

NATIONAL DIOXIN STUDY

STUDY DESIGN

TIER 1 - 245-TCP PRODUCTION SITES AND ASSOCIATED WASTE DISPOSAL SITES

TIER 2 - SITES WHERE 245-TCP WAS USED TO MAKE PESTICIDE PRODUCTS

TIER 3 - SITES WHERE 245-TCP WAS FORMULATED INTO PESTICIDE PRODUCTS

TIER 4 - COMBUSTION SOURCES

TIER 5 - SITES WHERE 245-TCP DERIVED PESTICIDES HAVE BEEN USED ON A
COMMERCIAL BASIS

TIER 6 - CHEMICAL AND PESTICIDE MANUFACTURING SITES WHERE 2378-TCDD COULD
HAVE BEEN INADVERTENTLY PRODUCED

TIER 7 - CONTROL SITES WHERE 2378-TCDD CONTAMINATION IS NOT SUSPECTED

TIER 4 - COMBUSTION SOURCES

BUDGET

APPROXIMATELY \$1.4 MILLION

- o \$715k IN FY-84
- o \$700K IN FY-85

ALSO MAY INCLUDE ANALYSIS OF ALL OR SOME OF SAMPLES COLLECTED UNDER TIER 4

OBJECTIVES

- (A) WHICH COMBUSTION SOURCE CATEGORIES EMIT 2378-TCDD?
- (B) AT WHAT CONCENTRATIONS IS 2378-TCDD EMITTED?
- (C) DO THESE CONCENTRATIONS POSE AN UNREASONABLE RISK TO THE PUBLIC?
- (D) IF SO, WHAT CAN BE DONE TO MINIMIZE THAT RISK? (SHORT TERM VS. LONG TERM)

Table 1: Tier 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	629-5585
Lisa Barrera	OANR - Washington, DC		382-7426
Jim Cummings	Dioxin Management Coordination Staff - Washington, DC	W-439	382-5363
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 Programs - Region V		886-6054
Garrett Smith	Air Programs - Region II		264-3407
Mike Dellarco	ORD - Washington, DC	M-3100	382-5763
Jack McGinnity	OAQPS - RTP, NC	MD-14	629-5504

TIER 4 - WORK PLAN

- (1) PERFORM LITERATURE REVIEW TO FIND WHICH COMBUSTION SOURCE CATEGORIES HAVE BEEN TESTED FOR 2378-TCDD.
- (2) IDENTIFY THOSE COMBUSTION SOURCE CATEGORIES THAT HAVE NOT BEEN TESTED AND WHICH HAVE A HIGH LIKELIHOOD FOR EMITTING 2378-TCDD.
- (3) CONDUCT A SOURCE TESTING PROGRAM TO COLLECT EMISSION DATA, OPERATING AND EMISSION CONTROL INFORMATION.
- (4) IN THOSE CASES WHERE 2378-TCDD IS FOUND, CONDUCT AN EXPOSURE AND RISK ANALYSIS (IN CONJUNCTION WITH SASD AND THE CHLORINATED DIOXIN WORK GROUP).
- (5) PREPARE A FINAL REPORT THAT SUMMARIZES THE RESULTS OF THE LITERATURE REVIEW AND THE SOURCE TESTING PROGRAM.
- (6) PROVIDE INPUT FOR REPORT SCHEDULED TO BE SUBMITTED TO CONGRESS, DECEMBER 1985.

TIER 4 - KEY STEPS

1. PERFORM LITERATURE REVIEW TO DETERMINE SOURCE CATEGORIES THAT HAVE BEEN TESTED (MARCH 1984).
2. PRIORITIZE AND SELECT SOURCE CATEGORIES FOR SOURCE TESTING (APRIL 1984).
3. WORK WITH REGIONAL OFFICES/STATES TO LOCATE SOURCES WITHIN EACH CATEGORY FOR TESTING (MAY-JUNE 1984).
4. PERFORM A PRE-TEST SURVEY AND PREPARE A SOURCE TEST PLAN FOR EACH SOURCE (VIA CONTRACT) (SUMMER 1984).
5. BEGIN SOURCE TESTING ONCE SOURCE TEST HAS BEEN APPROVED BY TIER 4 WORK GROUP (FALL 1984). TESTING WILL INCLUDE STACK EMISSIONS, BEFORE/AFTER CONTROLS, OPERATING PARAMETERS.
6. IF 2378-TCDD IS FOUND, EXPOSURE ANALYSIS AND RISK ASSESSMENT WILL BE NECESSARY. SASD SUPPORT ANTICIPATED AND COORDINATION WITH THE CHLORINATED DIOXIN WORK GROUP THAT HAS DONE THE RISK ASSESSMENT FOR MUNICIPAL WASTE INCINERATORS.
7. IF HIGH RISK SITUATION IS FOUND, SOME SHORT TERM OR LONG TERM TECHNOLOGICAL SOLUTION MAY BE NEEDED TO ABATE PUBLIC CONCERN.
8. RESULTS OF SOURCE TESTS WILL BE DOCUMENTED AND WILL BE SUMMARIZED AT THE END OF THE PROJECT, ALONG WITH RESULTS OF LITERATURE REVIEW (FALL 1985).

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

Activities	1983					1984					1985					1986				
	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J
Begin project	o																			
Initial Work Group Meeting*	o																			
Perform literature review	o																			
Select source categories for testing																				
Select individual sources for testing																				
Hold ASTM Conference and prepare source test protocol																				
Prepare individual source test plans; conduct source testing and prepare source test reports																				
Prepare draft final Tier 4 report																				

* Tier 4 Work Group will meet periodically (bi-monthly) throughout the study period.

METHODOLOGY

- PREPARE A LIST OF COMBUSTION SOURCES ALREADY TESTED FOR PCDD
- REVIEW POSTULATED PCDD FORMATION MECHANISMS
- PRODUCE COMBUSTION SOURCE LIST WITH NECESSARY CRITERIA FOR PCDD FORMATION
- SCREEN PRELIMINARY LIST
- RANK FINAL SOURCE LIST

SUMMARY OF AVAILABLE DATA

SOURCES TESTED

MUNICIPAL WASTE INCINERATORS
HAZARDOUS WASTE INCINERATORS
SEWAGE SLUDGE INCINERATORS
RDF BOILERS
COAL UTILITY BOILERS
WASTE OIL BOILERS
INDUSTRIAL SLUDGE (K001) INCINERATORS
BOILERS COFIRING INDUSTRIAL WASTES
CARBON REACTIVATION
DOMESTIC WOOD COMBUSTION
MOBILE SOURCES
WIRE RECLAMATION
LIME/CEMENT KILNS COFIRING HAZARDOUS WASTES
ACCIDENTAL TRANSFORMER FIRE

TABLE 1. TCDD ANALYSIS

Source	Number of Facilities Tested	Sample	Mean	Range
HW Ships	1	Stack	114,900 ng/m ³	11,000 - 19,500 ng/m ³
SS Incinerator	1	Stack (PCDD)	739 ng/m ³	483 - 1,130 ng/m ³
Contaminated Waste Oil	6	Stack	66.7 ng/m ³	* ND - 1,400 ng/m ³
MSW (USA)	6	Stack	45.41 ng/m ³	ND - 240 ng/m ³
MSW (European)	6	Stack	35.05 ng/m ³	0.62 - 128 ng/m ³
Industrial Boilers (Waste Fired)	4	Stack	10.13 ng/m ³	ND - 40.5 ng/m ³
HW (Land Based)	2	Stack	0.56 ng/m ³	ND - 2.5 ng/m ³
Accidental Fire	2	Scraping	44,000 ppb	ND - 195,000 ppb
K001 Sludge	1	Composite Ash	25 ppb	0.8 - 3.4 ppb
Domestic Wood	4	Chimney Scraping	0.329 ppb	ND - .777 ppb
Wire Reclamation	1	Stack		ND - .410 ppb
Mobile Sources	8	Exhaust	4x10 ⁻³ ppb	ND - 2x10 ⁻² ppb
Carbon Regeneration	1	Stack	1.25x10 ⁻⁵ ppb	ND - 5x10 ⁻⁴ ppb
Lime/Cement Kilns	1	Stack	ND	
Coal Boilers	7	Stack	ND	

* ND = None Detected

POTENTIAL FACTORS EFFECTING PCDD EMISSIONS
BASED UPON LITERATURE SURVEY RESULTS

- PCDD IN FEED
- PCDD FORMED BY INCOMPLETE COMBUSTION/THERMAL
REARRANGEMENTS
 - PRESENCES OF PRECURSORS
 - PRESENCE OF CHLORINE
 - LOW COMBUSTION TEMPERATURE (500-600°C)
 - LOW OXYGEN AVAILABILITY (PRIMARY COMBUSTION ZONE)
 - SHORT RESIDENCE TIME
 - NO SUPPLEMENTAL FUEL
 - DEGREE OF FEED PROCESSING/FUEL CHARACTERISTICS

COMBUSTION SOURCES CONSIDERED

COAL FIRED BOILERS	CHARCOAL MANUFACTURING
OIL FIRED BOILERS	CARBON BLACK
NATURAL GAS FIRED BOILERS	COKE MANUFACTURING
LPG BOILERS	COAL GASIFICATION
OIL PROCESS HEATERS	BLACK LIQUID BOILERS
NG PROCESS HEATERS	ASPHALT MANUFACTURING
REFINERY GAS PROCESS HEATERS	COFFEE ROASTING
GAS TURBINES (OIL)	MEAT SMOKE HOUSES
GAS TURBINES (NG)	BAGASSE BOILERS
WOOD BOILERS	HOME HEATING
BARK-FIRED BOILERS	- OIL
RDF BOILERS	- NG
MSW INCINERATORS	- COAL
- MODULAR	- FIREPLACE
- WATERWALL	- WOODSTOVE
- DOMESTIC	- KEROSENE
HW INCINERATORS (LAND BASED)	STATIONARY ENGINES
HW INCINERATOR SHIPS	MOBILE ENGINES
SS INCINERATORS	ACCIDENTAL FIRE
BOILERS & PROCESS HEATERS	OPEN BURNING
FIRED WITH HAZARDOUS WASTES	IND. WASTE
- CONTAMINATED WASTE OILS	INCINERATORS
- OFF SPEC PRODUCTS	
- DISTILLATION BOTTOMS	
- TARS	
CEMENT/LIME KILN (WITH HW)	
RESOURCE RECOVERY (METALS)	
CATALYTIC CRACKING	
CARBON REACTIVATION	
PATHOLOGICAL INCINERATORS	

SCREENING OF COMBUSTION SOURCE LIST

EXCLUSIONS:

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- COAL: TESTED EXTENSIVELY BY EPA
No PCDD DETECTED
- NG AND LPG: CLEAN BURNING
No CHLORINE
- CLEAN OIL: LOW CHLORINE
- SMALL/INTERMITTENT SOURCES:

CARBON BLACK
PATHOLOGICAL INCINERATORS
INCINERATION SHIPS
ASPHALT
COFFEE ROASTING
MEAT SMOKE HOUSES
BAGASSE BOILERS
OPEN BURNING
CATALYTIC CRACKING
COKE MANUFACTURING
COAL GASIFICATION
ACCIDENTAL FIRE

PRELIMINARY SOURCE LIST

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<u>SOURCE</u>	<u>REASONING</u>
HAZARDOUS WASTE INCINERATORS	PCDD DETECTED
MUNICIPAL WASTE INCINERATORS	PCDD DETECTED
RDF BOILERS	PCDD DETECTED
COMMERCIAL WASTE OIL BOILERS	PCDD DETECTED
INDUSTRIAL BOILERS COFIRING HW	PCDD DETECTED
WIRE RECLAMATION INCINERATORS	PCDD DETECTED
ACTIVATED CARBON REGENERATION	PCDD DETECTED
PCP SLUDGE INCINERATORS	PCDD DETECTED
SEWAGE SLUDGE INCINERATORS	PCDD DETECTED
MOBILE SOURCES	PCDD DETECTED
WOOD STOVES/FIREPLACES	PCDD DETECTED
WOOD/BARK BOILERS	EXPERIMENTAL RESULTS WITH PCP TREATED WOOD
CHARCOAL	EXPERIMENTAL RESULTS WITH PCP TREATED WOOD
BLACK LIQUOR	PCBS IN EFFLUENT
CEMENT/LIME KILNS (WITH HW)	PRECURSORS PRESENT
SMALL SPREADER-STOKER COAL BOILERS	FAVORABLE COMBUSTION CONDITIONS

PROPOSED RANKING CRITERIA

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- MEASURED TCDD LEVELS
- NUMBER OF PREVIOUS TESTS
- PRESENCES OF PCDD PRECURSORS
 - CHLOROPHENOLS
 - PCBs
 - CHLOROBENZENE
- SIZE OF SOURCE CATEGORY
 - NUMBER OF FACILITIES
 - QUANTITY OF FUEL BURNED
- FACILITY LOCATION AND POTENTIAL EXPOSURE
- COMBUSTION CHARACTERISTICS
 - TEMPERATURE
 - LOCAL AIR AVAILABILITY
 - AUXILLARY FUEL
 - RESIDENCE TIME
- FUEL CHARACTERISTICS
 - C:H RATIO (AROMATICS)
 - CHLORINE CONTENT
 - FUEL PROCESSING
 - MOISTURE CONTENT

TESTING PROTOCOL AND COSTS

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- SAMPLING PROCEDURES WILL BE BASED ON THE ASME PROTOCOL.
 - TRIPLICATE SAMPLES
 - SAMPLE QUANTITIES WILL ALLOW FOR INITIAL ANALYSIS AND ARCHIVED SAMPLES
 - SAMPLES WILL INCLUDE:
 - TOTAL GASEOUS AND PARTICULATE STACK EMISSIONS
 - INLET/OUTLET OF CONTROL DEVICES
 - FEED GRAB SAMPLES
 - BOTTOM ASH GRAB SAMPLES
 - ASH OR SLURRY FROM CONTROL DEVICES
- STANDARD EPA METHOD 5 TRAIN, MODIFIED TO INCORPORATE A SORBENT MODULE CONTAINING XAD-2.
- EMISSIONS CHARACTERIZATION.
 - STACK TEMPERATURE
 - MOISTURE CONTENT
 - CO₂, CO
 - O₂ CONTINUOUS MONITORING
 - TOTAL PARTICULATES
- COSTS
 - ESTIMATED SAMPLING COSTS: \$70,000 - \$90,000