plans to collect over the next 18 months to improve our current understanding of combustion sources which may emit dioxin to the ambient air. This report also describes the rationale used in designing the studies which make up the project plan, as well as alternative approaches considered. While source sampling and analytical methods and procedures to be used during the study are identified, this report is not intended to describe these procedures in detail. References are made to other documents where these methods and procedures are more fully described.

1.2 Background

There are 75 different chlorinated dioxin isomers, divided into eight homologues, each with different physical and chemical properties.¹ One of the 22 isomers with four chlorine atoms is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD).^{*} There are three reasons why this isomer has been selected as the principal focus of the National Dioxin Strategy:

1. It is believed to be the most toxic of the chlorinated dioxins,
2. It is the isomer most often associated with exposure and potential health risks to humans, and

*Throughout this work plan, the terms dioxin and dioxins are used generically to indicate chlorinated dioxin compounds as distinguished from 2378-TCDD, the specific isomer of major concern.

3. There is sufficient associated health and exposure information available to allow a targeted study to be developed.

On December 15, 1983, EPA released a Dioxin Strategy² which provides a framework under which EPA will:

1. Study the nature and extent of contamination of 2378-TCDD and the associated risks to humans and the environment;
2. Implement or compel necessary cleanup actions at contaminated sites; and
3. Further evaluate regulatory alternatives to prevent future contamination, as well as disposal alternatives to alleviate current problems.

To implement the strategy, EPA has formed seven study tiers, ordered by the decreasing potential for 2378-TCDD contamination:

Tier 1 - 2,4,5-trichlorophenol (245-TCP) production sites and associated waste disposal sites;

Tier 2 - Sites (and associated waste disposal sites) where 245-TCP was used as a precursor to make pesticidal products;

Tier 3 - Sites (and associated waste disposal sites) where 245-TCP and its derivatives were formulated into pesticidal products;

Tier 4 - Combustion sources;

Tier 5 - Sites where pesticides derived from 245-TCP have been and are being used on a commercial basis;

Tier 6 - Certain organic chemical and pesticide manufacturing facilities where improper quality control on certain production processes could have resulted in the formation of a 2378-TCDD contaminated product waste stream; and

Tier 7 - Control sites where contamination from 2378-TCDD is not suspected.

1.3 Management Of The National Dioxin Strategy

Overall responsibility for the management of the Strategy has been assigned to the Assistant Administrator for the Office of Solid Waste and Emergency Response (OSWER). OSWER is also managing the investigations for sites in Tier 1 and 2 of the study. The Office of Water Regulations and Standards (OWRS) is managing Tiers 3, 5, 6 and 7, while the Office of Air and Radiation (OAR) is responsible for Tier 4. The Office of Research and Development (ORD) is responsible for sampling and analytical guidance. ORD is also responsible for providing analytical support and plans to do so via an arrangement with three EPA laboratories (Duluth; Bay St. Louis; and Research Triangle Park), collectively known as the TROIKA. As described later, EPA's Regional Offices will be responsible for implementing various aspects of the National Dioxin Strategy, including portions of Tier 4.

1.4 Project Approach

Clearly, there are many data gaps in the available information concerning emissions of dioxins from combustion sources,³ and a number of different approaches could be taken to fill these data gaps. After considering various alternatives, the Agency has decided to focus the Tier 4 effort on the collection of data from a number of combustion source categories which are believed to have some potential to emit 2378-TCDD. Detailed stack test data and ash samples will be collected and analyzed for 2378-TCDD and the higher dioxin homologues (i.e., tetra, penta, hexa, hepta, and octa). Such efforts are needed to broaden our understanding of emissions of dioxins from combustion sources. The primary objective of the Tier 4 project thus, is one of problem definition what source categories emit dioxin and at what concentrations? The investigations are not designed to answer what can be done to minimize emissions.

This approach is believed necessary for a number of reasons. Only a limited number of combustion source categories have previously been tested to determine if they emit dioxins including 2378-TCDD to the ambient air. While these dioxin compounds have been found in the stack emissions and fly ash from some source categories, they have not been detected at all of the source categories which have been tested. Ranges of test values have been shown to be very broad (orders of magnitudes). Some of the ranges may be due, of course, to source subcategorization [e. g., mass burn versus refuse derived fuel (RDF) as subcategories of municipal incinerators; dry process versus wet process as subcategories of RDF, etc.] but data again are insufficient to support such conclusions. Also test methods have varied considerably within the data base now available. These and other factors, not surprisingly, have led to conflicting theories on how and when dioxins are formed. In summary, currently available data do not clearly define the scope of the problem, or if indeed there clearly is one.³

The scope of the Tier 4 study must be limited, for several practical reasons. While the Tier 4 budget of \$1.4 million is a considerable sum, it does not allow the Agency to implement a comprehensive study program designed to examine all aspects of dioxin emissions from combustion sources. A key factor is the high cost of stack sampling which is estimated to cost approximately \$90,000* for each source tested, not including similarly expensive analytical work. Because of these high costs and the limited resources available, the scope of the study must be sharply focused.

*\$90,000 is an estimate based on a typical source test, and does not include any laboratory analysis for dioxins, homologues or isomers. Actual costs will vary depending on source configuration, specific analytical work done., etc. Each work plan for individual sites will have individual estimates and costs will be optimized.⁴

Also of considerable impact is consideration for the fact that the National Dioxin Strategy is a two year effort scheduled to end in December 1985.² At that time, a report to Congress is planned which will summarize the results of the study. This schedule limits the types of activities which can be initiated and completed by that date. Certain research studies, such as, developing and validating a mechanistic model of dioxin formation in combustion sources, would likely take years to design and complete, and would not be practical to consider for this study.

However, because all aspects of the dioxin issue cannot be considered, follow up studies may be needed. The Tier 4 results should provide a more reasonable basis for more studies if needed.

1.5 Basis For Investigation Of Combustion Sources

There are several unproven hypotheses concerning dioxin emissions from combustion processes. Dow Chemical's "Chemistries of Fire" theory proposes that dioxins are a natural byproduct of fire and will be formed at some quantities in all combustion processes.⁵ However, experimental results by Buser and Rappe and an evaluation of data from the literature³ suggests that dioxins are emitted only under limited conditions. The most prevalent theories, including Esposito's formation mechanism, involve the incomplete combustion of polychlorinated dibenzo dioxin (PCDD's) or PCDD precursors. Although there is some disagreement on the definition of precursors, PCDD precursors are defined in this work plan as chlorinated aromatics that can produce PCDD's through bimolecular reactions and thermal rearrangements. Examples include chlorinated phenols and chlorinated benzenes. When PCDD's are in the feed of a combustion source, they can escape with the fine particulate when the thermal destruction efficiency is low.³ Additionally, PCDD precursors may be thermally rearranged during incomplete combustion to form PCDD's.³

Neither the Dow hypothesis or the precursor hypothesis have been conclusively supported or refuted.^{3,5} Recent studies involving pyrolysis of wood with and without chlorination, in conjunction with the studies of pyrolysis of chlorinated coal, suggest that inorganic chlorine at high levels with any organic material may very well lead to PCDD formation. Since combustion sources are ubiquitous and are fairly concentrated in urban areas, it is conceivable that a large portion of the United States population may be exposed to dioxins including 2378-TCDD in the ambient air. More data are needed to determine the magnitude and extent of exposure to dioxins from combustion sources. While current evidence does not suggest that an unreasonable risk exists, the Dioxin Strategy provides an opportunity to perform a more orderly and thorough investigation of the issue. An assessment of risk from each source tested with inferences to the source category will be produced as a part of this effort and be included in the Tier 4 report generated as input to the study's report to Congress.

1.6 Summary Of Tier 4 Program Plan

Two levels of source sampling are planned in Tier 4. First, relatively inexpensive ash samples (screening) will be collected from combustion source categories listed in Table 1-1. As explained later, these source categories are believed to have a reasonable likelihood of emitting dioxins. Samples are also expected to be collected from a limited number of additional source categories as may be identified by EPA Regional and State Officials. Ash samples will be collected from three different sources in each source category selected. These samples will generally consist of hopper ash from control devices, or "bottom" ash where no control devices are present. These samples will be analyzed to determine the total polychlorinated dioxins (PCDDs) present in the ash, as well as 2378-TCDD and the higher dioxin homologues. These data will be used to provide a qualitative indication of the likely presence of dioxins in the flue

Table 1-1. Combustion Source Categories Where Ash Samples

Will Likely Be Collected

Source Categories:*

Chemical Sludge Incinerators

Carbon Regeneration Unit (at industrial source)

Charcoal Manufacturing

Wire Reclamation

Wood Stoves

Wood Boilers Burning PCP Treated Wood

Spreader-Stoker Coal Boiler

Hazardous Waste Incineration

Lime/Cement Kiln Burning Hazardous Wastes

Forest Fires

Apartment House Flue Fed Incinerators

Agricultural Burning

*To be supplemented by other categories identified by State and Regional Officials with reasonable likelihood of emitting 2378-TCDD.

gas emissions. Because of the nature of these samples, they cannot be used to estimate the magnitude of 2378-TCDD emissions, nor can they be used to determine absolutely that 2378-TCDD is not present in the emissions. It is expected, however, that these data will provide data to examine further the usefulness of ash analyses as a viable means to assess relative the magnitude of dioxin emissions from combustion sources.

A limited number of combustion source categories have been selected for detailed source testing based on available data and information. Because of the limited budget and the cost involved with stack testing, only about 12 different sources can be tested. These stack tests will be performed using EPA's modified Method 5 and source testing procedures consistent with those described in the recently developed American Society of Mechanical Engineers (ASME) sampling protocol for energy recovery facilities.⁶

Samples to be collected during the stack testing program are discussed in Section 3 and are briefly summarized here. They include gaseous and particulate stack emission samples (both before and after controls), ash samples from the control device and firebox ash hoppers, samples of the feed or fuel, and samples of nearby soils. Precombustion air samples will also be collected at those sources where precursors are suspected to be present in significant concentration in the air from other nearby sources.

Stack, ash and precombustion air samples will be analyzed for the 2378-TCDD isomer, total dioxin, and totals for each of the higher homologues of dioxin (i.e., tetra, penta, hexa, hepta, and octa). Precombustion air and feed samples will also be analyzed for selected suspect dioxin precursors. Feed and waste water samples will also be analyzed for 2378-TCDD and total polychlorinated dioxins. Sufficient quantities or duplicates of all samples will be collected in the event that other analyses are needed at a later date. Furans, for example,

will not be analyzed under this program due to costs but are of serious concern but sufficient samples will be collected and may be so analyzed later.

Samples will be collected primarily by EPA contractors who will ship the them to the designated TROIKA laboratory for analysis. Procedures for the collection and shipping of samples, as well as the analytical and quality control procedures to be followed, are discussed elsewhere.⁷ A summary of the samples to be collected during stack testing and the analyses to be performed under Tier 4 are outlined in Table 1-2. Although not noted in the table, an additional number of samples (approximately 20 percent) will be collected and analyzed for quality assurance/quality control purposes.

The Agency has already performed an analysis to identify those combustion source categories which have the greatest potential to emit 2378-TCDD.³ These source categories are listed in Table 1-3. Source categories rated as "Rank A Sources" will be stack tested as soon as possible. Testing of source categories ranked B and C will be deferred until the results of the ash screening program are available. These data will be used to re-examine the current ranking of source categories, so the final listing of B and C ranked source categories could change the final selection of residual source tests can be made at that time. Figure 1-1 presents the anticipated schedule for the Tier 4 project.

At the conclusion of the Tier 4 study, the Agency will have collected either screening samples or detailed stack samples from a number of combustion source categories. These data will provide the Agency with a better understanding of the source categories which emit 2378-TCDD to the atmosphere. Further, the detailed stack test data will allow the Agency to determine the magnitude of the 2378-TCDD emissions from these sources and calculate the risk to which the people are exposed.

Table 1-2. SAMPLING AND ANALYSES MODEL

Sample	Method	Samples	Analyses	Total Samples ^a for Analyses
Inputs				
Precombustion Air	XAD-2 (PUFF) ^b	0-1 ^c	2378-TCDD, PCDD ^d , TOCL ^e , Cl-phenols, Cl-benzenes	1 ^c
Feed/Fuel	Grabs	Daily Composite	PCDD Scan, Cl-phenols Cl-benzenes, PCB, TOCL	3 ^f
Outputs				
Stack (before control)	MMST ^g	2 trains -Back Half Daily Composite -condenser Rinse -adsorbent Basin -Front Half Daily Composite -cyclone Catch -filter -probe Rinse	2378-TCDD, Homologues ^h (tetra - octa), PCDD	6
Stack (after control)	MMST	2 trains -Back Half Daily Composite -condenser Rinse -adsorbent Basin -Front Half Daily Composite -filter Catch -probe Rinse	2378-TCDD, Homologues (tetra - octa), PCDD	6
Bottom Ash	Grabs	Daily Composite	2378-TCDD, Homologues (tetra - octa), PCDD	3
Ash From Control Device	Grabs	Daily Composite	2378-TCDD, Homologues (tetra - octa), PCDD	3
Quench Water Effluent	Grabs	Daily Composite	2378-TCDD, Homologues (tetra - octa), PCDD	3
Other				
Soils (in vicinity)	Borings	1 Composite	2378-TCDD, Homologues (tetra - octa), PCDD	1
				Total 26ⁱ

^aBased on 3 sampling days.^bXAD-2 (PUFF) denotes a modified high volume air sampler with a special sampling head for ambient organic compounds.^cSample to be collected if there is a significant source of suspected precursors in vicinity of sampling site.^dPCDD - Polychlorinated dibenzo dioxin.^eTOCL - Total organic chlorine.^fAnalysis by contractor.^gMMST is a modified EPA "Method 5" train as defined in the ASME protocol.^hHomologues - Analyses done on higher (tetra through octa) PCDD's as a total for each group only.ⁱMultiple analyses for each sample will have a multiplier effect on the analytical costs also. Total does not include quality assurance samples (approx. 20%).

Table 1-3. Ranked Source Category List

Rank A Source Categories:

Sewage Sludge Incinerators
Black Liquor Boilers
Commercial Boilers Firing Fuels Contaminated with Chlorinated
Organic Wastes

Rank B Source Categories:

PCP Sludge Incinerators
Carbon Regeneration (industrial)
Charcoal Manufacturing
Wire Reclamation

Rank C Source Categories:

Wood Stoves
Boilers (Firing PCP treated Wood)
Mobile Sources
Small Spreader-Stoker Coal Boiler
Hazardous Waste Incinerators
Lime/Cement Kilns Co-fired with Chlorinated Organic
Wastes

Rank D Source Categories:

Municipal Solid Waste (MSW) Incineration
Industrial Boilers Co-firing Wastes

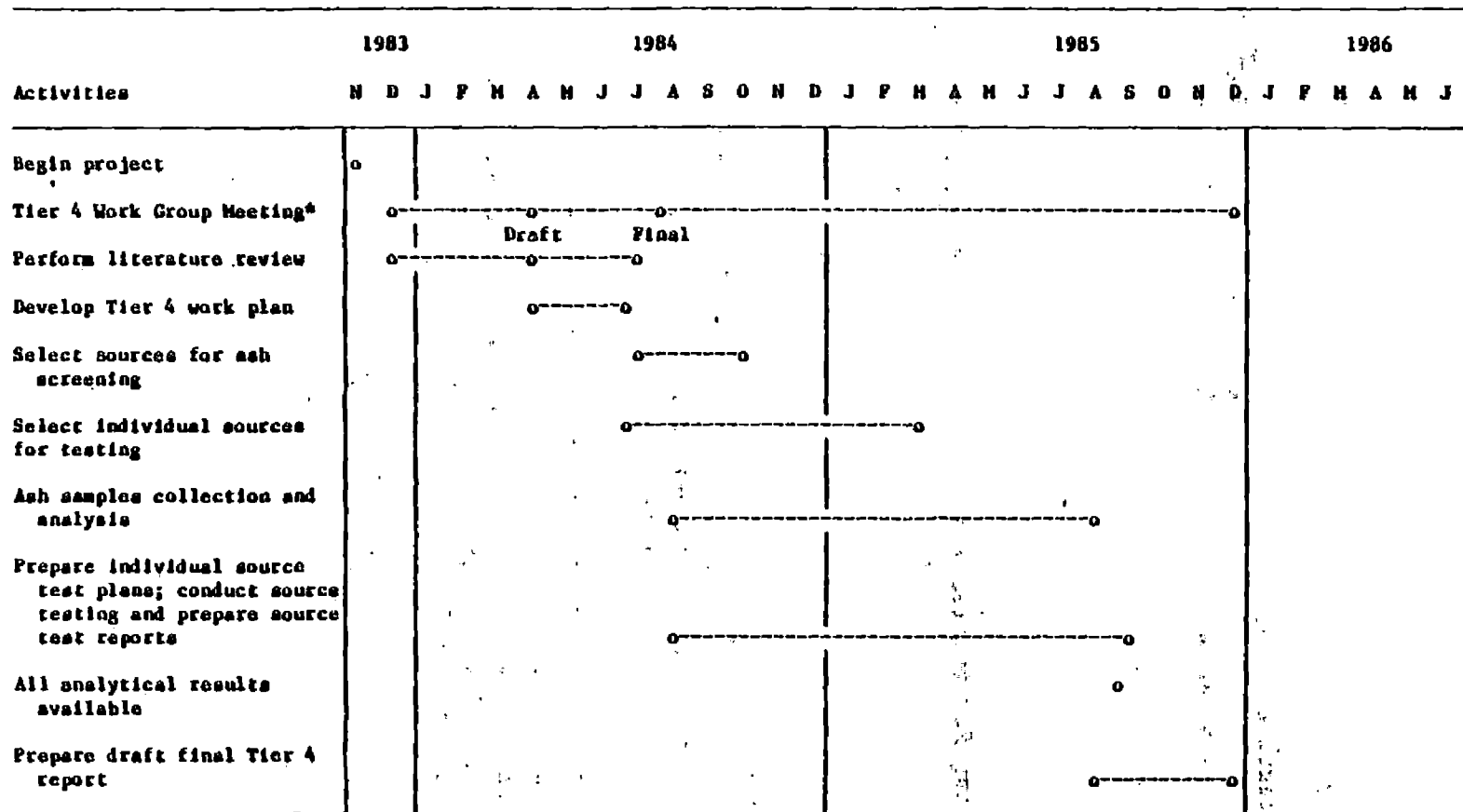
Rank A: Large source categories (greater than 1 million tons of fuel and/or waste burned annually) with elevated dioxin precursor contamination of feed/fuel. These categories are judged to have the highest potential to emit TCDD.

Rank B: Small source categories (less than 1 million tons of fuel and/or waste burned annually) or source categories with limited dioxin precursor contamination of feed/fuel. These categories have a high potential to emit TCDD.

Rank C: Source categories less likely to emit TCDD.

Rank D: Source categories which have already been tested three or more times.

Figure 1-1. Schedule: National Dioxin Study - Tier 4 - Combustion Sources



*Tier 4 Work Group will meet periodically throughout the study period.

Note: This schedule is very skeletal and will be further defined with the individual test efforts and subproject work plan.

The information collected under Tier 4 will be summarized in a final report.

The report will also summarize the state of knowledge of dioxin (particularly 2378-TCDD) emissions available from combustion sources. The status of ongoing studies will be given and available results of such studies will be reported upon in the final Tier 4 report. For example, the stack test data being collected from various combustion sources by New York State and others will be included, if available. Any preliminary results from the three million dollar three year effort being initiated by Environment Canada to examine the significance of various operating conditions on dioxin emissions from municipal incinerators will be particularly of interest. An updated list of recommendations for future testing and study will be provided at that time if warranted.

1.7 Possible Results Of The Tier 4 Study

While the previous paragraphs have briefly described the objective of Tier 4, it is worth noting what the study may or may not be able to accomplish.

The primary objective of the Tier 4 effort is problem definition. The degree to which Tier 4 can satisfy this objective depends in large measure on the magnitude and pervasiveness of the 2378-TCDD emissions found during the study. For example, a possible outcome of the study is that ash sampling and analysis may be validated as an effective tool to test to verify that 2378-TCDD is not emitted from a source or source category. Also, the stack test data and subsequent risk assessments may indicate, at least for the sources or source categories tested, that 2378-TCDD emissions do not likely result in an unreasonable risk to the public. Assuming these are the findings, some general conclusions about the scope of the problem are expected to be drawn from the Tier 4 study. Such conclusions will obviously need to be stated carefully, acknowledging the possibility that some untested sources may exist which may emit elevated levels of 2378-TCDD. Nevertheless, the Tier 4 study is intended to

provide information for the Agency to realistically define the scope and magnitude of the problem.

A more likely outcome is that the ash sampling program will identify a number of source categories with a sufficient probability of having levels of 2378-TCDDs present in the ash which merit further concern. As a result, these source categories may warrant further stack testing programs to obtain more definitive results. Similarly, the stack test program which can be conducted under Tier 4 may identify relatively high emission rates from some of the sources which are tested, thereby indicating a need for a number of other which sources should be tested. Since there are inadequate resources available under Tier 4, for the large amount of testing this would require, such further developments will likely depend upon followup studies to define more fully the magnitude of such problems.

In summary, it is likely that the Tier 4 study will better define the scope of the problem but may not provide sufficient definition to adequately define the magnitude of the problem nor will it develop any regulatory program, that might be need. More detailed study may be needed in such cases.

1.8 Format Of This Report

This section has provided a brief overview of the scope and purpose of the Tier 4 program under the National Dioxin Strategy. Section 2 discusses various alternatives which were considered in the design of the study. Section 3 provides further detail on how the source categories to be tested under Tier 4 were identified, the number and types of samples to be collected and the various analyses planned. Section 4 describes implementation issues, such as how the individual sources will be selected for testing and how the various samples will be collected.

Section 2

Alternative Study Plans Which Were Considered

The previous section presented a brief overview of the scope and purpose of the Tier 4 study. In designing of the study, the Agency considered various alternatives. The most frequently recommended alternatives are described below, along with the reasons why they were not included in the final Tier 4 plan.

2.1 Alternative 1: Focus The Tier 4 Effort Primarily on Municipal Waste Incinerators

The most frequently suggested alternative was to focus the Tier 4 study, in whole or in part, on determining the magnitude of dioxin emissions from various municipal waste incinerators. There were several reasons for this.

First, of the combustion source categories which have been tested, dioxin emissions are much greater for this source category than for others. This source category is, therefore, viewed with much interest and concern. Second, a number of urban areas are presently considering the permitting of new municipal incinerators, primarily as resource recovery units, due to the limitations associated with land disposal. Solid waste program representatives and other government officials, representatives of industry, and the public are concerned about the potential exposure and risk from dioxin emissions from these proposed facilities. As a result, it has been recommended that a number of municipal waste incinerators be tested in order to gain a better understanding of the magnitude of the dioxin problem from this source category.

After careful consideration, the Agency has decided to focus the Tier 4 effort primarily on combustion source categories other than municipal waste incinerators. While the Agency plans to test one municipal incinerator under

Tier 4, a broader study of municipal incinerators has not been included for the following reasons:

(1) Six of the approximately 40 large conventional (non-modular) municipal waste incinerators in the United States have been tested.³

As such, this source category is by far the most tested of all combustion source categories.

(2) Based on the results of these previous tests, the Agency has concluded that the emissions from well operated facilities do not pose a public health problem to those persons living in the vicinity of these sources. This position was initially contained in a report entitled "Interim Evaluation Of Health Risks Associated With Emissions Of Tetrachlorinated Dioxin From Municipal Waste Resource Recovery Facilities,"⁸ and was recently reaffirmed by the Agency in December 1983.⁹

(3) It is possible that other source categories may emit similar or larger quantities of 2378-TCDD or have a greater exposure and risk associated with them than municipal waste incinerators. This cannot be determined unless resources are devoted to testing other source categories, and

(4) There appears to be considerable local interest in testing specific municipal waste incinerators, so that resources external to this study will likely be available to test these facilities, even if municipal waste incinerators are not tested under Tier 4. At present, approximately ten municipal waste incinerators are under consideration for testing, primarily by Region III, individual States, other agencies and by Environment Canada.

For these reasons, the Agency has decided not to focus the Tier 4 effort on municipal incinerators. At this time, the Agency, tentatively plans to test only one incinerator (Hempstead, New York,) as part of Tier 4 to fulfill a

previous commitment. However, the data collected from the various other tests of municipal incinerators by other agencies will be obtained, and included in the final Tier 4 report.

2.2 Alternative 2: Investigate Conditions Which Increase/Decrease Dioxin Emissions

Another alternative considered was to include a study in the Tier 4 program designed to examine the significance of various combustion device operating parameters on the magnitude of dioxin emissions. Under this option, detailed stack sampling would be performed at one or two facilities. Operating conditions such as percent load and percent excess would be carefully monitored over a range and emissions measured for correlation.

It is recognized that such work is useful and necessary to understand how dioxin emissions can be minimized, however, such a study has not been included in Tier 4. Again, the primary reason is limited project resources. There are clearly insufficient funds available to characterize both a broad number of combustion source categories and to perform the type of stack testing which would be needed to determine quantitatively the significance of various operating parameters on emission rates.

Further, other agencies already have projects underway which are designed to address this specific issue. Environment Canada, for example, has recently initiated a three year, \$3 million study designed to investigate the significance of changes of various operating conditions upon emissions of 2378-TCDD at three municipal waste incinerators. Also, the ASME plans a series of tests at a United States incinerator designed to provide data to develop a relationship between various operating parameters and 2378-TCDD emissions. For these reasons, Tier 4 studies are not desired to collect additional field data specifically to characterize the significance of operating parameters. Rather, Tier 4 will obtain the results of other studies that are underway and as previously

conducted and summarize their findings in the final Tier 4 report. Operating data from all sources tested under Tier 4 will however, be carefully monitored and documented so they can be included in the data base for generally analyzing the effects on emissions of 2378-TCDD.

2.3 Alternative 3: Develop A Mechanistic Model To Estimate 2378-TCDD Emissions

Since resources to conduct detailed stack tests for each candidate combustion source category would not be within reason, it has been suggested that an empirical or mechanistic model be developed which could be used to estimate emissions of 2378-TCDD from source categories which could not be adequately tested. While such models may be of value in estimating emissions, this alternative was not included in the final Tier 4 plan for the following reasons:

(1) The design of a mechanistic or empirical model prior to any data collection effort may require a substantial amount of time. Given the current schedule of the National Dioxin Strategy, it is clear that there is not sufficient time to (a) design such a model, (b) collect the source test data, (c) validate the model, and (d) estimate dioxin emissions for many source categories;

(2) It is not entirely clear, at this time, if a single model could be developed which would be applicable to all combustion source categories, or whether a number of models would need to be developed for various types or groups of combustion source categories. If the latter case is true, considerable funds may be needed for development and validation. Certain theoretical models now exist, but the practical field application of these models is believed limited at this time; and

(3) The development and validation of such models may not be possible or successful, given the limited amount of test data which can be collected under Tier 4.

For these reasons, the Agency has decided not to include the development of mechanistic or empirical models as part of the Tier 4 program. However, it is anticipated that a project to further examine the feasibility of developing a practical empirical or mechanistic model(s) will be likely later. Such efforts could use the data collected under Tier 4 and other projects as a framework to design such a model development and validation program.

2.4 Alternative 4: Collect Ash Samples From A Large Number Of Source Categories

In order to address which source categories emit 2378-TCDD, it has been suggested that ash samples be collected from a large number of combustion source categories. Under this alternative, ash sampling would become the primary activity of Tier 4. While the initial Tier 4 program has been modified as a result of this comment to include more extensive ash sampling than originally planned, a totally comprehensive ash sampling program was not included in Tier 4 because ash samples have a limited value in identifying sources which may emit 2378-TCDD.³ In a few cases where 2378-TCDD has been measured in the flue gas, it was not measured in the ash. Further, concentrations of 2378-TCDD from available data do not correlate sufficiently with emissions data to allow them to be used to estimate 2378-TCDD concentrations in the flue gas. There are also cases where 2378-TCDD was not detected in the ash but was measured in the stack gasses. Although the data available tend to suggest a "trend," ash sampling has limited value, even to address which sources emit 2378-TCDD. It is expected that the additional data collected at the stack sampling sites for Tier 4 will provide the basis for revaluation of this correlation at the end of the study.

The Tier 4 study has been designed in such that ash sampling will complement the stack testing program. The ash samples will be used with other information to prioritize the source categories believed to have the greatest potential to emit 2378-TCDD for stack testing. Suggestions are, nevertheless, solicited from the Regional Offices and other reviewers of this document on whether other source categories which have a reasonable likelihood of emitting 2378-TCDD should be included under the ash sampling program.

2.5 Alternative 5: Analyze Samples For Specific Isomers And Homologues Of Furans

It has been suggested that the samples collected under Tier 4 be analyzed for furans, as well as 2378-TCDD and higher dioxin homologues. While there is general agreement that information on furans would be beneficial, these analyses have not been included in the work plan, primarily because of resource and time constraints. If furan analyses are included, fewer dioxin analyses are possible.

The Dioxin Strategy has been designed to focus on 2378-TCDD. Although it recognizes the possible importance of other dioxin isomers and "dioxin-like" compounds and has initiated a program to assess what should be done concerning the other isomer issue, the Strategy further recognizes that implementation of any other isomer program is contingent upon availability of adequate resources. At this time, Tier 4 has been allocated approximately 700 analyses from the TROIKA. These allocated analyses are currently planned for 2378-TCDD or dioxin homologues. If furan analyses were included, only about half of the planned dioxin analyses could be complete. For this reason, furans have not been included in Tier 4. However, sufficient samples will be collected and splits or or extracts stored for possible follow up analysis.

Section 3

The Tier 4 Work Plan

3.1 Overview

This section describes the process which was used to identify those combustion source categories which are likely to have the greatest potential to emit dioxin to the ambient air. These source categories are candidates for source sampling under Tier 4. The process initially involved a literature review of information related to dioxin emissions from combustion sources.³ The information was reviewed to determine (a) which combustion source categories had already been tested for dioxin and (b) which factors appear to be most important with respect to dioxin being emitted from combustion sources. Criteria were then applied to prioritize those source categories believed to have the greatest potential to emit dioxin.

3.2 Literature Review And Evaluation

An initial literature search for dioxin emission information was made in 1983 for OAR/EPA.¹⁰ This search was used as the starting point for a more specific search concerning dioxin emissions from combustion sources. Contacts were made to identify recently performed or ongoing studies which could be used to supplement the data base. While the full results of the literature review are reported elsewhere, the following paragraphs provide a summary of the key findings of the search.³

3.3 Summary Of Available Data

A review of the literature³ has identified 12 combustion source categories which have been tested for dioxins and for which data are available. Table 3-1 lists these source categories and the concentrations which have been measured.

TABLE 3-1. COMBUSTION SOURCES FOR WHICH TCDD TEST DATA ARE AVAILABLE

Source Category	Number Of Facilities Tested	Sample	TCDD ^a		2378-TCDD ^a		References
			Mean	Range	Mean	Range	
Municipal Waste Combustors							
o USA	6	Stack	3.5 ng/m ³	ND-240 ng/m ³	3.5 ng/m ³	0.30 - 9.4 ng/m ³	11 - 15
o European	13	Stack	25.6 ng/m ³	ND-120 ng/m ³	- ^b	-	16 - 20
Hazardous Waste Incinerators							
o Incinerator Ship	2	Stack	ND ^c	ND	-	-	21, 22
o Land Based Incinerators	10(7) ^d	Stack	0.56 ng/m ³	ND-2.5 ng/m ³	ND	ND	23 - 26
Sewage Sludge Incinerators	1	Stack	†	†	-	-	27
Utility Coal Boilers	7	Stack	ND	ND	-	-	12, 13
Commercial Boilers (Waste Fired)	6(6) ^d	Stack	§	§	-	-	28
Industrial Boilers (Waste Fired)	6(1) ^d	Stack	10.13 ng/m ³	ND-40.5 ng/m ³	18,000 ppt ^h	ND-55,000 ppt	5, 29 - 31
Activated Carbon Regeneration	1	Stack	0.013 ppt	ND-0.050 ppt	0.019 ppt	ND-0.083 ppt	32
Residential Combustion ⁱ	4	Scrapings	329 ppt	ND-777 ppt	242 ppt	26-600 ppt	5, 33
Mobile Sources ^j	9(4) ^d	Exhaust	4.0 ppt	ND-20 ppt	3.0 ppt	*	5, 34
Waste Reclamation Incinerators	1	Scrapings	234 ppt	58-410 ppt	-	-	35
Lime/Cement Kilns (Waste Fired)	1(1) ^d	Stack	§	§	-	-	36
Accidental Electrical Equipment Fires ^k	2	Wall Swipes	44 ppm ^l	ND-195 ppm	0.059 ppm	*	37, 38

^aTCDD = Tetrachlorodibenzo-p-dioxin.^bND = No data.^cND = None detected (detection limits vary).^dNumber of tests which have been performed, but for which the results have not been officially reported.^e* = One datum, no range available.^fPCDD scan only. PCDD concentrations ranged from 463 ng/m³ to 1,140 ng/m³ with a mean of 739 ng/m³.^gResults have not yet been officially reported.^hppt = Parts per trillion by weight.ⁱFuels include wood, wood/oil mixture, and natural gas.^jFuels include diesel, unleaded and leaded gasoline. In one test series exhaust scrapings were analyzed, in the other series, filter medium from exhaust samples.^kIncludes PCB transformers and capacitor batteries.^lppm = Parts per million by weight.

General operating characteristics of the sources which were tested are summarized in Table 3-2 and are used below to identify combustion related parameters which may affect the likely presence and magnitude of dioxin emissions from combustion sources.

Dow Chemical's "Chemistries of Fire" hypothesis proposes that polychlorinated dibenzo dioxins (PCDD's) are a common and natural byproduct of fire.⁵ However, an evaluation of data from the literature suggests that PCDD's are emitted during the incomplete combustion of either (a) dioxins or (b) dioxin precursors. Although uncertainty remains, dioxin precursors are defined for purposes of this work plan as chlorinated aromatics which can produce dioxins through bimolecular reactions and thermal rearrangements. Examples include chlorinated phenols and chlorinated benzenes. Based on the literature review,³ the following appear to affect dioxin emissions:

- °PCDD in feed,
- °Precursors in feed,
- °Chlorine in feed, (i. e., chlorinated compounds cannot be formed without chlorine present);
- °Combustion temperature,
- °Residence time,
- °Oxygen availability,
- °Feed processing,
- °Supplemental fuel.

3.3.1 PCDD In Feed³

2378-TCDD is an impurity that can result from the manufacture of trichlorophenol, which is used to make the herbicide 2,4,5-trichlorophenoxy acetic acid (245-T). Pentachlorophenol (PCP) production can also result in a PCDD contaminant, primarily octachlorodibenzo-p-dioxin (OCDD). The primary end use

Table 3-2. Characteristics Of Sources Tested For Dioxins

Source	Precursors	Furnace Type	Temperature	Available Air ^a
Municipal Waste Combustors				
o Conventional	Cl-aromatics	Waterwall	500-1000°C	Low
o Refuse Derived Fuel Boilers	Cl-aromatics	Spreader-Stoker	1000°C	Excess
Hazardous Waste Incinerators				
o Land Based	PCBs, PCPs	Rotary Kiln	1200°C	Excess
o Incinerator Ships	PCBs, PCPs	Dual Chamber	1600°C	Excess
Sewage Sludge Incinerators	PCBs, Cl-aromatics	Multiple Hearth	450-950°C	Low
Utility Coal Boilers	Coal, Low Chlorine	Pulverized Coal	1200°C	Excess
Commercial Boilers (waste-fired)	TCP	Small Fire Tube	1000°C	Excess
Industrial Boilers (waste-fired)	PCP, Cl-aromatics	Liquid Injection/Stoker	1300°C	Excess
Activated Carbon Regeneration	PCBs	Fluidized Bed	750-1000°C	Limited
Residential Wood Combustion	Low Chlorine	Wood Stove/Fireplace	<500°C	Low
Mobile Sources	Low Chlorine	Internal Combustion Engine	1800-2500°C	Excess
Wire Reclamation Incinerators	PCBs, PVCs	Batch/Conveyor	500°C	Limited
Lime/Cement Kilns (waste-fired)	Cl-organics	Rotary Kiln	1400°C	Excess
Accidental Transformer Fire	PCBs, Cl-benzene	Uncontrolled PCB Oil Fire	NA ^b	NA

^a Excess: High air/fuel ratio with efficient mixing.
 Low: High air/fuel ratio with inefficient mixing.
 Limited: Designed for low air/fuel ratio.

^b NA: Not Available

for PCP is as a wood preservative. It is anticipated that limited dioxin contamination will also occur during the manufacturing of other similar chlorinated aromatics, particularly if the manufacturing process is inefficient or not well controlled. Therefore, dioxins are expected to enter the environment as a contaminant of commercial products, such as wood preservatives and pesticides.

The widespread use of these products increases the possibility of finding dioxins in the feed of a combustion process. For example, PCP treated wood may be used to fire boilers. Runoff may carry pesticides containing dioxins to water treatment facilities where the organics are incorporated into a sludge. The sludge may then be incinerated. Likewise, contaminated waste streams from manufacturing processes may be incinerated as an energy recovery procedure. Two examples are PCP sludge incinerators used at wood preserving facilities and black liquor recovery boilers used at paper mills.

Boiler studies discussed in the literature review³ demonstrate that if PCDD's have been detected in combustion source emissions with PCDD's in the feed of an inefficient or poorly controlled combustion process, it is very likely that they will be released to the atmosphere.

3.3.2 Precursors In Feed

Most of the experiments reviewed focused on the formation of dioxins and furans from precursors. Esposito et al. presented detailed descriptions of the formation mechanisms of chlorinated dioxins from precursors.³⁹ This work organizes dioxin precursors into three classes:

Class I - Polyhalogenated phenols, primarily with a halogen ortho to the hydroxyl group, with a high probability of dioxin formation;

Class II - Ortho-halophenols and ortho-halophenyl esters where the substituted groups are a mixture of halogens and nonhalogens; and

Class III - Other chemicals having the possibility, but less likelihood, of dioxin formation, including chlorinated aromatic compounds.

The majority of experimental work to date has centered on three classes of precursors: chlorinated phenols, chlorinated benzenes, and PCB's. Dioxin formation from the combustion of chlorinated phenols has been tested extensively by Rappe⁴⁰ Jansson⁴¹, and Ahling^{42,43}. Dechlorination of highly chlorinated homologues can result in formation of the more toxic 2378-TCDD isomer. Chlorinated phenols are used as wood preservatives, herbicides, and for sap stain control. Wood or vegetation sprayed with chlorophenols may be disposed of by incineration or used as a supplemental fuel in boilers. In addition, chlorophenol wastes are often disposed of in sludge incinerators and industrial boilers. The identified references above provide a reasonable basis for considering these combustion sources as candidates for the Tier 4 testing program.

Buser investigated the formation of PCDD's and PCDF's from the pyrolysis of chlorobenzenes.⁴⁴ The formation mechanism included a chlorophenol and a polychlorinated diphenyl ester (PCDFE) intermediate. Chlorobenzenes are used in solvents, dyes, pharmaceuticals, and rubber production. Such products make up much of the organic chlorine found in municipal waste incinerator feed. The associated waste products may also be disposed of in other incinerators or boilers.

Buser also investigated the formation of PCDF's from the pyrolysis of PCB's.^{45,47} No experimental work has been identified on PCDD formation from PCB's. However, several studies have been identified that found PCDD's emitted from PCB fires.^{23,37,38} In addition, PCB's are frequently in solution with hexachlorobenzenes which have been shown to form PCDD's. PCB's have been used as dielectric fluids, in transformers and capacitors hydraulic fluids, plasticizers, and dyes. The incineration of PCB's at waste disposal facilities or in boilers may result in PCDD and PCDF emissions.

3.3.3 Chlorine In Feed

The chlorine content of fuel is obviously an important parameter affecting the formation of PCDD's or PCDF's. Shih et al. developed a ranked priority list of conventional combustion systems emitting polycyclic organic matter including PCDD's and PCDF's.⁴⁹ The rationale presented for source ranking is based on fuel characteristics and combustion conditions. Shih's work places great emphasis on both the chlorine content of the feed and the concentration of aromatics in the feed.

Other authors have demonstrated the effect of chlorine on dioxin emissions. Mahle et al. demonstrated that PCDD's were emitted from coal combustion only when chlorine was added.⁵⁰ Tiernan et al. found PCDD formation during the combustion of pine in the presence of HCl, but no PCDD's were detected during the combustion of pine alone.⁵¹ Liberti studied the combustion of vegetables.⁵² When inorganic chlorine or PVC is added, PCDD's and PCDF's were detected in the feed. While there is general acceptance that some chlorinated compounds are conclusive to dioxin formation, these inorganic chlorine studies demonstrate that the specific mechanisms involved in PCDD formation are complex and not well understood. However, it can be generally stated that chlorine must be present for the formation of PCDD, and general trends suggest that increased chlorine concentrations in the feed may improve the possibilities of PCDD emissions.

3.3.4 Combustion Conditions

The remaining factors that affect PCDD emissions are combustion conditions. These are combustion temperature, residence time, mixing, use of supplemental fuel, and fuel processing. The combustion efficiency is a function of all of these factors. In order to destroy PCDD's or prevent their formation, the combustion efficiency must be high. This requires a combination of high temperatures, available oxygen, high heat content fuel, and long residence times. Each factor is discussed separately below.

3.3.4.1 Combustion Temperature

Experimental evidence suggests that temperatures of 500-800°C promote PCDD formation, while temperatures greater than 800°C destroy PCDD's.^{5,43,47} Buser et al. showed that PCB pyrolysis at 550-650°C forms PCDF.⁴⁷ However, pyrolysis at temperature greater than 700°C cause 99 percent destruction of PCB's and no PCDF formation.³⁸ Ahling et al. produced similar results for both PCDD's and PCDF's during the combustion of chlorophenols.⁴²

Combustion temperature is a function of the BTU (British Thermal Unit) content of the fuel or supplemental fuel, the available air, and the degree of fuel processing. Municipal waste incinerators are considered a significant combustion source of PCDD's.¹⁴⁻¹⁹ These large mass burn units are characterized by low combustion temperatures, due in part, to the high moisture, low BTU fuel; poor air/feed mixing due to the lack of feed processing; and lack of supplemental fuel. In comparison, many hazardous waste incinerators and high efficiency boilers are designed for very efficient combustion. These units burn high BTU fuels and/or add high BTU supplemental fuels; and, even if the air/fuel ratio is low, the air/fuel mixing is efficient. The fuels are processed to decrease moisture and improve mixing. In many cases, high temperature afterburners are used for the combustion of offgases. Several studies have been identified that demonstrate the effects of high combustion temperatures on PCDD's and PCDD precursors.^{22,23,26} For example, no PCDD's were detected in the emissions of the Vulcanus incinerator ship during the combustion of PCDD contaminated Herbicide Orange.²² The combustion temperature during this project was 1600°C.

3.3.4.2 Residence Time

The residence time necessary to destroy PCDD's and the combustion temperature are inversely related. The higher the combustion temperature, the shorter the required residence time for PCDD destruction. Likewise, a low temperature source will require a long residence time for destruction of PCDD's.

Sachdev et al. showed that an increase in both temperature and residence time decreased the formation of PCDD's from chlorophenol combustion.⁵³ Similar results have been found at hazardous waste incinerators that run with 1.5-2.0 second residence times. Combustion sources with longer residence times and high temperatures are less likely to form products of incomplete combustion, such as dioxins.

3.3.4.3 Oxygen Availability

Oxygen availability is a function of both the air/fuel ratio and air/fuel mixing efficiency, both of which are of concern when burning solid fuels. Solid fuels and high viscosity liquid fuels (waste tars, etc.) burn as particulates or large droplets, and therefore portions of the fuel are burned in low oxygen or pyrolysis conditions. A low air/fuel ratio or poor air/fuel mixing will promote poor combustion conditions and the formation of PCDD's. Jansson demonstrates that an insufficient air supply increases PCDD emissions from chlorophenol combustion.⁴¹ Municipal waste combustors are usually fired with excess air. However, large mass burn units have poor air/fuel mixing due to the lack of fuel processing. Activated carbon regeneration and wire reclamation incinerators are both designed with limited air (some wire reclamation is done, in poorly designed nearly open chambers which are conducive to low temperatures and mixing). All of these cases have been shown to emit dioxins.^{14,32,35} Available oxygen will be considered during the source ranking. Sources with a low air/fuel ratio or poor air/fuel mixing will be considered potential sources of PCDD emissions.

3.3.4.4 Feed Processing

The feed material for a combustion source may be a liquid, a solid, or a gas. Both liquid and gaseous fuels can be easily mixed with air resulting in a high combustion efficiency; solid feeds usually require some processing to

improve combustion. Often solid feeds require drying, shredding, or separation to improve combustion. Similarly, high viscosity fuels, for example waste tars, require some preparations including preheating and atomization prior to combustion.

Feed processing will determine, in part, both oxygen availability and residence time. Fine, homogeneous feed particles will improve air/fuel mixing and combustion. Larger particles will require longer residence times and may result in local oxygen deficiencies due to poor mixing. High moisture will also decrease combustion efficiency. Therefore, highly processed homogeneous feeds are less likely to emit products of incomplete combustion, such as PCDD's.

3.3.4.5 Supplemental Fuel

When burning a low BTU fuel, the addition of supplemental fuel will increase the combustion temperature and improve combustion. Haile et al. tested a boiler cofiring RDF with coal.¹² The boiler temperature was 1200°C, and no PCDD's were detected. Dow Chemical tested an industrial incinerator burning waste tars without supplemental fuel and found parts per billion (ppb) levels of TCDD's in the fly ash.⁵ After the addition of a supplemental fuel, no TCDD's were detected.

When selecting sources for the Tier 4 testing program, sources fired with high BTU supplemental fuel are considered less likely to emit PCDD's. Sources burning low BTU wastes without supplemental fuels are high candidates for testing.

3.4 Identification Of Source Categories With A Potential To Emit Dioxin

The previous paragraphs have identified a number of parameters which are likely to affect either the presence and/or magnitude of dioxins emitted from combustion sources. In the analysis described below, combustion source categories are reviewed to determine which exhibit characteristics more closely

associated with these parameters. Source categories so identified are higher priority candidates for source sampling under Tier 4.

A broad list of combustion source categories is provided in Table 3-3.

These source categories were examined in a somewhat judgmental manner with the combustion related parameters previously described. This process resulted in a listing of combustion source categories (see Table 3-4) which are considered to be associated with these parameters. This listing also identifies those source categories where dioxin has previously been found to be emitted. Source categories in Table 3-4 represent the combustion source categories which are candidates for source sampling under Tier 4.

A number of the source categories initially listed in Table 3-3 do not appear in Table 3-4. For example, fossil fuel-fired boilers, process heaters, and gas turbines have been excluded due to their use of fuel with low chlorine content. For the same reason, industrial processes using low chlorine fossil fuels, such as the production of carbon black and coal gasification, have not been included.

Sources burning a low annual tonnage of fuels, such as coffee roasting, pathological incinerators, meat smoke houses or open burning, also have not been included in Table 3-4. Similarly, intermittent sources, such as structural fires have been excluded. While some of these sources may possibly emit 2378-TCDD, these source categories are not expected to pose as great an exposure problem as would be expected from large sources which operate continuously.

3.5 Development Of Criteria For Prioritizing The Candidate Source List

It will not be possible to stack test each of the candidate combustion source categories listed in Table 3-4 Tier 4. Therefore, a method for prioritizing the candidate source categories by groups was developed. The process

Table 3-3. Combustion Sources

<u>Fossil Fuel Boilers, Process Heaters, or Engines</u>	<u>Waste Disposal Operations</u>
Boilers	Bagasse Boilers
--- coal-fired	Wood Waste Burners
--- oil-fired	Refuse Derived Fuel Boilers
--- natural gas-fired	Municipal Waste Incinerators
--- liquefied petroleum gas	Hazardous Waste Incinerators
--- wood	--- land based
Process Heaters	--- incinerator ship
--- oil	Sewage Sludge Incinerators
--- natural gas	Waste Oil Boilers
--- refinery gas	Cement/Lime Kilns (Waste Fired)
Turbines	Wire Reclamation Incinerators
--- oil	Carbon Reactivation
--- natural gas	Pathological Incinerators
Internal Combustion Engines	Black Liquor Boilers
--- stationary	Open Burning
--- mobile	Agricultural Burning
Home Heating	
--- oil	
--- natural gas	
--- coal	
--- wood stoves/fireplaces	
<u>Industrial Processes</u>	<u>Accidental Fires</u>
Catalytic Cracking	Electrical Transformers
Charcoal Manufacturing	Structural Fires
Carbon Black Manufacturing	Forest Fires
Coke Manufacturing	
Coal Gasification	
Asphalt Manufacturing	
Coffee Roasting	
Meat Smoke Houses	
Black Liquor Boilers (paper mills)	

Table 3-4. Combustion Source Categories Believed To Have
The Greatest Potential To Emit Dioxins

<u>Source</u>	<u>Rationale</u>
Hazardous Waste Incinerators	TCDD ¹ Detected
Municipal Waste Incinerators	TCDD Detected
RDF ² Boilers	TCDD Detected
Commercial Waste Oil Boilers	TCDD Detected
Industrial Boilers Co-firing Wastes	TCDD Detected
Wire Reclamation Incinerators	TCDD Detected
Activated Carbon Regeneration	TCDD Detected
PCP ³ Sludge Incinerators	TCDD Detected
Sewage Sludge Incinerators	PCDD ⁴ Detected
Mobile Sources	TCDD Detected
Wood Stoves/Fireplaces	TCDD Detected
Wood/Bark Boilers	Experimental results with PCP treated wood
Charcoal Manufacturing	Experimental results with PCP treated wood, combustion conditions
Black Liquor Boilers	PCB's ⁵ in effluent, PCPs in feed
Cement/Lime Kilns Co-firing Wastes	Precursors present
Small Spreader-Stoker Coal Boilers	Favorable combustion conditions for dioxin formation

¹TCDD refers to the tetra homologues as a group. Available analyses are mixed, with some researches reporting "total tetras" and others reporting 2378-TCDD or both. The presence of TCDD's generally indicates some likelihood of 2378-TCDD being present.

²RDF = Refuse Derived Fuel.

³PCP = Pentachlorophenol.

⁴PCDD = Total of all dioxin homologues or Polychlorinated dibenzo dioxins. While detection of PCDD's does not necessarily indicate presence of TCDD or 2378-TCDD, there are sufficient data to infer such in this case.

⁵PCB = Polychlorinated biphenyls.

used was subjective, since no realistic assignment of weighting factors could be made for the ranking criteria. Criteria and the "decision tree" used to prioritize the candidate source categories are illustrated in Figure 3-1.

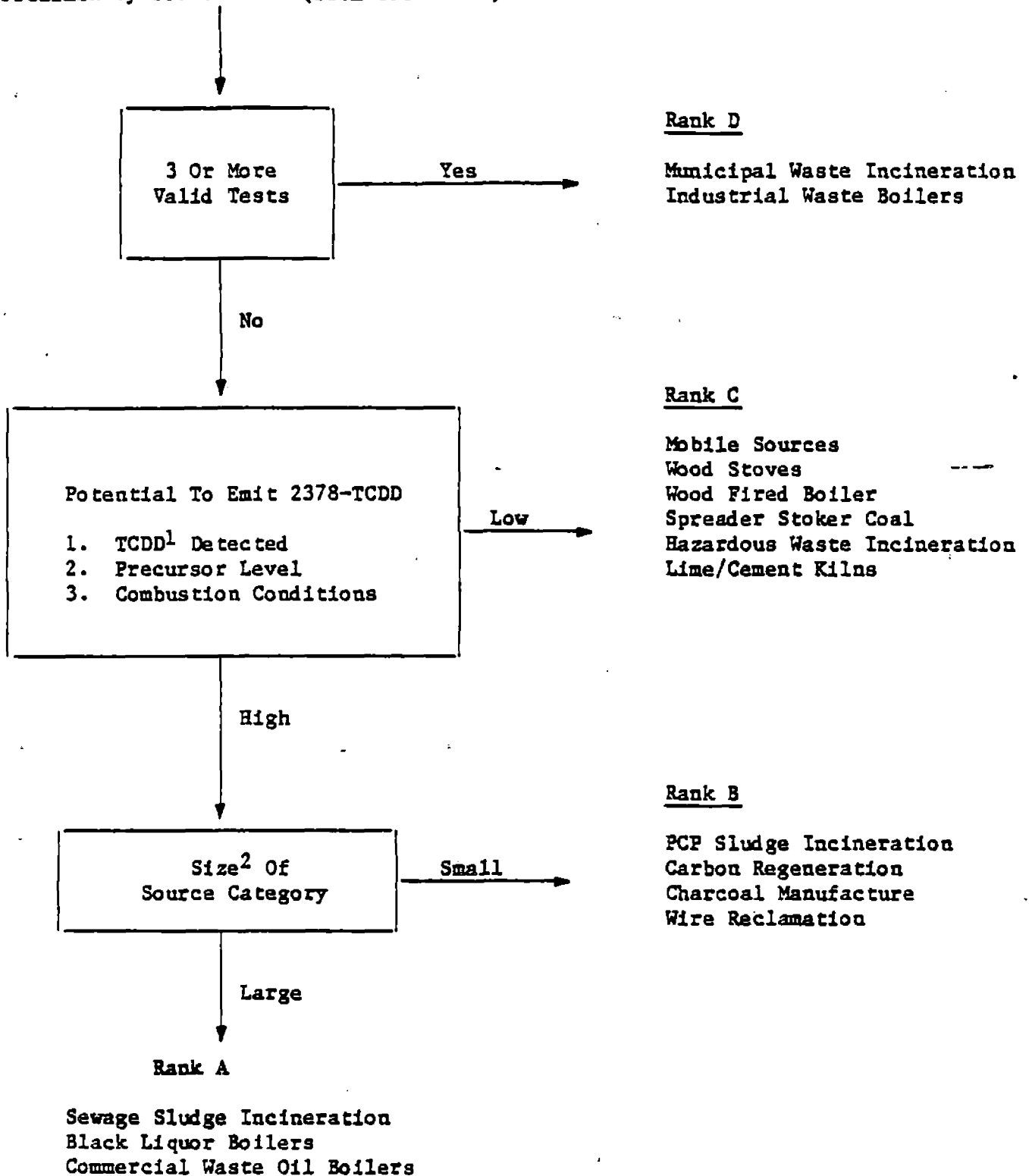
Based on these criteria, candidate source categories were placed into one of the four groups listed in Table 3-5. Table 3-5 also presents the grouped source category list. The source categories within a particular group are not listed in any particular order. The Rank A group is expected to be the most likely to emit 2378-TCDD and have the greatest potential for human exposure. Rank B and C groups also have a fairly high likelihood of emitting 2378-TCDD but are hypothesized to present less of an exposure problem. Rank D source categories have been tested three or more times.*

3.5.1 Rank D Source Categories

Rank D source categories include municipal waste incinerators and industrial boilers co-firing wastes. Six municipal waste incinerators have been tested in the United States.¹¹⁻¹⁵ Several fly ash and stack tests have also been conducted in Canada and Europe.¹⁶⁻²⁰ A total of six, wastefired, industrial boiler tests will be available after re-analyzing archived samples from industrial boiler tests. Because more than three stack tests have been conducted for each of these source categories, they were not considered for additional testing under Tier 4, beyond that required to fulfill previous commitments of the agency.

*As described in Appendix A, it is believed that data from three different sources provides a reasonable amount of data to characterize a particular source category for this effort. Appendix A also demonstrates that it will not be possible to obtain statistically significant results under Tier 4, since it is not possible to test enough sources under this program to obtain a rigorously representative sample to be able to develop meaningful confidence limits and account for variabilities that exist among sources.

Preliminary Source List (From Table 3-4)



¹Some researchers have reported only the total for the tetra homologue. The presence of TCDD is assumed for this ranking procedure to be adequate to indicate the potential to emit 2378-TCDD.

²"Size" of category takes into consideration the number of sources, their emission volume and general location with respect to exposed populations.

Figure 3-1: Ranking Criteria and Decision Tree

Table 3-5. Ranked* Source Category List

Rank A Source Categories:

Sewage Sludge Incinerators
Black Liquor Boilers
Commercial Boilers Firing Fuels Contaminated with Chlorinated
Organic Wastes

Rank B Source Categories:

PCP Sludge Incinerators
Carbon Regeneration (Industrial)
Charcoal Manufacturing
Wire Reclamation

Rank C Source Categories:

Wood Stoves
Wood Boilers (Firing PCP treated wood)
Mobile Sources
Small Spreader-Stoker Coal Boiler
Chlorinated Organic Waste Incinerators
Lime/Cement Kilns Co-fired with Chlorinated Organic
Wastes

Rank D Source Categories:

Municipal Solid Waste (MSW) Incineration
Industrial Boilers Co-firing Wastes

*Ranking is by group, not by sources within a group.

Rank A: Large source categories (greater than 1 million tons of fuel and/or waste burned annually) with elevated dioxin precursor contamination or feed/fuel. These categories have a high potential to emit TCDD and population exposure is expected to be high.

Rank B: Small source categories (less than 1 million tons of fuel and/or waste burned annually) or source categories with limited dioxin precursor contamination of feed/fuel. These categories have a high potential to emit TCDD but population exposures are expected to be low.

Rank C: Source categories less likely to emit 2378-TCDD.

Rank D: Source categories which have been tested three or more times.

3.5.2 Rank C Source Categories

Rank C source categories are those which have been judged to be less likely to emit 2378-TCDD, when compared to the other candidate source categories. This is based on the following factors: (a) the level of 2378-TCDD detected in previous tests, (b) the anticipated level of precursors in the fuel/feed, and (c) the likelihood of conditions favorable to incomplete combustion. Rank C source categories include mobile sources, wood stoves, wood boilers, small spreader-stoker coal boilers, hazardous waste incinerators, and lime/cement kilns.

Mobile sources have been tested in two earlier studies.^{5,34} In both cases, 2378-TCDD was detected at the part per trillion (ppt) level in particulate matter scraped from exhaust systems or in filtered exhaust samples. Chlorine content of the gasoline and diesel fuels are also low (0-100 ppm). Based on those earlier tests and chlorine content, mobile sources have been ranked C.

Wood stoves have been tested by Dow Chemical.^{5,33} 2378-TCDD was detected in chimney scrapings up to 100 ppt. The chlorine content of wood is less than 100 ppm. Although the combustion conditions found in wood stoves favor the formation of dioxins, the low chlorine concentrations and the low levels of dioxins detected in earlier studies indicate that this category may not emit high levels of 2378-TCDD. Nevertheless, 48 million tons of wood are burned annually, so the potential exposure could be considerable. Wood-fired boiler (burning untreated wood) are more efficient combustion systems and are also ranked C.

Small, spreader-stoker coal boilers have also been placed in the Rank C category. This source category was ranked in this manner because of combustion conditions which favor dioxin formation (e.g., relatively low combustion temperatures and poor air/fuel mixing due to large feed size). It

should be noted that tests on high temperature, coal-fired utility boilers have not detected dioxins in stack emissions.

Both hazardous waste incinerators and lime/cement kilns co-firing wastes have been ranked C. Elevated levels of chlorinated dioxin precursors can be expected in the feed of these source categories. However, previous tests have shown that relatively low levels of dioxin are emitted.^{23-26,36} This is due to combustion conditions which are not favorable to dioxin formation. Generally, combustion temperatures for these sources are greater than 1000°C, and the residence time for fuel ranges from one to two seconds. The use of high BTU supplemental fuel and afterburners also decreases the likelihood of dioxin emissions from these sources.

3.5.3 Rank B Source Categories

Sources with high potential to emit are ranked A or B. Rank B source categories are smaller source categories (less than one million tons of fuel burned per year) or are categories with lower concentrations of precursors in the feed. These include PCB sludge incineration, carbon regeneration, charcoal manufacturing, and wire reclamation.

PCP waste incineration has been evaluated in two studies.^{30,54} In both cases, PCDDs were detected in fly ash samples. Through experimental studies, PCPs have been shown to form octachlorodibenzo-p-dioxins (OCDD) during combustion.⁴¹ Dechlorination of OCDD can result in TCDD's and thus 2378-TCDD.²⁹ Annually, 19,000 tons of PCP are used to preserve wood.⁵⁵ Only a small percentage of this is incorporated in sludge which must be disposed. Typically, the sludge is incinerated at the wood preserving plant, along with scrap wood. The lack of feed processing and the high moisture content of the sludge can result in poor combustion conditions. Therefore, PCP sludge incineration is a potential source of dioxin.

Activated carbon regeneration was also been ranked B. In order to prevent the combustion of the carbon during the carbon regeneration process, the air/fuel ratio and the combustion temperature (800°C) are kept low.⁵⁶ These conditions are conducive to incomplete combustion. The thermal regeneration of activated carbon has been studied at one source, where the spent carbon had been used to treat a water supply system.³² Ppt levels of TCDDs were detected in the fly ash. Precursor levels in the carbon are low in comparison to what may be expected in carbon used to treat an industrial waste stream.

Charcoal manufacturing is a source category with combustion conditions which favor dioxin formation. Furnace temperatures are kept low (500°C), and both air/fuel ratio and air/fuel mixing are poor.⁵⁷ Source category surveys indicate that charcoal manufacturers are now heavily using scrap wood from saw mills.⁵⁷ Much of this wood may have been treated with PCP products for sap stain control. The combustion conditions, along with the potential use of PCP treated wood, indicate that this source category has a high potential to emit dioxins. Approximately three to four million tons of wood are used annually in the production of charcoal.⁵⁷ However, not all of this wood is PCP treated. In addition, the majority of charcoal manufacturing facilities are located in rural settings. For these reasons, this source category was placed in the Rank B category.

The final Rank B source category is wire reclamation incinerators. In previous tests, ppt levels of TCDDs were detected in fly ash samples.³⁵ As with carbon regeneration and charcoal manufacturing, both the combustion temperature and available oxygen are kept low in this process.⁵⁸ Wire insulation incinerated during the process often contains PCBs and polyvinyl chloride.

3.5.4 Rank A Source Categories

The remaining source categories were ranked A. These are sewage sludge incinerators, black liquor boilers, and commercial boilers co-firing chlorinated wastes.

Approximately 1.5 million tons of sewage sludge are incinerated annually.⁵⁹ The high moisture content of the feed can result in poor combustion conditions. In addition, sewage from an industrial area may contain elevated levels of PCBs and other chlorinated aromatics. In an earlier Canadian study, PCDDs were detected in stack emissions.²⁷ Many newer units are operated on a fuel efficient system. In order to save energy, both the combustion temperature and the available oxygen are held low.

Black liquor recovery boilers are also Rank A sources. Approximately 13 percent of all fuel used in large industrial boilers is pulping liquor.⁶⁰ Some 42 million tons of pulping liquor are recovered by burning in boilers of which black liquor boilers are a subcategory.⁶¹ Due to wood treatment at saw mills and biocides used in the pulping operation, the potential for chlorophenol contamination is high. In order to prevent smelt oxidation, the temperature is kept relatively low in these boilers. In addition, earlier studies have detected PCBs in the emissions from these boilers.⁶²

The final Rank A source category is commercial boilers co-firing wastes. Approximately 20 million tons of Resource Conservation and Recovery Act (RCRA) wastes are disposed of in boilers annually.⁶³ Many of these wastes are chlorinated aromatics. Commercial size boilers are estimated to account for about one-third of this waste disposal. These boilers are less efficient than the larger industrial boilers, and are more likely to produce products of incomplete combustion, such as dioxins. They are also generally urban oriented sources with low stacks.

The ranking procedure described above is highly subjective. As discussed later, ash screening tests will be conducted on Rank B and C source categories in order to help further definitize a ranked source list. As a result, the final ranking of B and C source categories may change, depending on the results of the screening tests.

3.6 Selection Of Certain Candidate Source Categories For Stack Testing

Since Tier 4 funds are only adequate to test about 12 sources, several options were considered for selecting the source categories for stack testing from the prioritized list. Three of the options which were considered are illustrated in Table 3-6. These include:

Option 1: Reasonable coverage (three sources tested) for each of the source categories ranked A, B, and C.

Option 2: Minimal coverage (1 source tested) for each of the source categories ranked A, B, and C.

Option 3: Reasonable coverage (three sources tested) for source categories ranked A, with the remaining source tests to be reserved until the results of the ash screening program are available for re-prioritizing source categories currently ranked B and C.

Option 1, which provides the most comprehensive test plan, cannot be selected due to the limited resources available for testing. As previously mentioned, Tier 4 can only fund about 12 stack tests - not the 32 or more needed to implement this option. Option 2 provides a more economical test plan, but it provides only a single stack test for each of 12 different source categories. More reliable results would be obtained if three sources within each source category were tested. Option 3, although not providing the broad coverage of source categories, attempts to collect a reasonable amount of data (i.e., three

TABLE 3-6. SOURCE TEST PLAN OPTIONS FOR STACK EMISSIONS

Source	Number of Recommended Tests		
	Option 1	Option 2	Option 3
<u>Rank A Sources</u>			
Sewage Sludge Incinerator	2	1	2
Black Liquor Boilers	3	1	3
Commercial Boilers	3	1	2
<u>Rank B Sources</u>			
PCP Sludge Incinerator	2	1	
Carbon Regeneration (Industrial)	2	1	
Charcoal Manufacturing	3	1	
Wire Reclamation	2	1	
<u>Rank C Sources</u>			
Mobile Sources*	2	1	4
Wood Stoves	3	1	
Wood Boilers (PCP Treated)	3	1	
Small Spreader-Stoker Coal Boiler	3	1	
Hazardous Waste Incineration	1	0	
Lime/Cement Kilns (w/Chlorinated Organic Wastes)	2	0	
<u>Rank D Sources</u>			
Municipal Solid Waste (MSW)	1	1	1
Industrial Boilers Co-firing Wastes	0	0	0
TOTAL	32	12	12

Option 1: Three-test coverage of potential source categories.

Option 2: Single-source coverage of potential source categories.

Option 3: Recommended stack test plan; focused on source categories with greatest potential.

*\$10k allocated to EPA's Environmental Sciences Research Laboratory, Research Triangle Park, North Carolina, for supplemental emissions testing.

sources tested) for a limited number of source categories. Option 3 has been selected by the Agency for implementation under Tier 4.

Stack testing under the program will be phased. EPA plans to initiate detailed stack tests in FY-84 of sewage sludge incinerators, black liquor recovery boilers, and small commercial boilers which co-fire chlorinated organic waste. Three black liquor boilers will be tested, while two sewage sludge incinerators and commercial boilers co-firing wastes will be tested. Two sources in these latter source categories will be tested, since a third source in both source categories is being tested by other groups. Selection criteria are under development which will allow optimization of characteristics of sources to be tested.

EPA plans to begin the process of locating specific sources for testing in each source category by July 1984. As explained in Section 4, the process of locating specific sources for testing will be coordinated with the EPA Regional Offices, as well as the appropriate State and local agencies.

Testing of the Rank A source categories will use seven of the available 12 source tests. Five* other source tests can be performed. At this time, EPA plans to postpone final selection of source categories for these five tests, until the results of the first phase of the ash sampling program are available. The information from the ash program will be used to re-evaluate the order of the B and C ranked source categories. It is anticipated that a final selection of source categories for these five tests will be made by the beginning of the 1985 calendar year. This selection will also take into account other stack tests underway or planned by others external to Tier 4.

*One of these source tests is currently reserved for testing the Hempstead, New York, incinerator. This facility is currently shut down and may reopen during the course of the Tier 4 study. If not, the source test will be reassigned to another source category. A decision on possible reassignment will be made by December 1984.

3.7 Types Of Samples To Be Collected Under The Stack Testing Program

The stack testing program is designed to obtain a quantitative measure of the 2378-TCDD emissions discharged to the atmosphere from a given source. Gaseous and particulate matter stack samples will be collected, both before and after existing control devices in most cases. Stack emissions will be sampled using methods similar to those described in the newly developed ASME sampling protocol.^{6,64} This protocol is based on use of an EPA modified Method 5 train with an XAD-2 sorbent.

A summary of the stack testing requirements contained in the draft protocol is outlined in Table 3-7. Three independent sampling runs will be made at each site over a period of about one week. Sample catches from both the front and back halves of the sampling train will be analyzed separately for each of the sampling runs. The analyses of stack samples will include the tetra and higher dioxin homologues (i.e., penta, hexa, hepta, and octa), as well as 2378-TCDD, and total dioxins (PCDD's). Samples will be analyzed to the low ppt level of detection (= 25 ppt). Sufficient samples will be taken to allow archiving a portion of the samples for possible followup analysis, primarily if resources become available to do additional isomer specific and/or furan analysis.

In addition to stack samples, ash, water, soil, and precombustion air samples will be collected. Ash samples will be periodically collected during each of the stack test runs and composited daily. As described later, comparisons of the magnitude of dioxin in the ash with that in the flue gas are planned. Analysis of ash samples will identify any potential disposal problem, which may exist if high levels of 2378-TCDD exist in the ash. Procedures for collection of ash samples are described in Standard Site Plan for Chlorinated Dioxin Sampling at Combustion Sources.⁶⁴

Limited soil borings will be collected at each of the sources, primarily around ash handling areas. Soil samples will be collected using standardized

Table 3-7. Summary Of Draft ASME Protocol* For Sample Collection

- o Sampling procedures will be based on the draft ASME protocol requirements.
 - Three separate test runs.
 - Sample quantities will allow for initial analysis and archived samples.
 - Each source will be tested and includes the following samples:
 - Total Gaseous and Particulate Matter Stack Emissions
 - Inlet/Outlet of Control Devices
 - Grab Samples of Feed/Fuel
 - Bottom Ash Grab Samples
 - Ash or Slurry from Control Devices
 - Precombustion Air
 - Quench Water Effluent
 - Soil
- o Standard EPA Method 5 train, modified to incorporate a sorbent module containing XAD-2.
- o Emissions Characterization:
 - Stack Temperature
 - Moisture Content
 - CO₂, CO)
 - O₂, NO_x, THC, SO_x, Opacity)----- Continuous Monitoring
 - Total Particulates)

*Data requirements set forth in the ASME protocol will be collected as a minimum. In many cases, other data will be collected. For example Total Volatile Compounds, HCl, Total Chlorine and other analyses may be generated at some sites. Operating parameters and conditions will be closely monitored and documented.

sampling procedures described in Sampling Guidance Manual for the National Dioxin Study.⁶⁵ Composite soil samples from the various sites will be analyzed for 2378-TCDD and dioxin homologues. If stack analyses and risk assessments indicate reason for serious concern, further sampling of soils downwind will be considered.

Precombustion air will be sampled at any source where significant dioxin precursors are suspected to be in the air as a result of site contamination. Some heavily industrialized areas for example, could have relatively high (ppb to ppm levels) concentrations of precursors of dioxin in the ambient air. The decision to test precombustion air will be made on a source-by-source basis during the pretest survey. Steps will be identified in the pretest survey protocol described in Section 4 as criteria for this decision. Precombustion air samples will be collected by the ambient sampler (e.g., modified high volume ambient sampler with an XAD-2 collection resin) described in guidance for dioxin monitoring.⁶⁵ Down wash from the stack sampled will be avoided. These samples will be analyzed for 2378-TCDD, the higher dioxin homologues, PCBs, chlorinated phenols, chlorinated benzenes, and total organic chlorine.

During the stack test, fuel/feed samples will be periodically collected and composited. The fuel/feed samples will be analyzed for total PCDDs, PCBs, total chlorine, chlorinated phenols, and chlorinated benzenes, since these compounds may be precursors of dioxin. If 2378-TCDD is detected in the stack emissions, the fuel samples will also be analyzed for 2378-TCDD and the higher homologues. The TROIKA will perform analyses for the dioxin compounds and the sampling contractor will analyze for the other compounds. Thus, the extent of non-dioxin analyses will affect the cost of each sample collected and consequently Tier 4's budget. Table 3-8 summarizes the analyses to be performed on each sample collected during the stack test. In addition to the number of

Table 3-8. SAMPLING AND ANALYSES MODEL

Sample	Method	Samples	Analyses	Total Samples* for Analysis
Inputs				
Precombustion Air	XAD-2 (PUFF) ^b	0-1 ^c	2378-TCDD, PCDD ^d , TOCL ^e , Cl-phenols, Cl-benzenes	1 ^f
Feed/Fuel	Grabs	Daily Composite	PCDD Scan, Cl-phenols Cl-benzenes, PCB, TOCL	3 ^f
Outputs				
Stack (before control)	HMST ^g	2 trains -Back Half Daily Composite -condenser Rines -adsorbent Basin -Front Half Daily Composite -cyclone Catch -filter -probe Rines	2378-TCDD, Homologues ^h (tetra - octa), PCDD	6
Stack (after control)	HMST	2 trains -Back Half Daily Composite -condenser Rines -adsorbent Basin -Front Half Daily Composite -filter Catch -probe Rines	2378-TCDD, Homologues (tetra - octa), PCDD	6
Bottom Ash	Grabs	Daily Composite	2378-TCDD, Homologues (tetra - octa), PCDD	3
Ash From Control Device	Grabs	Daily Composite	2378-TCDD, Homologues (tetra - octa), PCDD	3
Quench Water Effluent	Grabs	Daily Composite	2378-TCDD, Homologues (tetra - octa), PCDD	3
Other				
Soils (in vicinity)	Borings	1 Composite	2378-TCDD, Homologues (tetra - octa), PCDD	1
				Total 26 ^f

*Based on 3 sampling days.

^bXAD-2 (PUFF) denotes a modified high volume air sampler with a special sampling head for ambient organic compounds.

^cSample to be collected if there is a significant source of suspected precursors in vicinity of sampling site.

^dPCDD = Polychlorinated dibenzo dioxin.

^eTOCL = Total organic chlorine.

^fAnalysis by contractor.

^gHMST is a modified EPA "Method 5" train as defined in the ASME protocol.

^hHomologues = Analyses done on higher (tetra through octa) PCDD's as a total for each group only.

ⁱMultiple analyses for each sample will have a multiplier effect on the analytical costs also. Total does not include quality assurance samples (approx. 20%).

samples listed in the table, an estimated additional 20 percent will be required for quality assurance/quality control purposes (blanks, duplicates, blinds etc.).

3.8 Ash Screening Program

The Tier 4 plan includes a program to collect ash screening samples from several combustion source categories which are listed in Table 3-9. This listing includes each of the source categories ranked B or C, as well as a few other combustion source categories which have been recommended for testing by EPA Regional Offices and others. For example, testing of agricultural burn areas was recommended by EPA's Region X office, while forest fire residues were recommended by an advisory group to Tier 4. Additional source categories that have a reasonable likelihood of emitting 2378-TCDD may be added to the screening list, based upon recommendations from the EPA Regional Offices and others. The rationale for performing the ash sampling program is based primarily on the need to refine the results of the admittedly subjective stack testing prioritization procedure. The ash sampling program is relatively inexpensive and will provide dioxin related information for several combustion sources.

Unfortunately, there is no reliable screening technique available to provide conclusive estimates of 2378-TCDD emissions from combustion sources. 2378-TCDD is hypothesized to be typically emitted either as a particulate, a gas or absorbed upon the fine particulate. If this is true, it would generally not be concentrated in the ash of a particulate control device. Data are available which indicate there is likely to be selective partitioning of homologues between those in the flue gas and those in the fly ash.²⁹ These data imply that, TCDD concentrates in the flue gas, while the higher dioxin homologues concentrate in the ash. As a result, ash samples can only provide a general indication of the presence of dioxin at a source. For example, if 2378-TCDD is found in the

Table 3-9. Combustion Source Categories Where Ash Samples
Will Likely Be Collected*

Source Categories:*

Chemical Sludge Incinerators

Carbon Regeneration Unit (at industrial source)

Charcoal Manufacturing

Wire Reclamation

Wood Stoves

Wood Boilers Burning PCP Treated Wood

Spreader-Stoker Coal Boiler

Hazardous Waste Incineration

Lime/Cement Kiln Burning Hazardous Wastes

Forest Fires

Apartment House Flue Fed Incinerators

Agricultural Burning

*To be supplemented by other categories identified by State and Regional officials with reasonable likelihood of emitting 2378-TCDD.

ash, it can only be assumed that 2378-TCDD was probably emitted in the flue gas. When 2378-TCDD is not found in the ash, it cannot be assumed that 2378-TCDD is not emitted in the flue gas. At least at one source, where both stack and ash data were collected from the same source, TCDD was found in the flue gas, even though no PCDD or TCDD was found in the fly ash,¹⁷ but the methodology and quality control procedures used have not been thoroughly examined. Ash samples can probably now best be used as a screening tool to identify those source categories which have a likelihood of emitting dioxin and which probably should be stack tested.

Despite the limitations associated with these samples, ash sampling is expected to be useful in providing data to supplement the ranking process described in the previous section. Ash and stack sample data collected by Tier 4 and from other studies being conducted by others may provide additional data to evaluate correlations. A more thorough examination of data relationships between homologues, source characteristics, etc., will be required before a hypothesis or further research plan can be developed, however.

Section 4

Implementation Of The Tier 4 Plan

4.1 Overview

The previous section identified the specific source categories to be sampled under Tier 4. This section focuses on how individual sources will be selected for testing and who will be responsible for various activities under Tier 4. This section also discusses the management and coordination aspects of Tier 4.

4.2 Selection Of Individual Sources For Testing

Generally, ash and/or stack samples will be collected from three sources within each of the source categories which has been selected for testing. The process of selecting individual sources for testing within each of the source categories will begin by Tier 4 identifying several sources or source category "models" which are believed to be representative or typical of each source category targeted. The EPA Regional staff will then be asked to recommend certain sources from amongst these sources or meeting the model criteria for screening or stack testing. In selecting these sites, the Regions and Tier 4 management will need to consider a number of practical constraints.

For example, accessibility to a site will be an important factor. While Section 114 Authority of the Clean Air Act may be used to gain access to a particular facility, if necessary, it would be more practical to select sites where accessibility is not a problem. The potential support and cooperation of State/local agencies should also be considered, since the ash sampling program is planned to be conducted by EPA Regional Offices for sources located within their jurisdiction. Selecting sites in those States which will provide assistance and cooperation would be beneficial.

4.3 Ash Sampling Program

Once individual sites have been approved for the ash sampling program, the appropriate Regional Office(s) will be asked to develop site plans for the collection of the ash samples. The purpose of the plans is to describe the specifics of how the ash samples and other information will be collected at the site(s) in accordance with guidelines to be furnished by Tier 4.

Specific guidance on the types of information to be collected and how the ash samples are to be collected is currently under development. Briefly, it is planned that Regional (or State/local) personnel will obtain the ash samples from a particular site. Samples should be collected from particulate matter control devices, or from the ash pit, in the event no control device is used. Samples will need to be collected in such a manner that they are indicative of long term operations which may require collection of multiple samples. Samples collected will be combined into a single composite. A portion of this composite sample will be stored for possible follow-up analyses.

Equipment and detailed procedures needed to collect, package and ship samples to the TROIKA for analysis will be provided by Tier 4. Each sample will be assigned a unique sample identification number by the Sample Control Center which has been established to manage the influx of samples to the TROIKA under the National Dioxin Study. Once samples are analyzed, the results will be validated by the laboratory before being released to Tier 4 and recorded in STORET.* Tier 4 will authorize the validated data to be made available to the Regional Office.

*STORET is a parametric data storage and handling system operated by the Office of Water. This system has been adopted by the National Dioxin Study management as the central repository for all data generated.

4.4 Source Testing Program

Similar procedures will be used to identify individual sources for the detailed stack testing program. Initially, OAR will identify general descriptions or specific candidate sources believed to be representative of the source category. This listing along with selection criteria and guidance will generally be sent to the EPA Regions, who will be asked to recommend specific sources for testing. Once selected, the Regions will be asked to initiate the process of coordinating with the State/local agencies and gaining access to the particular sources within the Region. Some tests may be added to existing test programs being conducted by IERL. After access to a site has been agreed upon, an EPA contractor will visit the source to make a pretest survey to obtain the necessary background information needed to plan the source test. A plan will be prepared by the contractor and submitted to OAR the Region, State, and the source to be tested prior to the actual testing. This plan will include:

- (a) reference to descriptions of the sampling procedures equipment to be used;
- (b) the number of individual source tests to be performed;
- (c) the number and types of samples (e.g., before or after controls, feed/fuel, ash, soil) which will be collected;
- (d) the location at the source of where each sample will be collected;
- (e) information on the various operating parameters which will be recorded during source testing;
- (f) procedures to be followed concerning the labeling, storage and shipment of the samples to the TROIKA for laboratory analysis; and
- (g) a Quality Assurance/Quality Control plan for the source testing program.

Once the plan is agreed upon, the contractor will make arrangements to proceed with the stack test. EPA personnel will oversee most of the stack sampling, which includes three separate test runs, which may last 5-10 days.

After the stack test has been completed, a report will be prepared for each source tested. A guidance manual, including an example Tier 4 source test report, is currently being developed which will be used to assure consistency and comparability among the reports assembled under Tier 4.

4.5 Quantitative Exposure And Risk Assessment

In the event that 2378-TCDD is detected in the stack emissions at any of the sources tested, a quantitative exposure and risk assessment will be performed for that site. Evaluation of inferences that can be made to other sources within this source category will also be performed. An revised exposure and risk methodology is currently under development by the Strategies and Air Standards Division (SASD), OAQPS who will perform this exposure and risk analysis.

4.6 Ambient Air Quality Study

At one of the sources where high levels 2378-TCDD is measured (if indeed such a case occurs) in the flue gas, a follow-up ambient air quality study is planned. The purpose of this study will be to measure mbient air quality levels of 2378-TCDD in the vicinity of the source. The study will be one to two months in duration during the spring/summer of 1985. Approximately three to five ambient monitors will be located at varying distances downwind from the source. Ambient samples will be collected on an alternate day schedule at each of the monitoring sites. Each sample collected will be initially screened for PCDDs. In the event PCDDs are detected, the ambient samples will be further analyzed for 2378-TCDD. Although insufficient data will be collected to "validate" exposure model predictions of 2378-TCDD concentrations, the measured data will

be compared to the model estimates and some general observations made. A decision on the location of the ambient air quality study should be made by March 1985.

4.7 Management Of Tier 4

The responsibility for managing Tier 4 has been assigned to the Office of Air and Radiation (OAR). Within OAR, the Tier 4 program manager is Edward J. Lillis, Chief, Air Management Technology Branch (AMTB). AMTB is part of OAR's Office of Air Quality Planning and Standards (OAQPS), Monitoring and Data Analysis Division (MDAD), Research Triangle Park, North Carolina. The Tier 4 program staff consists of James H. Southerland, William H. Lamason, William B. Kuykendal and Edward Hanks within the Air Management Technology Branch.

An advisory Tier 4 Work Group, comprised of representatives of various EPA program offices (Table 4-1), has been formed to:

- (a) assist OAR in the design and implementation of Tier 4;
- (b) seek technical expertise and guidance from other EPA representatives on issues which arise during the project;
- (c) provide suggestions on how to accomplish the study objectives;
- (d) review and comment on the adequacy of protocols, sampling strategies, source test reports, and other material which may be prepared; and
- (e) keep other EPA officials apprised of the status of the project.

4.8 Coordination With The EPA Regional Offices

EPA's Regional Offices are expected to play a key role in the implementation of the Tier 4 program. Regional contacts have been identified in each of the Region, to establish and maintain lines of communication. A current list of Regional Office contacts is provided in Table 4-2. Briefly, their role is to:

Table 4-1Tier 4 Work Group

<u>Name</u>	<u>Organization</u>	<u>Mail Code or Room Number</u>	<u>Telephone Number (FTS)</u>
Edward J. Lillis	OAQPS - RTP, NC	MD-14	629-5586
James H. Southerland	OAQPS - RTP, NC	MD-14	629-5575
William Lamason	OAQPS - RTP, NC	MD-14	629-5575
Jim Cummings	Dioxin Management Coordination Staff - Washington, DC	W-439	382-4686
Mike Slimak	OWRS/OW - Washington, DC	E-829	382-7051
Don Barnes	Chlorinated Dioxin Work Group - Washington, DC	E-635	382-2897
Bob Olexsey	IERL - Cincinnati, OH		684-7696
Dave Sussman	OSW/OSWER - Washington, DC	WSM-S2811	382-7927
Paul des Rosiers	ORD - Washington, DC	W-621	382-2722
Boniface Thayil	Air And Radiation - Region V		886-6054
Garrett Smith	Solid Waste - Region II		264-3407
Mike Dellarco	ORD - Washington, DC	M-3100	382-5794
Jack McGinnity	OAQPS - RTP, NC	MD-14	629-5504
Israel Milner (Interim)	Air Programs - Region III	3AM12	597-9090

Table 4-2

Regional Office Contacts - Tier 4

<u>Region</u>	<u>Name</u>	<u>Organization</u>	<u>FTS Number</u>
I	Margaret McDonough	Air Programs Branch (RM 2313)	223-4870
II	Garrett Smith	Solid Waste Branch (2AWM-SW)	264-3407
III	Israel Milner (Interim)	Air Branch (3AM12)	597-9090
IV	Brian Beals	Air Management Branch	257-3454
V	Boniface Thayil	Air and Radiation Branch	886-6054
VI	Doug Holy	Air Branch (6AWAT)	729-2825
VII	Bill Fairless	Surveillance and Analysis (KC Lab)	926-3884
VIII	Norm Huey	Air Programs Branch	327-3763
IX	Kathleen Shimmin	Field Operations Branch	454-7466
X	Dana Davoli	Air Programs Branch (532)	399-1495

- (a) coordinate with Tier 4 on Regional and State plans for dioxin sampling of combustion sources;
- (b) recommend combustion source categories for dioxin sampling;
- (c) identify potential sampling sites for combustion source categories;
- (d) obtain access to sites selected for ash and stack sampling;
- (e) collect ash samples at screening sites;
- (f) appraise other Regional Office staff on the scope, objectives and status of Tier 4; and
- (g) coordinate with other Regional Office dioxin staff and the designated public affairs liason on community relations issues of Tier 4.

4.9 Additional Information

For additional information on Tier 4, please contact James Southerland or William Lamason at FTS 629-5575.

References*

1. Dioxins, EPA-600/2-80-197, U. S. Environmental Protection Agency, Cincinnati, OH, November 1980.
2. Dioxin Strategy, Office Of Water Regulations And Standards and the Office Of Solid Waste And Emergency Response, U. S. Environmental Protection Agency, Washington, DC, November 28, 1983.
3. Review And Evaluation Of Available Dioxin Emission Data And Testing Options For Combustion Sources (Draft), EPA Contract Number 68-02-3513, Radian Corporation, Research Triangle Park, NC, June 1984.
4. "Dioxin Test Costs", Memorandum from Bob Parks, Radian Corp., Research Triangle Park, NC, to Bill Lamason, Office Of Air Quality Planning And Standards, U. S. Environmental Protection Agency, Research Triangle Park, NC, April 3, 1984.
5. The Trace Chemistries Of Fire - A Source Of And Routes For The Entry Of Chlorinated Dioxins Into The Environment, Chlorinated Dioxin Task Force, Michigan Division of Dow Chemical, U. S. A., Midland, MI, 1978.
6. Environmental Standards Workshop, American Society of Mechanical Engineers, McLean, VA, January 23-25, 1984.
7. Analytical Procedures And Quality Assurance Plan For The National Dioxin Study (Draft), Office Of Research And Development, U. S. Environmental Protection Agency, Washington, DC, January 1984.
8. "Interim Evaluation Of Health Risks Associated With Emissions Of Tetra-chlorinated Dioxins From Municipal Waste Recovery Facilities", EPA Environmental News, U. S. Environmental Protection Agency, Washington, DC, November 19, 1981.
9. "TCDD Emissions From Municipal Waste Combustors", Memorandum from Michael B. Cook, U. S. Environmental Protection Agency, Washington, DC, to Division Directors, Regions I-X, U. S. Environmental Protection Agency, December 16, 1983.
10. Summary Of A Literature Search To Develop Information On Sources Of Chlorinated Dioxin And Furan Air Emissions (Draft), EPA Contract Number 68-02-3513, Radian Corporation, Research Triangle Park, NC, September 1983.
11. C. L. Haile, et al., Assessment Of Emissions Of Specific Compounds From A Resource Recovery Municipal Refuse Incinerator, EPA Contract Number 68-015915, Midwest Research Institute, Kansas City, MO, November 1983.

*Some of these reference citations are incomplete and will be amended or corrected in the final work plan.

12. Comprehensive Assessment Of The Specific Compounds Present In Combustion Processes, Volume 1, Pilot Study of Combustion Emissions Variability, EPA-560/5-83-004, Office Of Toxic Substances, U. S. Environmental Protection Agency, Washington, DC, June 1983.
13. Comprehensive Assessment Of The Specific Compounds Present In Combustion Processes, Volume 3, National Survey Of Organic Emissions From Coal Fired Utility Boiler Plants, EPA-560/5-83-006, Office Of Toxic Substances, U. S. Environmental Protection Agency, Washington, DC, September 1983.
14. G. H. Higgins, An Evaluation Of Trace Organic Emissions From Refuse Thermal Processing Facilities, EPA Contract Number 68-01-6071, Systech Corporation, Xenia, OH, July 1982.
15. T. O. Tiernan, et al., "Characterization Of Toxic Components In The Effluent From A Refuse-fired Incinerator", Resources And Conservation, 9:343-354, 1982.
16. A. Cavallaro, et al., "Sampling, Occurrence And Evaluation Of PCDDs And PCDFs From Incinerated Solid Urban Waste", Chemosphere, 9(10):611-621, 1980.
17. A. Cavallaro, et al., "Summary Of Results Of PCDD Analyses From Incinerator Effluents", Chemosphere, 11(9):859-868, 1982.
18. F. Gizzi, et al., "Polychlorinated Dibenzo-p-dioxins (PCDD) And Polychlorinated Dibenzofurans (PCDF) In Emissions From An Urban Incinerator - 1, Average And Peak Values", Chemosphere, 11(6):577-583, 1982.
19. J. Janssens, et al., "Qualitative And Quantitative Analysis Of Emissions Of A Municipal Incineration Installation", presented at CEC Physico-chemical Behavior Of Atmospheric Pollutants, 2nd Symposium, Varese, Italy, September 29 - October 1, 1981.
20. K. Olie et al., "Polychlorinated Dibenzo-p-dioxins And Related Compounds In Incinerator Effluents", Pergamon Series On Environmental Science.
21. D. G. Ackerman, et al., At-sea Incineration Of PCB Containing Wastes. Onboard The "M/T Vulcanus", EPA-600/7-83-024, U. S. Environmental Protection Agency, Research Triangle Park, NC, April 1983.
22. D. G. Ackerman, Destruction Efficiencies For TCDD During At-sea Incineration Of Herbicide Orange, EPA Contract Number 68-02-2660, Radian Corporation, Research Triangle Park, NC, March 1979.
23. PCB Disposal By Thermal Destruction, PB82-241860, National Technical Information Service, Springfield, VA, Research Triangle Park, NC, June 1981.
24. H. O. Rghei and G. A. Eiceman, "Adsorption And Thermal Reactions Of 1,2,3,4-Tetrachlorodibenzo-p-dioxin On Fly Ash From A Municipal Incinerator", Chemosphere, 11(6):569-676, 1982.

25. "Results of Silvex Test Burn DREs", letter from K. H. Jones, PhD., Roy F. Weston Associates, Westchester, PA, to Morris Hunt, Rollins Environmental Services, Inc., Bridgeport, NJ, September 9, 1983.
26. Performance Evaluation Of Full Scale Hazardous Waste Incinerators (Draft - Final Report), prepared for Incineration Research Division, U. S. Environmental Protection Agency, Cincinnati, OH, NC January 1984.
27. Sewage Sludge Task Force Report, Office of Water, U.S. Environmental Protection Agency, Washington, DC. Unpublished.
28. P. F. Fennelly, et al., Environmental Characterization Of Disposal Of Waste Oils In Small Combustors (Draft), EPA Contract Number 68-02-3168, GCA Technology, Bedford, MA, August 1983.
29. C. Castaldini, et al., Emissions Testing Of Industrial Boilers Co-firing Hazardous Wastes - Sites A, D, E, G, EPA Contract Number 68-02-3176, Acurex Corporation, Mountain View, CA, 1983.
30. B. DaRos, et al., Measured Multi-media Emissions From The Wood Preserving Industry, EPA Contract Number 68-03-2567, Acurex Corporation, Mountain View, CA, March 1981.
31. J. Hall, et al., Evaluation Of PCB Destruction Efficiency In An Industrial Boiler, GCA-TR-81-82-G, GCA Corporation, Bedford, MA, April 1981.
32. J. E. Howes, et al., Determination Of Dioxin Levels In Carbon Reactivation Process Effluent Streams, EPA Contract Number 68-02-3487, Battelle, Columbus, OH.
33. T. J. Nestrick, 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.
34. Dioxins In Mobile Sources Particles, memorandum from John E. Sigsby, Chief, to Karl H. Hellman, Control Technology and Application Branch, U. S. Environmental Protection Agency, Ann Arbor, MI, February 23, 1982.
35. D. O. Bryhorczuk, et al., "A Wire Reclamation Incinerator As A Source Of Environmental Contamination With Tetrachlorodibenzo-p-dioxins And Tetrachlorodibenzofurans", Archives Of Environmental Health, 36(5): 228-234, 1981.
36. J. A. Peters, Evaluation Of Hazardous Waste Incineration In Cement Kilns At San Juan Cement Company, Monsanto Research Corporation, EPA Contract Number 68-03-3025, Dayton, OH, January 1983.
37. R. L. Harless, High Resolution Mass Spectrometry Methods Of Analysis For Chlorinated Dibenzop-dioxins And Dibenzofurans, Human And Environmental Risks Of Chlorinated Dioxins And Related Compounds, 1983.

38. Polychlorinated Biphenyls (PCBs); Manufacture, Processing, Distribution in Commerce and Use Prohibitions; Use in Electrical Transformers, 49 FR 11070, March 23, 1984.
39. M. P. Esposito, et al., Dioxins: Volume I - Sources, Exposure, Transport, And Control, EPA-600/2-80-156, U. S. Environmental Protection Agency, Cincinnati, OH, June 1980.
40. C. Rappe, et al., "Formation Of Polychlorinated Dibenzo-p-dioxins (PCDDs) And Dibenzofurans (PCDF) By Burning Or Heating Chlorophenates", Chemosphere, 7(3):269-281, 1978.
41. B. Jansson, et al., "Formation Of Polychlorinated Dibenzo-p-dioxins During Combustion Of Chlorophenol Formulations", The Science Of The Total Environment, 10(3):209-217, 1978.
42. B. Ahling and A. Lindskog, "Emission Of Chlorinated Organic Substances From Combustion", Pergamon Series on Environmental Science, 1982, pp. 215-225.
43. B. Ahling, et al., "Formation Of Polychlorinated Dibenzo-p-dioxins And Dibenzofurans During Combustion Of A 2,4,5-T Formulation", Chemosphere, 6(8):461-468, 1977.
44. H. R. Buser, "Formation Of Polychlorinated Dibenzo-p-dioxins (PCDDs) And Dibenzofurans (PCDFs) From The Pyrolysis Of Chlorobenzenes", Chemosphere, 8(6):415-424, 1979.
45. H. R. Buser, et al., "Identification Of Polychlorinated Dibenzofuran Isomers In Fly Ash And PCB Pyrolyses", Chemosphere, 7(5):419-429, 1978.
46. H. R. Buser, et al., "Formation Of Polychlorinated Dibenzofurans (PCDFs) From The Pyrolysis Of PCBs", Chemosphere, 7(1):109-119, 1978.
47. H. R. Buser and C. Rappe, "Formation Of Polychlorinated Dibenzofurans From The Pyrolysis Of Individual PCB Isomers", Chemosphere, 8(3):157-174, 1979.
48. C. Rappe, et al., "Polychlorinated Dioxins, Dibenzofurans, And Other Polynuclear Aromatics Formed During PCB Fires", Chemica Scripta, 20:56-61, 1982.
49. C. Shih, et al., POM Emissions From Stationary Conventional Combustion Processes, With Emphasis On Polychlorinated Compounds Of Dibenzo-p-dioxin (PCDDs), Biphenyl (PCBs), And Dibenzofuran (PCDFs), EPA Contract Number 68-02-3138, Radian Corporation, Research Triangle Park, NC, September 1979.
50. N. Mahle and L. Whiting, "The Formation Of Chlorodibenzo-p-dioxins By Air Oxidation And Chlorination Of Bituminous Coal", Chemosphere, 9(11):693-699, 1980.
51. M. L. Tiernan, et al., "Chlorodibenzodioxins, Chlorodibenzofurans, And Related Compounds In The Effluent From Combustion Processes", Chemosphere, 12(4/5):565-606, 1983.

52. A. Liberti, et al., "PCDD And PCDF Formation In The Combustion Of Vegetable Wastes", Chemosphere, 12 (4/5);661-663, 1983.
53. A. K. Sachdev, Thermal Destruction Of Chlorophenol Residues, Project Number KE 111-1-0008, Dearborn Environmental Services, Mississauga, Ontario, Canada, July 1983.
54. C. Rappe and S. Marklund, "Thermal Degradation Of Pesticides And Xenobiotics: Formation Of Polychlorinated Dioxins And Dibenzofurans, Pesticide Chemistry: Human Welfare And Environment", Procedures Of The 5th International Congress On Pesticide Chemistry, 3:317-322, 1983.
55. K. R. Rao (editor), Pentachlorophenol: Chemistry, Pharmacology, And Environmental Toxicology, Plenum Press, New York, 1978.
56. S. Kulkarni, "Pollution Aspects Of The Thermal Regeneration Of Spent Activated Carbon", Radian Corporation, Research Triangle Park, NC, 1983. Unpublished.
57. P. B. Hulman, et al., Screening Study On Feasibility Of Standards Of Performance For Wood Charcoal Manufacturing, EPA Contract Number 68-02-2608, Radian Corporation, Research Triangle Park, NC, August 1978.
58. B. G. Liptak, Environmental Engineers Handbook, Volume 3, Chilton Book Company, Ontario, Canada, 1974, p. 283.
59. R. M. Dykes, A Review Of Standards Of Performance For New Stationary Sources - Sewage Sludge Incinerators, EPA Contract Number 68-02-3816, Radian Corporation, Research Triangle Park, NC, January 1984.
60. Report On The 1980 Manufacturing Industries Energy Consumption Study And Survey Of Large Combustors, DOE/EIAI-0358, U. S. Department of Energy, Washington, DC, January 1983.
61. Kraft Pulpig: Control Of TRS Emissions From Existing Mills, EPA-450/2-78-003b, U. S. Environmental Protection Agency, Research Triangle Park, NC, March 1979.
62. Application Of Combustion Modifications To Industrial Combustion Equipment, EPA-600/7-79-015a, U. S. Environmental Protection Agency, Research Triangle Park, NC, January 1979.
63. Impact Of Burning Hazardous Waste In Boilers, SCA Chemical Services, Inc., Boston, MA, August 1982.
64. Standard Site Plan For Chlorinated Dioxin Sampling At Combustion Sources (Draft), EPA Contract Number 68-02-3513, Radian Corporation, Research Triangle Park, NC, June 1984.
65. Sampling Guidance Manual For The National Dioxin Study, Office Of Water Regulations and Standards, U. S. Environmental Protection Agency, Washington, DC, May 1984.

Appendix A

Number Of Sources To Be Tested In A Source Category

The number of individual sources to be tested within each source category depends upon several factors, including the purpose of the testing, the number of sources in the source category which have been tested previously, and the available resources. Calculations have been made to estimate the number of sources within a particular category which should be tested in order to characterize statistically the emissions from the source category.

In order to determine the number of tests needed, information concerning the variability of emissions from the source categories is needed. Since emission data are not available for many source categories, the municipal waste incinerator source category was chosen as an example in Figure A-1 to estimate the number of sources within this category which should be tested. Based on these data, it has been determined that to characterize this source category in a statistically significant manner (i.e., at a 95 percent confidence), between 14-39 tests would be required (see attached). More specifically, 39 tests would be required if the results of each of the six previous tests are used in the analysis. Fourteen tests would be required if certain source tests believed to be nonrepresentative are not considered in the analysis. Assuming a cost of \$90,000 per source test (including non-dioxin analyses), it is clear that the entire Tier 4 budget could be spent testing emissions from only one source category for statistically representative results.

While it will not be possible under Tier 4 to sample enough sources to obtain rigorous and statistically significant results, a reasonable number of stack test and ash samplings should be performed in each source category. The

Figure A-1. Determination of Sample Size From Municipal Waste Incinerators

PROBLEM: Determine number of municipal waste combustors that should be tested in order to estimate the average dioxin emission rate within a 5 ng/m³ interval with 95 percent confidence.

Municipal Waste Combustors: Total population = 40

<u>Site</u>	<u>TCDD (ng/m³)</u>
A	240
B	29.7
C	6.3
D	3.15
E	1.2
F	ND

Assume: Sampling from a finite population without replacement

$$n = \frac{N z^2 SD^2}{d^2 (N-1) + z^2 SD^2}$$

n = sample size

N = population size = 40

Z = reliability coeff = 2 (95% confidence)

SD = standard deviation

d = confidence interval = 5 ng/m³

Case I: (all sites listed)

$$\bar{x} = 46.7$$

$$SD = 87.0$$

$$n = \frac{40 (2)^2 (87)^2}{5^2 (40-1) + (87)^2} = 39$$

$$5^2 (40-1) + (87)^2$$

Case II: (drop sites with highest and lowest average TCDD levels)

$$\bar{x} = 10.1$$

$$SD = 11.46$$

$$n = \frac{40 (2)^2 (11.46)^2}{5^2 (40-1) + 2^2 (11.46)^2} = 14$$

$$5^2 (40-1) + 2^2 (11.46)^2$$

SOLUTION: In order to estimate average dioxin emission rate for municipal waste combustions, 14-39 sources should be tested. Based on 95% confidence, results would be within 5 ng/m³ of true mean.

confidence intervals around these mean emissions should be fairly narrow to allow comparison among source categories. The confidence interval around a mean is given by:

$$\bar{X} \pm \frac{t_{\alpha} S}{\sqrt{n}}$$

The size of the confidence interval, therefore, varies with the size of the sample (n) and the value of the t statistic. The size of the t value varies with the degrees of freedom (number of samples minus one) and the confidence level chosen. Some example values of the t statistic are shown below.

<u>Number of Samples</u>	<u>t Statistic</u>		
	<u>95% C.I.</u>	<u>90% C.I.</u>	<u>t.05/√n</u>
2	12.706	6.314	8.99
3	4.303	2.920	2.48
4	3.182	2.353	1.59
5	2.776	2.132	1.24

Inspection of the above shows that, beyond three samples, there are diminishing returns. Similarly, the effects of 1/n diminish beyond n=3. For this reason, and for practical considerations (i.e., resources), a sample size of three tests will be considered optimal for the purposes of this study. This approach applies to the number of sources where ash samples or stack samples would be collected.

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