EFFECT OF COMBUSTION TEMPERATURE ON THE ATMOSPHERIC STABILITY OF
POLYBROMINATED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS

Parag Birla

Department of Environmental Sciences and Engineering

School of Public Health

University of North Carolina

Chapel Hill, North Carolina 27599-7400

ABSTRACT

The incineration of materials containing polybrominated diphenyl ether (PBDPE) flame retardants can potentially lead to the formation of polybrominated dibenzo-*p*-dioxins and furans (PBDDs and PBDFs). Some of these compounds may exhibit toxicities similar to those of their chlorinated analogues. Little is known about the atmospheric stability of PBDDs and PBDFs. In this study PBDDs and PBDFs produced from the combustion of polyurethane foam containing 4.4% PBDPEs were injected into outdoor teflon film chambers and aged in the presence of sunlight under typical atmospheric conditions. Combustion temperatures in the range of 400-450°C were categorized as "low temperature" experiments and those in the range of 650-750°C as "high temperature" experiments. PBDDs and PBDFs have been found to occur predominantly in the particulate phase, thus filter samples were collected over time to ascertain the atmospheric stability of these compounds. Production of

PBDFs, namely, tetrabrominated-*p*-dibenzofuran (TBDF) and pentabrominated-*p*-dibenzofuran (PeBDF) and decay of tetrabrominated-*p*-dioxin (TBDD) was observed in "low temperature" experiments. Production of TBDF and PeBDF is believed to occur from photolysis of unburnt PBDPEs. TBDF, PeBDF and TBDD emissions from "high temperature" experiments were stable. Validation of PBDF and PBDD behavior was done by collecting particulate- and gas-phase samples of polycyclic aromatic hydrocarbons (PAHs). Particle-bound PAHs from "low temperature" experiments degraded while corresponding PAHs from "high temperature" experiments were stable. Particle formation and composition from the two kinds of experiments have been investigated to explain these differences. These observations suggest that under typical incinerator conditions particulate-bound emissions of these compounds will be transported over long distances. Incineration temperatures around 450°C can lead to unstable emissions with atmospheric half-lives of 1-2 h. The dependence of the atmospheric stability of incineration-generated pollutants on the combustion temperature is an important finding of this study.

ACKNOWLEDGEMENTS

I want to thank Prof. Kamens, my advisor, whose valuable guidance and patience made my work possible. I am grateful to everyone in my research group as they contributed immeasurably in my understanding of the principles related to analytical and atmospheric chemistry. I owe special thanks to Dr. Bagnell in the Pathology Department for his help with the scanning electron microscope and G. Dean Marbury for assistance in mass spectrometry analyses. Finally, I wish to thank Dr. Leith and Dr. Christman, who as readers, provided valuable suggestions in refining my work.

Funding for this project was received from The Office of Exploratory Research, Washington, D.C. (Grant# 5-35435). This grant financed my education at The University of North Carolina at Chapel Hill.

CONTENTS

LIST OF ABBREVIATIONS	(i), (ii)
PURPOSE	1
BACKGROUND	1
Formation of PBDDs and PBDFs	2
Gas/Particle Partitioning of PBDDs and PBDFs	3
Existing Work on Photodegradation of PXDDs and PXDFs	8
MATERIALS AND METHODS	13
Chamber Description	13
Ignition Vessel Description	16
Instrumentation	18
Sampling Procedure	19
Sample Extraction and Enrichment	22
Quantification of Sample Extracts	28
RESULTS AND DISCUSSION	41
PBDD and PBDF Analysis	41
PAH Analysis	69
Comparison of Particle Characteristics	77
CONCLUSIONS	92
RECOMMENDATIONS FOR ADDITIONAL RESEARCH	94
REFERENCES	95

LIST OF ABBREVIATIONS

BaA	Benz[a]anthracene
BaP	Benz[a]pyrene
BbF	Benz[b]fluoranthene
BkF	Benz[k]fluoranthene
BghiP	Benzo[ghi]perylene
DBA	Dibenz[a,h]anthracene
DCM	Dichloromethane
DD	Dibenzodioxin
DESE	Department of Environmental Sciences and Engineering
EAA	Electrical Aerosol Analyzer
ECD	Electron Capture Detector
Fluor.	Fluoranthene
GC	Gas Chromatograph
HpCDD	Heptachloro Dibenzo-p-dioxin
HRGC	High Resolution Gas Chromatography
HRMS	High Resolution Mass Spectrometry
HxBDPE	Hexabromo Diphenyl Ether
HxCDD	Hexachloro Dibenzo-p-dioxin
IP	Indeno[1,2,3-cd]pyrene
LAS	Laser Aerosol Spectrometer
OCDD	Octachloro Dibenzo-p-dioxin
PAH	Polycyclic Aromatic Hydrocarbon
PBB	Polybrominated Biphenyl
PBDD	Polybrominated Dibenzo-p-dioxin
PBDF	Polybrominated Dibenzofuran
PBDPE	Polybrominated Diphenyl Ether

PCDD	Polychlorinated Dibenzo- <i>p</i> -dioxin
PCDF	Polychlorinated Dibenzofuran
PCDPE	Polychlorinated Diphenyl Ether
PeBDD	Pentabrominated Dibenzo- <i>p</i> -dioxin
PeBDF	Pentabrominated Dibenzofuran
PeBDPE	Pentabrominated Diphenyl Ether
PeCDPE	Pentachlorinated Diphenyl Ether
PFK	Perfluorokerosene
Phenan.	Phenanthrene
PIC	Product of Incomplete Combustion
PUF	Polyurethane Foam
PXDD	Polyhalogenated Dibenzo- <i>p</i> -dioxin
PXDF	Polyhalogenated Dibenzofuran
SEM	Scanning Electron Microscope
SIM	Selected Ion Monitoring
SSA	Specific Surface Area
TBDD	Tetrabrominated Dibenzo- <i>p</i> -dioxin
TBDF	Tetrabrominated Dibenzofuran
TBDPE	Tetrabrominated Diphenyl Ether
TCDD	Tetrachlorinated Dibenzo- <i>p</i> -dioxin
TCDF	Tetrachlorinated Dibenzofuran
UNC	University of North Carolina at Chapel Hill

PURPOSE

This study assesses the effect of combustion temperature on the atmospheric stability of polybrominated dibenzo-*p*-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) on realistic soot particles generated from small scale combustion of materials containing brominated organics.

BACKGROUND

Polyhalogenated dibenzo-*p*-dioxins (PXDDs) and polyhalogenated dibenzofurans (PXDFs) are the by-products of certain chemical manufacturing or combustion processes involving precursor compounds and heat. Incineration of brominated or chlorinated organics can lead to the formation of PBDDs, PBDFs, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) as well as the mixed halogenated species. It has also been suggested that these chemicals may be ubiquitous as a consequence of trace chemical processes during combustion (Shaub and Tsang, 1983). In fact, Bacher and Ballschmiter (1991) have detected PXDDs and PXDFs in vehicle exhaust particulates, wood combustion and metal reclaiming processes. Over the last two decades, these contaminants have become a focus of concern on a worldwide basis because of their highly toxic properties (Schmidt, 1992).

The toxicity of PBDDs and PBDFs has not been as extensively studied as that of PCDDs and PCDFs. Current indications suggest that PBDDs and PBDFs are at least, if not more toxic to animals than PCDDs and PCDFs (Mason et al., 1987; Moore et al., 1979,

Ramalingam et al., 1986). Toxicity is related to halogen substitution in the lateral positions i.e. 2,3,7 and 8. Toxicity decreases as the number of substituents increases (Mason et al., 1987; Rappe, 1983). The ability of 2,3,7,8 TBDF to kill guinea pigs is similar to that of 2,3,7,8 TCDF (Moore et al., 1979) and 2,3,7,8 TBDD is a more potent inducer of enzymes affecting toxicity in chick embryos, arylhydrocarbon hydroxylase and 7-ethoxyresorufin diethylase than 2,3,7,8 TCDD.

Formation of PBDDs and PBDFs:

PBDD and PBDF emissions have three principal sources: (1) they can be present in the waste feed and pass through the combustion process without being destroyed, (2) they can be formed in the combustion process as products of incomplete combustion (PICs), and (3) they can be formed "de novo" in cooler areas downstream of the combustion products from elements and compounds that act as precursors (Acharya et al., 1991). The major routes of formation for PBDDs and PBDFs would be from combustion of chemically related compounds such as bromobenzenes, bromophenols, polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDPEs) (Buser, 1987; Shaub and Tsang, 1983). PBDFs have also been found to be formed from photolysis of PBDPEs (Lutes et al., 1992; Watanabe et al., 1987).

Currently bromine exists in municipal waste streams at levels that are 2-4% of chlorinated organics (Schafer and Ballschmiter, 1986). The industrial production of brominated organic precursors is increasing (Ramalingam et al., 1986),

particularly with respect to PBDPEs. In this study PBDPEs (industrial grade DE-71 consisting primarily of penta and tetra congeners as a 4.4% w/w component of polyurethane foam (PUF), Olympic Products, Greensboro, NC) are used as precursors to PBDDs and PBDFs. PBDPEs are used as flame retardants and are added to plastic, textiles, carpets, and other materials to reduce flammability and protect these materials in case of fire accidents. Production of PBDPEs was around 75 million pounds in 1988 at a growth rate of 15%/annum. The increased production of precursors to PBDDs and PBDFs coupled with increased use of incineration as a waste disposal technology are likely to increase atmospheric concentrations of PBDDs and PBDFs. Figure 1.1 depicts the mechanisms by which PBDDs and PBDFs can be formed from pyrolysis of PBDPEs (Bieniek et al., 1989; Lindahl et al., 1980). Figure 1.2 elucidates formation of PBDFs from photolysis of PBDPEs. Photodegradation of PBDPEs into PBDFs is dominated by debromination followed by ring closure to PBDFs (Norstorm et al., 1976).

Gas/Particle Partitioning of PBDDs and PBDFs:

Partitioning of PBDDs and PBDFs between gas and particle phases is important from the following standpoints: (1) chemical reactivity in the atmosphere is governed by the phase in which the contaminant is present, (2) deposition processes are different for gas-phase and particulate-phase species and (3) health effects of a pollutant are dependent on gas/particle partitioning of a contaminant. Experimental values of ϕ

FIGURE 1.1 MECHANISMS FOR FORMATION OF PBDDs AND PBDFs FROM PYROLYSIS OF PBDPEs

FIGURE 1.2 PHOTOLYSIS OF PBDPEs INTO PBDFs

$\phi = [\text{particulate phase}] / ([\text{particulate phase}] + [\text{vapor phase}])$ for TBDF, PeBDF and TBDD have been determined to be greater than 0.95 (Lutes, 1991). This implies that in the atmosphere PBDDs and PBDFs will be primarily bound to particulate mass.

Theoretical predictions of gas-particle partitioning have been based on Langmuirian adsorption isotherm (Bidelman et al., 1986; Junge, 1977; Pankow, 1987; Yamasaki et al., 1982). Junge (1977) derived the following equation to predict ϕ :

$$\phi = c_j \theta_j / (p_o + c_j \theta_j), \text{ where} \quad (\text{equation 1})$$

$$c_j = 760RTN_s e^{(Q_d - Q_v)/RT}$$

$$\theta_j = \text{concentration of aerosol surface area (cm}^2\text{cm}^{-3}\text{)}$$

$$p_o = \text{saturation vapor pressure at T (torr)}$$

$$R = \text{gas constant (=82cm}^3\text{atm mole}^{-1}\text{K}^{-1}\text{)}$$

$$T = \text{temperature (K)}$$

$$N_s = \text{moles of sorption sites per cm}^2 \text{ of aerosol}$$

$$= 1/N_o s_o, N_o = \text{Avagadro's number (= } 6.02 \times 10^{23} \text{ /mole)},$$

$$s_o = \text{surface area per sorption site (cm}^2\text{)}$$

$$= 3.33 \times 10^{-15} \text{ (Shaub and Tsang, 1985)}$$

$$Q_d = \text{enthalpy for desorption directly from surface (Kcal/mole)}$$

$$Q_v = \text{enthalpy of vaporization of the liquid (Kcal/mole)}$$

Equation 1 was used to predict values of ϕ for PBDDs and PBDFs. Comparison of experimental values from Lutes et al. (1992) to the theoretical values obtained from equation 1 was also done (shown in Table 1.1). It was found that a $(Q_d - Q_v) = 2$ kcal/mole led to theoretical values of ϕ that were in congruence

TABLE 1.1

EXPERIMENTAL AND THEORETICAL VALUES OF GAS-PARTICLE PARTITIONING

COMPOUND	Qd-Qv (Kcal/mole)	Po=PI (torr)	Surface Area (cm ² cm ⁻³)	PHI (TH.)	PHI (EX.)
TBDD	1	3.91E-07	5.68E-04	0.9869	0.998
TBDF	"	1.13E-06	"	0.9632	0.996
PeBDF	"	1.13E-07	"	0.9962	0.994
TBDD	2	3.91E-07	5.68E-04	0.9974	0.998
TBDF	"	1.13E-06	"	0.9924	0.996
PeBDF	"	1.13E-07	"	0.9992	0.994
TBDD	3	3.91E-07	5.68E-04	0.9996	0.998
TBDF	"	1.13E-06	"	0.9989	0.996
PeBDF	"	1.13E-07	"	0.9999	0.994

NOTES:

(1) Bidelman and Foreman (1987) suggest that the value of Po should be that of the sub-cooled liquid as opposed to solid.

(2) PI values were obtained from Mill (1989).

(3) Aerosol surface area concentration and PHI (EX.) were obtained from Lutes (1991).

with the observed values by Lutes et al. Bidelman and Foreman (1987) have cited experimental evidence that (Qd-Qv) is no more than 2 to 4 Kcal/mole for PAHs and organochlorines.

Since PBDDs and PBDFs occur primarily in the particulate-phase, the focus of research on the atmospheric stability of these compounds is relevant to their occurrence on atmospheric aerosols. Therefore, in this study the atmospheric stability of PBDDs and PBDFs has been determined by analyzing for their concentrations on the particles generated from incineration experiments.

Existing Work on Photodegradation of PXDDs and PXDFs:

Wingerter (1989) has predicted increased use of incineration through expansion of existing municipal waste combustors (MWCs) and construction of new ones due to a drastic shortfall in landfill space. Several studies have reported emissions of toxic air pollutants from existing MWCs equipped with air pollution control devices. Therefore, the atmospheric stability of toxic organic compounds emitted from MWCs is central to the use of incineration as a viable waste disposal technology. This issue is important because atmospheric fate and transport from source to sink ultimately results in biological exposure and uptake.

Currently a paucity of data exists on the atmospheric stability of PXDDs and PXDFs under realistic conditions. Indirect methods such as structural activity relationships, source receptor differences in congener or isomer distributions, and photolysis on glass surfaces or in solutions have been used

and photolysis on glass surfaces or in solutions have been used to estimate the extent of atmospheric reactions (Buser, 1988; Dulin et al., 1986; Nestricks et al., 1980; Podoll et al., 1986). In a recent work by Lutes et al. (1992) the atmospheric stability of PBDDs and PBDFs was ascertained using the smog chamber facility operated by the University of North Carolina at Chapel Hill (UNC).

A review of existing work on photodegradation of PXDDs and PXDFs has been included in Table 1.2, perusal of which reveals the following trends: (a) half-lives of PCDD and PCDF as compared to their brominated analogues are higher (b) PXDFs usually have shorter half-lives than their corresponding PXDDs and (c) solution-phase experiments usually yield shorter half-lives than the solid-phase experiments.

An important observation related to the current work in photodegradation of PXDDs and PXDFs is the effect of the reaction media on the photolysis of PXDDs and PXDFs. Buser (1988) has suggested that the first step in photodegradation of PXDFs and PXDDs is debromination and generation of their lower brominated radicals. This reaction is enhanced in the presence of good proton donors. Therefore, the nature of the media is an important variable as it can influence photodegradation through its ability to donate protons. The relative stability of PXDDs and PXDFs on solid-phase experiments as compared to the solution-phase experiments may imply that the latter have higher proton donating capacity. The effects of reaction media also elucidates

TABLE 1.2

REVIEW OF EXISTING LITERATURE ON PHOTODEGRADATION OF PXDDs AND PXDFs

INVESTIGATOR/S	ANALYTES	MEDIUM	IRRADIATION SOURCE	CONCENTRATION	HALF-LIFE
Buser (1988)	1,2,3,4 TBDD	i-octane	sunlight	5 ng/ μ l	3 min
	1,2,3,4 TCDD	"	"	"	380 min
	2,3,7,8 TCDD	"	"	"	14 min
	1,2,3,4 TCDF	"	"	"	180 min
	2,3,7,8 TCDF	"	"	"	220 min
	1,2,7,8 TCDF	"	"	"	600 min
	1,2,3,4 TBDD	"	"	1 ng/ μ l	2 min
	2,3,7,8 TBDD	"	"	"	0.8 min
	2,3,7,8 TBDF	"	"	"	0.7 min
	2,3,7,8 TCDD	"	"	"	200 min
	TCDD/F	"	artificial	5,1 ng/ μ l	28 days
	TBDD/F	"	lab. light	5,1 ng/ μ l	8 days
	1,2,3,4 TCDD	dispersed	sunlight		65 hr
	2,3,7,8 TCDD	as	"		300 hr
	1,2,3,4 TCDF	solid	"		95 hr
	2,3,7,8 TCDF	film	"		120 hr
Choudhry & Webster (1989)	1,2,3,7 TCDD	ACN	reactor		8.73 days
	1,3,6,8 TCDD	"	output		1.47 days
	PeCDD	"	290-310 nm		76.8 days
	HxCDD	"			31.9 days
	HpCDD	"			2392 days
	OCDD	"			863 days
Crosby et al. (1971)	2,3,7,8 TCDD	methanol	sunlight	5 mg/l	3 hr
	"	"	UV light	"	6 hr
	OCDD	"	"	2.2 mg/l	>24 hr
Dulin et al. (1986)	2,3,7,8 TCDD	water:ACN	313 nm	$3.61 \cdot 10^{-7}$ M	20 hr
	"	(90:10)	sunlight	"	26.3 hr
	"	hexane	313 nm	$3.36 \cdot 10^{-7}$ M	3 hr
Lutes et al. (1992)	PBDDs/ PBDFs	incinerator soot*	sunlight		175- 650 min

N.B.: ACN-acetonitrile

*"-using smog chambers

TABLE 1.2 (contd.)

REVIEW OF EXISTING LITERATURE ON PHOTODEGRADATION OF PXDDs AND PXDFs

INVESTIGATOR/S	ANALYTES	MEDIUM	IRRADIATION SOURCE	CONCENTRATION	HALF-LIFE
Kleatiwong et al. (1990)	2,3,7,8 TCDD	i-octane	310 nm	$3.1 \cdot 10^{-6}$ M	4 min
Liberti et al. (1978)	2,3,7,8 TCDD	glass surface	mercury lamp		2.3 hr
Muto et al. (1991)	2,3,7,8 TCDD	fly ash in water	254 nm		22.12 hr
Nestrick et al. (1980)	2,3,7,8 TCDD	glass surface	sunlamp (280-400 nm)	2ng/cm ²	8400 min
	1,2,3,9 TCDD	surface	"		121 min
	2,3,7,8 TCDD	n-hexa-decane	"	0.06ng/ μ l	56.8 min
	1,2,3,9 TCDD	decane	"	0.041ng/ μ l	584 min
Podoll et al. (1986)	2,3,7,8 TCDD	water	sunlight		21 hr *
	"	"	"		118 hr **

N.B.: *-summer, **-winter

the different half-life values obtained by Buser (1988), Crosby et al. (1971), Dulin et al. (1986), Nestrick et al. (1980) and Podoll et al. (1986) for solution-phase photolysis of 2,3,7,8 TCDD. These investigations used different media for the photolysis experiments (Table 1.2).

The disparity between the solid-phase and solution-phase experiments highlights the need for more realistic values of half-lives for PXDDs and PXDFs that are applicable to atmospheric aerosols. Preliminary work in this direction was carried out by Lutes et al. (1992) and revealed that half-lives for PBDDs and PBDFs on realistic soot particles are more comparable to the solid-phase experiments than to the solution-phase experiments. The study showed stable behavior of PBDDs and PBDFs obtained from combusting PBDPEs contained in PUF at combustion temperatures ranging from 640-760°C. Moreover, typical combustion temperatures in a MWC can vary widely (Benefenati et al., 1983; Hiraoka et al., 1987; Ozvacic et al., 1985; Tiernan et al., 1983). Minimal combustion temperatures have been reported to range from 320-1010°C. The effect of combustion temperature on the atmospheric stability of toxic emissions from incinerators is an unexplored area in air pollution research. This study addresses the effect of combustion temperature on the atmospheric stability of PBDDs and PBDFs on realistic atmospheric aerosols. Polycyclic aromatic hydrocarbons (PAHs) generated from the combustion experiments have also been quantified to gain a better insight into the behavior of PBDDs and PBDFs.

MATERIALS AND METHODS

Chamber Description:

The chambers selected for use in this study are located at the UNC smog chamber facility in Pittsboro, N.C. All but one of the experiments were conducted using identical 25m³ (see Figure 2.1) chambers referred to as East and West, which allowed for the performance of two simultaneous experimental runs under identical atmospheric conditions. One of the experiments was conducted in a 190m³ chamber (see Figure 2.2) designated as the Aerosol chamber. This chamber is equipped with two sets of gas and aerosol sampling manifolds that facilitate the collection of two sets of samples from the same experiment. Notwithstanding the dissimilarity in the geometries of the chambers, they are otherwise similar in the materials used in their construction. The framework of each chamber is enclosed by five mil Teflon FEP film (Livingstone Corp., Charlotte, N.C.). Jeffries et al. (1990) have shown that the five mil Teflon film transmits greater than 70% of the incident light (measured normal to the sun) from 300 to 700 nm and greater than 50% of the incident light at 350 nm between a 0° and 70° angle between the film plane and the sun. The chamber floors are covered with aluminium foil overlaid by Teflon film, hence light entering the chamber can be reflected off the floor and added to the total light flux inside the chamber. Sampling manifolds run down from the chambers to the sampling devices located in the laboratory. Chambers are equipped with exhaust fans and vents for air exchange with the

FIGURE 2.1 EAST AND WEST CHAMBERS

FIGURE 2.2 AEROSOL CHAMBER (Chamber Volume = 190m³)
(drawing not to scale)

rural air. Several air exchanges were performed before and after each experiment. Mixing fans inside the chambers ensure proper mixing of the air parcel to be studied. Dilution rate, as determined with an SF_6 tracer, was about 5%/hr for the Aerosol chamber and about 10%/hr for East and West chambers.

Ignition Vessel Description:

An ignition vessel was custom-built in the workshop of Department of Environmental Sciences and Engineering (DESE) at UNC for the of this study (Figure 2.3). The inside diameter of the ignition vessel was 5", the outside diameter was 8" and it was 15" high. Combustion was contained inside the incinerator by stainless steel walls which were insulated with kaolinite wool from the external surface. The walls of the incinerator could withstand temperatures as high as 1500°C. The flame was generated by a flat burner using liquified petroleum gas as the fuel. Air inlets were provided below the burner through which air entered the combustion region. The amount of air entering the combustion zone could be regulated by controlling the opening at the inlet. No provision was made for a secondary air source. Heat distribution grids were provided for equitable distribution of heat and thus stable temperatures were attainable over short periods of time. The temperature in the combustion vessel was measured via a thermocouple (Omega, Stamford, CT). Thermocouple wires were made of Nickel-Chromium and Nickel-Aluminium respectively. The reference junction was maintained at 0°C by immersing the junction in iced water. The thermocouple was

FIGURE 2.3 LONGITUDINAL SECTION OF THE IGNITION VESSEL

capable of measuring temperatures up to 1250°C. The sample was introduced into the combustion zone by means of a plunger and the combustion occurred on a grid located 4" above the burner. The thermocouple was positioned so as to record the temperature prevalent near the sample grid. Fluctuations in combustion temperature were avoided by combusting small amounts of PUF i.e. about 0.5g at a time.

Instrumentation:

Instruments were available in the laboratory below the chamber for characterization of experimental conditions and particles generated from the combustion of PUF (containing PBDPE mixture DE-71). Chamber ozone and oxides of nitrogen were monitored with chemiluminescent monitors (Bendix Model 8101-B and 8002 analyzers, Lewisburg, WV). Relative humidity and chamber temperatures were measured by a thermohygrometer (Hanna Model# 8564, Fisher Instruments, Raleigh, NC). A total solar radiation sensor (an Epply, Newport, RI, black and white pyranometer) was located on the floor of the chamber. Particle size distribution data were taken with an Electrical Aerosol Analyzer, EAA, (TSI, Inc., St. Paul, MN) and a Laser Aerosol Spectrometer, LAS, (PMS, Inc., Boulder, CO). In addition to real time monitoring of aerosols, 0.1 μm nucleopore filter samples were collected and analyzed on Scanning Electron Microscope, SEM, located in the Pathology Department at UNC. Dilution rates were measured by a gas chromatograph/electron capture detector (GC/ECD) using SF_6 as a tracer.

Sampling Procedure:

Emissions from the ignition vessel were injected into the chambers by a flexible steel rimmed transfer manifold (5 cm internal diameter). Valves were used to direct the air parcel into the appropriate chamber for aging. During the aging period, air samples were collected by passing chamber air via a 15mm glass manifold through a sampling train that contained 47mm T60 A20 Teflon impregnated glass fiber filters (Pallflex, Putnam, CT), for the collection of particulates followed by a 4" x 1.5" PUF (Olympic Products, Greensboro, NC) vapor trap for collection of gas-phase pollutants. The PUF used for sample collection did not contain PBDPEs and was Soxhlet extracted in toluene and dried prior to use. Samples were collected for periods ranging from 30 to 50 minutes at flow rates of 35 to 50 lpm (face velocities ranging from 34-48 cm/s) over approximately four hour durations. Filter weights were determined using a three place milligram balance (Sartorius balance model 4503-MP6). Background samples were collected during each experiment to estimate background concentrations of analytes. Background concentrations of the analytes of interest were below 1% of the concentration in the filter samples collected from the various experiments. Background filter mass suggested background aerosol concentrations of 20-30 $\mu\text{g}/\text{m}^3$.

Gas samples for NO_x and O_3 meters were drawn through a 12 mm i.d. glass tube extending from the chamber to the laboratory. The top of the manifold is in the shape of a "U tube" and permits

TABLE 2.1**COMPARISON OF EXPERIMENTAL CONDITIONS**

	AUG. 21, 1991 East Chamber	AUG. 21, 1991 West Chamber	NOV. 5, 1991 East Chamber	NOV. 5, 1991 West Chamber
Chamber Temperature (deg. C)	32.5-40.5	30-42	19.5-22.2	20.2-21.8
Relative Humidity (%)	76-83	73-76	10-13	11-13
Incinerator Temperature (deg. C)	400	745	780	780
Total Solar Radiation (cal./cm ² /min)	0.32-0.85	NA	0.08-0.63	NA
NO Concentration (ppm)	0-0.002	0-0.32	0-0.074	0-0.094
NO ₂ Concentration (ppm)	0.01-0.016	0.02-0.16	0.01-0.061	0.01-0.074
O ₃ Concentration (ppm)	0-0.07	0-0.24	0-0.06	0-0.05
Injection Time	10:01 a.m.	10:12 a.m.	10:58 a.m.	11:01 a.m.
Mass of PUF Combusted (g)	1.4899	1.6945	0.4841	0.6378

TABLE 2.1 (contd.)**COMPARISON OF EXPERIMENTAL CONDITIONS**

	MAY 21, 1992 Aerosol Chamber	OCT.03, 1992 East Chamber	OCT.03, 1992 West Chamber
Chamber Temperature (deg. C)	26.3-26.7	23.9-27.4	24.1-27.1
Relative Humidity (%)	46-45	42-39	42-39
Incinerator Temperature (deg. C)	470	470	470
Total Solar Radiation (cal./cm ² /min)	0.26-0.93	0.24-0.86	NA
NO Concentration (ppm)	0-0.002	0-0.016	0-0.013
NO ₂ Concentration (ppm)	0-0.005	0.01-0.026	0.01-0.021
O ₃ Concentration (ppm)	0-0.045	0-0.041	0-0.014
Injection Time	9:49-10:05 a.m.	10:15 a.m.	10:25 a.m.
Mass of PUF Combusted (g)	3.9123	2.0876	1.9672

the attachment of a 47mm Teflon film holder. Pallflex (T60 A20) Teflon impregnated glass fiber filters were used to exclude particles in the gas stream before air entered the gas sampling manifold. Sampling lines from the chambers were also connected to aerosol sizing instruments.

Table 2.1 shows a comparison of the experimental conditions. Experiments conducted in the temperature range 700-800°C have been categorized as "high temperature" experiments/burns and those in the range 400-500°C as "low temperature" experiments/burns. Variation in solar radiation during the course of these experiments is depicted in Figures 2.3 and 2.4.

Sample Extraction and Enrichment:

Procedure for PBDDs and PBDFs:

Procedures for the analysis of PBDDs and PBDFs were based on EPA method 8290 (Stanley and Sack, 1986). Isotopically labeled, $^{13}\text{C}_{12}$ PBDDs and PBDFs (Cambridge Isotope Laboratory, Woburn, MA) were used as internal standards. 12.5 ng of each species was added to the filter samples from a standard solution in toluene that contained each species at a concentration of 50pg/ μl . After addition of the internal standard, the particulate samples were extracted in 400 ml of toluene (all solvents were Fisher Optima grade, Pittsburgh, PA). The toluene extracts were then evaporated and solvent exchanged until they were contained in approximately 5 ml of hexane (Buchi Rotovapor R-110). The extracts were then passed through a series of three gravity columns; acidic silica gel, florisil and carbon/celite to enrich

FIGURE 2.4 TOTAL SOLAR RADIATION VS. TIME

FIGURE 2.5 TOTAL SOLAR RADIATION VS. TIME

the content of PBDDs and PBDFs in the soxhlet extract. This eased the process of quantitation as possible interferences like PBDPEs were separated. All laboratory work was carried out under conditions that excluded natural light. Artificial lights shielded against ultraviolet radiation were used in the laboratory. As a further precaution the samples were kept wrapped in foil to exclude light. The samples were stored in a refrigerator at 5°C when they were not being worked upon.

In order to perform the silica gel column cleanup the column packing (Bio-sil A, 100-200 mesh, Bio-Rad Laboratories, Richmond, CA) required activation. Activation involved heating the material in the oven at a 180°C for 90 minutes. After being allowed to cool, the material was washed with methanol and dichloromethane (DCM). The material was then reheated at slow temperature gradient spanning from 50°C to 180°C so that solvent was vaporized. The activated silica gel was stored in a dessicator. The silica gel column was prepared by plugging the tip of a 25 ml pipet (from which the upper constriction had been cut off) with glass wool and adding 8 g of silica gel (Bio-Sil A) and a 1 to 2 cm layer of sodium sulfate. The column was then washed with three 10 ml portions of hexane and the eluate solvent was discarded. All of the following eluate was then collected. The sample extract, in about 5 ml of hexane, was loaded along with two 5 ml rinses of the sample container. This was followed by elution with 120 ml of hexane. The eluate was rotary evaporated to approximately 5 ml in hexane for further

enrichment.

The next step in analysis for PBDDs and PBDFs was the florisil column cleanup. This separation was performed in a specially prepared piece of glassware consisting of a 250 ml round bottom flask fused to the top of a 100 ml buret, referred to as a reservoir column (University Research Glassware, Chapel Hill, NC). The column was plugged with glass wool and 30g of florisil (60-100 mesh, Fisher Chemical) was added, followed by a 1 inch layer of sodium sulfate. The eluate from the silica gel column was then loaded onto the florisil column and allowed to settle for 1 to 2 minutes. The round bottom was rinsed four times with 5 ml of hexane which was also added to the column. Following this 250 ml of hexane was eluted through the column and discarded. The eluate obtained by running 250 mls of 35/65 v/v DCM/hexane was collected for further analysis. This eluate was solvent exchanged to hexane and transferred to a 15 ml tube where it was reduced to 1 ml by nitrogen evaporation. This led to the last step in the cleanup of samples for PBDD and PBDF analysis i.e. the carbon column.

The carbon column was prepared by cutting a 2 ml pipet at the 1.8 ml mark. A carbon celite mixture was prepared from 62 g of celite 545 (Fisher, Pittsburgh, PA) and 5.35 g of Carbon AX-21 (Anderson Development Co., Adrian, MI). The column was plugged with glass wool to the 0.53 ml mark, filled with carbon/celite mixture to the 0 ml mark and a glass wool plug was then placed on top. Three solvent mixtures were prepared and designated as

follows: A - 50/50 v/v benzene (Fisher certified 99%)/ethyl acetate, B - 50/50 v/v DCM/cyclohexane and C - 50/50 v/v DCM/hexane. The column was pre-eluted with 2 ml of A, 1 ml of B and 2 ml of hexane. The sample, in 1 ml of hexane, was then loaded. The sample container was rinsed twice with 0.5 ml portions of hexane and loaded onto the column. The sample tube was also rinsed with a 2 ml portion of C and a 2 ml portion of A each of which were added to the column. After elution of these rinses, the column was reversed and PBDDs and PBDFs were eluted with 10 ml toluene. This fraction was then evaporated under nitrogen to approximately 1 ml and then transferred to a 1.5 ml vial. Following this the sample was nitrogen evaporated to near dryness. A 50 μ l aliquot of toluene was added and the sample was stored for analysis. Isotopically labeled ^{13}C hexachlorinated dibenzo-p-dioxin was added as an external standard immediately prior to analysis as a recovery standard.

Procedure for PBDPEs:

Enrichment procedure for PBDPE analysis was similar to that for PBDD and PBDF, except that the carbon column was excluded in the chromatographic process. Smith et al. (1984) have found that polychlorinated diphenyl ethers (PCDPEs) are retained by the carbon column, therefore, it is expected that PBDPEs can also be retained by the carbon column.

Procedure for PAHs:

β,β -binaphthyl was used as the internal standard for PAH analysis. Each filter was spiked with 10 μ l of a standard

solution containing β,β -binaphthyl at a concentration of 10ng/ μ l. Soxhlet extraction for PAHs was done in 30 ml of DCM. Loss of analytes due to volatilization can be of concern for compounds having low volatility like phenanthrene (Daisey et al., 1986). This fact prompted the use of DCM for extraction of particulate samples for PAHs. The extract was then blown down to a volume of 2 ml using a Kuderna-Danish column. Following this the entire sample was transferred to a centrifuge tube and the sample container was rinsed thrice with approximately 1 ml of DCM for a total rinsing volume of 3 ml. These were also transferred to the centrifuge tube. After further reduction of this extract by nitrogen evaporation, solvent exchange was performed with acetonitrile to a final volume of 100 μ l. This was used for further analysis.

Quantification of Sample Extracts:

PBDD & PBDF Analysis:

Quantification of samples for PBDDs and PBDFs was done by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) in accordance with EPA Method 8290 (Stanley and Sack, 1986). A Hewlett Packard 8290 Series II gas chromatograph interfaced to a VG 70-SEQ hybrid mass spectrometer was used for this purpose. Analysis was set up on a selected ion monitoring (SIM) mode at a resolving power of 10,000 (10% valley definition) and a dwell time of 50 msec/ion. Gas chromatographic separation of the PBDDs and PBDFs was obtained by using a 30m, 0.32 mm ID DB-5 column (J&W Scientific, Folsom, CA) and fused

TABLE 2.2

PBDDs & PBDFs Monitored in HRGC/HRMS and Time Windows

Group 1 - 5:00 - 16:50 minutes

<u>MASS</u>	<u>ANALYTE</u>	<u>ION TYPE</u>
401.856	*Hexachlorodibenzo-p-dioxin	M+2
403.853	*Hexachlorodibenzo-p-dioxin	M+4
481.698	Tetrabromodibenzofuran	M+2
483.696	Tetrabromodibenzofuran	M+4
493.738	*Tetrabromodibenzofuran	M+2
495.736	*Tetrabromodibenzofuran	M+4
497.692	Tetrabromodibenzo-p-dioxin	M+2
499.690	Tetrabromodibenzo-p-dioxin	M+4
509.733	*Tetrabromodibenzo-p-dioxin	M+2
511.731	*Tetrabromodibenzo-p-dioxin	M+4
565.620	Pentabromodiphenyl ether	M+6
643.530	Hexabromodiphenyl ether	M+6
466.973	PFK (lock mass)	

Group 2 - 16:50 - 22:00 minutes

<u>MASS</u>	<u>ANALYTE</u>	<u>ION TYPE</u>
561.606	Pentabromodibenzofuran	M+4
563.604	Pentabromodibenzofuran	M+6
573.646	*Pentabromodibenzofuran	M+4
575.644	*Pentabromodibenzofuran	M+6
577.601	Pentabromodibenzo-p-dioxin	M+4
579.599	Pentabromodibenzo-p-dioxin	M+6
589.641	*Pentabromodibenzo-p-dioxin	M+4
591.639	*Pentabromodibenzo-p-dioxin	M+6
643.530	Hexabromodiphenyl ether	M+6
721.441	Heptabromodiphenyl ether	M+6
566.966	PFK (lock mass)	

Group 3 - 22:00 - 30:00 minutes

<u>MASS</u>	<u>ANALYTE</u>	<u>ION TYPE</u>
641.514	Hexabromodibenzofuran	M+6
643.512	Hexabromodibenzofuran	M+8
657.509	Hexabromodibenzo-p-dioxin	M+6
659.507	Hexabromodibenzo-p-dioxin	M+8
669.549	*Hexabromodibenzo-p-dioxin	M+6
671.547	*Hexabromodibenzo-p-dioxin	M+8
721.441	Heptabromodiphenyl ether	M+6
801.349	Octabromodiphenyl ether	M+8
616.963	PFK (lock mass)	

N.B.: '*' denotes ¹³C labeled analytes

silica on column injection. The temperature program was 150°C for 1 min, increased at a rate of 20°C/min to 170°C and then 6°C/min to 300°C followed by a 8 min. hold. The column head pressure was maintained at 25 PSI yielding a helium flow rate of 0.13 ml/min. This temperature facilitated elution of the analytes in three distinct time windows. Table 2.2 describes each time window and the ions monitored in the window. High resolution permitted identification of fragment ions of PBDPEs that can appear at the same exact mass of PBDFs as interferences. The ratio between the halogen containing fragments, the absence of interfering ions and the relative retention time were used as criteria to confirm the presence of PBDDs and PBDFs. Since standards for all of the possible TBDD, TBDF and PeBDF isomers were not available, therefore, identification of such compounds excluded the criterion involving relative retention time.

A six point calibration curve was obtained for each set of samples. The analytical procedure has been characterized by Lutes (1991). Standards used for construction of the calibration curves are described in Table 2.3. An additional five point calibration curve for TBDF was obtained so that response factors, defined as the ratio of the area of unlabeled analyte to the area of the internal standard, were comparable to some concentrated samples. Typical calibration curves of PBDDs and PBDFs quantified are shown in Figures 2.6 and 2.7.

PBDPE Analysis:

Quantitation for PBDPEs was done on the same instrumental

FIGURE 2.6 CALIBRATION CURVE FOR 2,3,7,8 TBDF

(Internal Standard at 250pg/μl)

Response Factor = Area of Analyte/Area of IS

FIGURE 2.7 CALIBRATION CURVE FOR 2,3,7,8 TBDD & 1,2,3,7,8 PeBDF
 (Internal Standard at 250pg/μl)
 Response Factor = Area of Analyte/Area of IS

TABLE 2.3

Standards Used for PBDD & PBDF Calibration Curves

Standard Name	Concentration of 13C IS				Concentration of 12C Native			
	TBDF	PeBDF	TBDD	PeBDD	TBDF	PeBDF	TBDD	PeBDD
1	250	250	250	250	1000	1000	1030	1270
2	250	250	250	250	500	500	515	635
3	250	250	250	250	50	50	51.5	63.5
4	250	250	250	250	10	10	10.3	12.7
5	250	250	250	250	1.25	1.25	1.29	1.59
6	250	250	250	250	0	0	0	0
7	250	0	0	0	5000	0	0	0
8	250	0	0	0	10000	0	0	0
9	250	0	0	0	50000	0	0	0
10	250	0	0	0	100000	0	0	0
11	250	0	0	0	1000000	0	0	0

N.B.: All Concentrations are in pg/μl

TABLE 2.4

PBDFs & PBDPEs Monitored in HRGC/HRMS and Time Windows

Group 1 - 5:00 - 16:50 minutes

MASS	ANALYTE	ION TYPE
401.856	*Hexachlorodibenzo-p-dioxin	M+2
403.853	*Hexachlorodibenzo-p-dioxin	M+4
481.698	Tetrabromodibenzofuran	M+2
483.696	Tetrabromodibenzofuran	M+4
483.714	Tetrabromodiphenyl ether	M+2
485.712	Tetrabromodiphenyl ether	M+4
493.738	*Tetrabromodibenzofuran	M+2
495.736	*Tetrabromodibenzofuran	M+4
563.622	Pentabromodiphenyl ether	M+4
565.620	Pentabromodiphenyl ether	M+6
643.530	Hexabromodiphenyl ether	M+6
466.973	PFK (lock mass)	

Group 2 - 16:50 - 25:00 minutes

MASS	ANALYTE	ION TYPE
561.606	Pentabromodibenzofuran	M+4
563.604	Pentabromodibenzofuran	M+6
563.622	Pentabromodiphenyl ether	M+4
565.620	Pentabromodiphenyl ether	M+6
573.646	*Pentabromodibenzofuran	M+4
575.644	*Pentabromodibenzofuran	M+6
643.530	Hexabromodiphenyl ether	M+6
645.528	Hexabromodiphenyl ether	M+8
566.966	PFK (lock mass)	

N.B.: '*' denotes 13C labeled analytes

set up as for PBDDs and PBDFs. Instrumental conditions were also the same although a different experiment was used for SIM (Refer to Table 2.4). Isotopically labeled internal standards were not available for the respective PBDPEs, therefore, quantitation was based on respective ^{13}C PBDFs. TBDPE was quantified with respect to ^{13}C TBDF and ^{13}C PeBDF was used as a surrogate for ^{13}C PeBDPE and ^{13}C HxBDPE. Identification of respective PBDPEs was based on isotope ratios of halogen fragments and on relative retention times.

Response factors were based on a one point calibration. It was assumed that the calibration curve was linear through the origin. Response factors were calculated by analyzing a solution of DE-71 (the precursor to PBDDs and PBDFs contained in the PUF combusted) at a known concentration. Samples contained the same isomers of PBDPEs as those present in the DE-71 solution. Response factors were obtained by introducing $1\mu\text{l}$ of DE-71 at $1405\text{ ng}/\mu\text{l}$ along with $1\mu\text{l}$ of a solution containing ^{13}C TBDF and ^{13}C PeBDF at $250\text{ pg}/\mu\text{l}$ (the concentration of internal standard in a $50\mu\text{l}$ extract of particulate samples assuming 100% extraction efficiency). Lutes (1991) has determined that TBDPE, PeBDPE and HxBDPE constitute 40%, 57% and 3% respectively of DE-71. This finding was utilized to arrive at response factors for TBDPE, PeBDPE and HxBDPE.

PAH Analysis:

PAHs were quantified by HRGC/HRMS on the same instrumental set up as used for other analyses. A different temperature

program was used for gas chromatographic separation of the analytes. The initial temperature was 120°C for 1 min., increased at a rate of 20°C/min. to 170°C and then 6°C/min. to 300°C followed by a four minute hold. The column head pressure was maintained at 15 PSI yielding a helium flow rate of 0.10 ml/min. Dwell time was set at 80 msec./ion at a resolution of 10,000. The elution of PAHs was categorized into four time windows as described in Table 2.5. One ion was monitored for each compound, therefore, identification of PAHs was based on their respective relative retention times.

Response factors for PAHs (area of PAH/area of β,β -binaphthyl) were obtained by using SRM 1647b (NIST, Gaithersburg, MD). A four point calibration curve was constructed by using 1:5, 1:10, 1:20 and 1:50 dilutions of SRM 1647b (see Table 2.6) containing the internal standard β,β -binaphthyl at 1 ng/ μ l. Typical calibration curves for PAHs quantified are shown in Figures 2.8, 2.9 and 2.10.

TABLE 2.5

PAHs Monitored in HRGC/HRMS and Time Windows

Group 1 - 4:00 - 11:00 minutes

<u>MASS</u>	<u>ANALYTE</u>	<u>ION TYPE</u>
128.063	Naphthalene	M+
152.063	Acenaphthylene	M+
154.078	Acenaphthene	M+
166.078	Fluorene	M+
161.990	PFK (lock mass)	

Group 2 - 4:00 - 11:00 minutes

<u>MASS</u>	<u>ANALYTE</u>	<u>ION TYPE</u>
178.078	Phenanthrene	M+
178.078	Anthracene	M+
202.078	Fluoranthene	M+
202.078	Pyrene	M+
192.989	PFK (lock mass)	

Group 3 - 11:00 - 20:00 minutes

<u>MASS</u>	<u>ANALYTE</u>	<u>ION TYPE</u>
228.094	Benz[a]anthracene (BaA)	M+
228.094	Chrysene	M+
252.094	Benzo[b]fluoranthene (BbF)	M+
252.094	Benzo[k]fluoranthene (BkF)	M+
252.094	Benzo[a]pyrene (BaP)	M+
254.110	β,β -Binaphthyl	M+
242.986	PFK (lock mass)	

Group 4 - 20:00 - 28:00 minutes

<u>MASS</u>	<u>ANALYTE</u>	<u>ION TYPE</u>
254.110	β,β -Binaphthyl	M+
276.094	Benzo[ghi]perylene (BghiP)	M+
276.094	Indeno[1,2,3-cd]pyrene (IP)	M+
278.110	Dibenz[a,h]anthracene (DBA)	M+
268.982	PFK (lock mass)	

TABLE 2.6

Standards Used for PAH Calibration Curves

ANALYTE	***** Dilutions of SRM 1647b *****			
	1:5	1:10	1:20	1:50
Naphthalene	3.96	1.98	0.99	0.396
Acenaphthylene	3.23	1.615	0.8075	0.323
Acenaphthene	3.978	1.989	0.9945	0.3978
Fluorene	1.552	0.776	0.388	0.1552
Phenanthrene	0.788	0.394	0.197	0.0788
Anthracene	0.94	0.47	0.235	0.094
Fluoranthene	0.984	0.492	0.246	0.0984
Pyrene	1.676	0.838	0.419	0.1676
BaA	0.788	0.394	0.197	0.0788
Chrysene	0.738	0.369	0.1845	0.0738
BbF	0.832	0.416	0.208	0.0832
BkF	0.94	0.47	0.235	0.094
BaP	0.984	0.492	0.246	0.0984
BghiP	0.752	0.376	0.188	0.0752
IP	0.874	0.437	0.2185	0.0874
DBA	0.728	0.364	0.182	0.0728
β,β -Binaphthyl	1	1	1	1

N.B.: All concentration are ng/ μ l

FIGURE 2.8 CALIBRATION CURVE FOR PHENANTHRENE

FIGURE 2.9 CALIBRATION CURVE FOR FLUORANTHENE & PYRENE

FIGURE 2.10 CALIBRATION CURVE FOR BaA & Chrysene

RESULTS AND DISCUSSION

PBDD and PBDF Analysis:

"High Temperature" Experiments:

As mentioned previously, "high temperature" experiments are categorized as burns carried out in the temperature range 700-800°C. Two "high temperature" experiments were carried out in order to demonstrate that the work of Lutes et al. (1992) could be repeated. TBDF, PeBDF and TBDD were the compounds detected. It was not possible to identify specific isomers since appropriate standards were not available. TBDF, PeBDF and TBDD isomers were detected in accordance with the identification criteria specified in the last chapter. In all experiments TBDF concentrations were greater than TBDD. Figure 1.1 evinces that formation of PBDDs from PBDPEs is an intermolecular process while the formation of PBDFs from PBDPEs is most likely an intramolecular process. This elucidates the predominance of PBDFs over corresponding PBDDs in the filter samples collected from our experiments. Buser (1986), Bieniek et. al. (1989), Czuczwa and Hites (1984), Visalli (1987) have also reported similar findings related to dioxin and furan concentrations in environmental samples.

As mentioned in the previous chapter, two "high temperature" experiments were carried out on August 21, 1991 and on November 5, 1991. Behavior of TBDF, PeBDF and TBDD over time in the presence of sunlight is shown in Figures 3.1, 3.2 and 3.3 respectively. Error bars around each point denote ± 2 standard

FIGURE 3.1 TBDF CONCENTRATION VS CHAMBER AGING TIME

FIGURE 3.2 PeBDF CONCENTRATION VS CHAMBER AGING TIME

FIGURE 3.3 TBDD CONCENTRATION VS CHAMBER AGING TIME

deviations (Lutes, 1991). Table 3.1 shows the results of regression analysis of concentration (mass of analyte/mass of particulate) against time on these curves. The units of slope in all cases is concentration per time, therefore, it may be ng/mg/hr or $\mu\text{g/mg/hr}$ depending upon the units of concentration for the particular compound. This format has been followed for other such analyses in this chapter.

From Table 3.1, it is evident that the slopes are insignificant at a 10% significance level. Hence, it can be concluded that there is no significant decay of these compounds. These results also support conclusions by Lutes et. al. (1992). Laboratory experiments performed by Buser (1988) for the photostability of PBDDs and PBDFs sorbed on solid surfaces are in better agreement with these observations as opposed to photodegradation experiments conducted in solutions. Solid phase photolysis involved dispersion of compounds as thin films in quartz vials. These experiments yielded half-lives of approximately 30 hrs for 1,2,3,4-TBDD, 2,3,7,8-TBDD and 2,3,7,8-TBDF. Half-lives were of the order of minutes when the same compounds were photolyzed in i-octane solution. Therefore, results from solution-phase experiments can underestimate the half-lives of PBDDs and PBDFs on atmospheric soot particles from high temperature combustion.

Perusal of Table 2.1 reveals that conditions with respect to relative humidity and chamber temperature for the experiment on August 21, 1991 differ largely from the one on November 5, 1991.

TABLE 3.1.

Significance of the Slopes of Concentration vs Time Plots

High Temperature* Experiments						
Compound	August 21, 1991			November 5, 1991		
	Slope	P-value	R-Sq.	Slope	P-value	R-Sq.
TBDF	-0.2371	0.3586	0.2116	-1.4436	0.1342	0.5808
PeBDF	-8.8167	0.3593	0.2111	-1.0836	0.322	0.3181
TBDD	0.1246	0.8344	0.0123	0.0126	0.7985	0.0253

PC-SAS was used for Linear Regression Analysis

Units of Slope are Concentration/Time

Level of Significance = 10%

However, the stable behavior of the analytes in both cases renders these parameters inconsequential in assessment of the atmospheric stability of brominated dioxins and furans.

"Low Temperature" Experiments:

"Low temperature" burns were conducted on August 21, 1991 and May 21, 1992. These experiments were carried out in the temperature range 400-500°C. No TBDD could be detected in the samples collected from the latter experiment, hence, a "low temperature" experiment was conducted on October 3, 1992 to verify TBDD behavior observed in August 21, 1991 experiment. The results from these experiments are presented in Figures 3.4, 3.5, 3.6 and 3.7. Linear regression analysis was performed on these curves to test for the significance of slopes and the appropriate p-values have been included in Table 3.2.

Significant negative slopes for TBDD is an indication of unstable behavior. Assuming a first-order decay of TBDD yields half-lives of 1.46 ($r^2=0.90$) and 2.06 ($r^2=0.51$) hrs for October 3, 1992 and August 21, 1991 experiments respectively. This is a departure from the stable TBDD behavior exhibited in "high temperature" experiments and the half-lives are more comparable to the solution-phase experiments by Buser (1988). This difference can be explained on the basis of particle characteristics.

Particulate matter collected on the filters revealed a different color for the two kinds of experiments. Particulate matter collected from the "high temperature" experiments were

FIGURE 3.4 TBDF CONCENTRATION VS CHAMBER AGING TIME

"LOW TEMPERATURE" PARTICLE

"HIGH TEMPERATURE" PARTICLE

FIGURE 3.8 POSTULATED COMPOSITION OF PARTICLES GENERATED FROM COMBUSTION EXPERIMENTS

while diesel soot has a thin organic coating of predominantly non-polar compounds (Japar et al., 1984; Schuetzle et al., 1981). McDow et al. (1991, 1992) have shown that the presence of methoxyphenols enhances the photodegradation of PAHs in solution.

Differences in physical and chemical properties of the particles generated from the "high temperature" and "low temperature" experiments may account for the incongruence in TBDD behavior between the two kinds of experiments. Absence of an organic layer coating in particles from "high temperature" experiments can be expected as most of the volatile organics should be oxidized and there should be very little PICs to form the organic layer. Thus particles from "high temperature" experiments mimic the solid-phase experiments carried out by Buser (1988) while particles from "low temperature" experiments may be similar to the solution-phase experiments as PBDDs and PBDFs may be dissolved in the organic layer surrounding the carbon core. For degradation of PBDDs and PBDFs dissolved in hydrocarbon solution reductive debromination has been suggested as the major decomposition pathway and occurs predominantly from the higher brominated carbon-ring and from the lateral-positions (Buser, 1988). The final products under these conditions are believed to be unsubstituted dibenzodioxin and dibenzofuran, which can undergo further reaction. A mechanism for such a pathway has been shown in Scheme 1. Such a mechanism for degradation of TBDD can also be prescribed for our experiments. Another possible mechanism of decay can involve generation of

SCHEME 1 POSSIBLE PATHWAY FOR TBDD PHOTODEGRADATION

SCHEME 2 POSSIBLE PATHWAY FOR TBDD DEGRADATION
INVOLVING CLEAVAGE OF DIOXIN LINKAGE

phenolic compounds by cleavage of the dioxin linkage (Hosaya et al., 1993). This mechanism has been depicted in Scheme 2.

Examination of Table 3.2 reveals that the slopes of TBDF and PeBDF are significant at a 10% level for all the experiments and the positive nature of the slope indicates that there is production of these compounds over time. Buser (1986) has shown that thermolysis of PBDPE flame retardants at temperatures of 510°C causes about 10% decomposition of the PBDPEs leading to the formation of PBDDs and PBDFs at a combined level of around 0.5-1%. These numbers should be reasonably valid for our "low temperature" experiments where temperatures are around 450°C. This implies that around 90% of the PBDPEs are unburnt which can photolyze to yield PBDFs and PBDDs. In fact, Lutes et. al. (1992) have demonstrated that there is 0.06% yield of TBDF over a four hour period from photolysis of flame retardant mixture DE-71 (exposed on filters in smog chambers), which is used in our system. Watanabe et. al. (1987) carried out solution-phase experiments for the formation of PBDDs and PBDFs from UV irradiation of decabromodiphenyl ether (DeBDPE). This study arrived at a yield of 20% over a sixteen hour period for the total amount of PBDFs. In another study photolysis of 2,2',4,4',5 pentachlorodiphenyl ether (PeCDPE) dissolved in cyclohexane yielded 14% TCDF after 4 hrs (Choudhry et al., 1977). These observations can be used to rationalize the production of TBDF in the "low temperature" experiments. Buser (1986) has also reported 96-97% destruction of PBDPEs at combustion temperatures

around 630°C, therefore, in "high temperature" experiments there should be very little unburnt PBDPEs in the chamber. Photolysis of this residual PBDPEs will yield insignificant amounts of PBDFs.

The major reaction pathway for formation of halogenated dibenzofurans from photolysis halogenated diphenyl ethers involves dehalogenation and ring closure to halogenated dibenzofurans (Norstorm et al., 1976; Watanabe et al., 1987). This implies that unburnt PeBDPE and HxBDPE from "low temperature" experiments can photolyze to yield TBDF. Formation of PeBDF can take place from photolysis of HxBDPE. Also, this implies that any degradation of PBDFs could have been confounded by this production.

In order to assess the production of TBDF from possible photolysis of residual PBDPEs, samples collected from the "low temperature" experiment on May 21, 1992 were split into two after the florisil column for PBDPE analysis. Smith et al. (1984) have mentioned the possibility of PCDPEs being retained by the carbon column, hence this was excluded for analysis of PBDPEs. Results from HRGC/HRMS analysis of PBDPEs are shown in Figures 3.9 and 3.10. Corresponding behavior of TBDF (ng/m^3) over time is plotted in Figure 3.11. In units of concentration as ng/m^3 , TBDF is stable over time. Therefore, the rate constant for TBDF concentration is zero. This rate constant is comprised of three components: a) production of TBDF due to ether photolysis (k_1) b) dilution of chamber air due to sampling, leaks and wall losses

FIGURE 3.5 PeBDF CONCENTRATION VS CHAMBER AGING TIME

FIGURE 3.6 TBDD CONCENTRATION VS CHAMBER AGING TIME

FIGURE 3.7 TBDF & PeBDF CONCENTRATION VS CHAMBER AGING TIME

TABLE 3.2.

Significance of the Slopes of Concentration vs Time Plots

"Low Temperature" Experiments									
Compound	August 21, 1991			May 21, 1992			October 03, 1992		
	Slope	P-value	R-Sq.	Slope	P-value	R-Sq.	Slope	P-value	R-Sq.
TBDF	-0.2371	0.3586	0.2116	17.7374	0.0005	0.9622	6.5104	0.0323	0.7214
PeBDF	-8.8167	0.3593	0.2111	8.6244	0.0015	0.9894	0.2419	0.0064	0.8727
TBDD	0.1246	0.8344	0.0123	N/A	N/A	N/A	-4.4803	0.0237	0.7595

PC-SAS was used for Linear Regression Analysis

Units of Slope are Concentration/Time

Level of Significance = 10%

dark brown or black in color while those from the "low temperature" experiments were light brown in color. Korfmacher et al. (1980) have argued that there may be an "inner-filter" effect: the darker substrates absorb more of the incident light which can reduce the rate of photolytic degradation of compounds adsorbed on the substrate. Another argument that can be put forward is the availability of higher specific area for the particles generated from "low temperature" experiments.

Particle composition is also a factor. There is a possibility that particles from "low temperature" experiments have an aerosol core with a coating of an organic layer with PBDFs and PBDDs dissolved in this organic layer as opposed to just an elemental core for particles from "high temperature" burns. An illustration of this concept is provided in Figure 3.8. Such a model would imply solution-phase photodegradation in the case of "low temperature" experiments. The organic layer may be constituted of products of incomplete combustion. It has been shown by Rau (1989) and Kamens et al. (1988) that wood smoke contains little elemental carbon and organics typically represent more than 90% of the total mass. In contrast, elemental carbon can constitute upto 50% of diesel exhaust (Watson, 1979). Further, Yu and Hites (1981) have found that only 10-40% of the mass is extractable in organic solvents. The chemical composition of the organic layer itself can influence the photodegradation. Wood smoke is composed of almost entirely polar organic material such as methoxyphenols (Hawthorne, 1989)

FIGURE 3.9 PeBDPE CONCENTRATION VS CHAMBER AGING TIME

FIGURE 3.10 HxBDPE CONCENTRATION VS CHAMBER AGING TIME

FIGURE 3.11 TBDF & SF₆ CONCENTRATION VS CHAMBER AGING TIME

(k_2) c) possible decay of TBDF (k_3). Since the net result of these processes is a stable concentration of TBDF, $k_1+k_2+k_3=0$.

Calculation of k_1 was done on the basis of results arrived at by Lutes et al. (1992) and Choudhry et al. (1977). Lutes obtained TBDF yields over a 4 hr period based on experiments involving exposure of DE-71 (the PBDPE mixture used in our experiments) spiked teflon impregnated glass fiber filters to sunlight. These experiments yielded TBDF yields of 0.06% (mass of TBDF formed/initial mass of PeBDPE and HxBDPE on the filter) over a 4 hr period, however, this work does not realistically represent the situation in the chambers. There is the possibility of PBDPE diffusing into the filter material and thus being shielded from sunlight. This is supported by the work of Kamens et al. (1985). BaP exposed to sunlight on filters had a much lower decay rate under summer outdoor light than BaP on wood soot particles. In our experiments photolysis is taking place with the ethers adsorbed on to the particles or in the gas phase. Choudhry et al. (1977) obtained a TCDF yield of 14% over a 4 hr period. Their work involved solution phase irradiation of 2,2',4,4',5 PeCDPE. Hence, this result may be equally unacceptable for our case as it involves extrapolation from the PCDPEs and the media is a solution. Moreover, TBDF yields from photolysis of HxBDPE cannot be estimated from the work of Choudhry et al. (1977). Due to lack of any further information on formation of PBDFs from photolysis of PBDPEs, it was decided to use these results. Initial concentration (C_0) of HxBDPE,

PeBDPE present in the particulate phase in the chamber was calculated from the curves plotted in Figures 3.9 and 3.10. These curves can be defined by an exponential function ($r^2 > 0.90$), hence C_0 can be calculated from the exponential equation defining the plots of PBDPEs vs time.

The amount of TBDF formed over a 4 hr period was calculated based on the initial amount of PBDPE (sum of PeBDPE and HxBDPE) present in the chamber and the yields arrived at from the results of Lutes et al. (1992) and Choudhry et al. (1977). The yield was converted into units of concentration by taking into account the fact that the chamber volume is 190 m^3 . It should be mentioned that TBDF yields have been calculated from photolysis of only the particulate phase PBDPEs. There can be PBDPE in the gas phase which can also photolyze to yield TBDF which can then be sorbed on the particles. However, this yield should be insignificant as most of the PBDPE should be on the particles analogous to the gas-particle partitioning of PBDFs and PBDDs. The value of k_1 , assuming that the rate of production of TBDF can be represented by a first-order rate constant, was then calculated. This analysis yielded k_1 values of $0.2\%/hr$ and $17.7\%/hr$ based on the works of Lutes et al. (1992) and Choudhry et al. (1977), respectively. Dilution rate from the chamber was determined using SF_6 tracer gas. This rate was evaluated to be $5.3\%/hr$ and the dilution curve is shown in Figure 3.11.

Values of k_3 can now be calculated since k_1 and k_2 have been determined and $k_1 + k_2 + k_3 = 0$. k_3 was found to be $5.1\%/hr$ and

-12.4%/hr based on the works of Lutes et al. (1992) and Choudhry et al. (1977) respectively. Therefore, if the effect of production of TBDF from photolysis of PBDPEs were to be excluded there may actually be decay of TBDF and a decay constant of the order of 12.4%/hr will support the degradation of TBDD in "low temperature" experiments. The proposed concept of the nature of particles formed (Figure 3.8) will support experiments conducted by Choudhry et al. (1977) in solution-phase for formation of TBDF from photolysis of PBDPE even though they used 2,2',4',5 PeCDPE in their experiments. The positive value of k_1 calculated from using a yield rate of 0.06%/hr as per Lutes et al. (1992) suggests that a yield of 0.06%/hr may actually be an underestimation for TBDF yields from photolysis of DE-71.

An interesting observation related to TBDF isomers for "low temperature" experiments involved changes in isomer distribution accounting for the total TBDF concentration at a given time. Identification of individual isomers not being possible, the four TBDF isomers are referred to as "TBDF1", "TBDF2", "TBDF3" and "TBDF4" respectively. Figure 3.12 is a chromatogram showing the order of elution of these isomers. Figures 3.13 and 3.14 show the variation in isomer distribution with time for "high temperature" and "low temperature" experiments respectively. In case of the former the distribution is relatively constant over time with the approximate contribution of each isomer to the total TBDF concentration being as follows: "TBDF1"-1-2%, "TBDF2"-25%, "TBDF3"-45% and "TBDF4"-30%. However, there is some

TBDF ISOMER VARIATION OVER TIME
 "LOW TEMPERATURE" BURN

FIGURE 3.12

FIGURE 3.13 VARIATION IN TBDF ISOMER DISTRIBUTION

FIGURE 3.14 VARIATION IN TBDF ISOMER DISTRIBUTION

indication that the contribution by "TBDF3" increases marginally over time while that by "TBDF2" declines over the corresponding period. For the "low temperature" experiments the contribution of each isomer to the total concentration of TBDF varies with time but the distribution appears to equilibrate to a pattern similar to the "high temperature" experiments. In this case there is a more pronounced variation in the contributions by "TBDF3" and "TBDF2" with the trend similar to that of "high temperature" experiments. Acharya et. al. (1991) and Townsend (1980, 1983) mention the possibility of isomer rearrangement. Such observations may reflect a kinetic equilibration process at work in the environment. Townsend in his articles compares observed and theoretical isomer group ratios in environmental samples and finds the comparisons numerically consistent. Theoretical predictions were based on quasi steady state kinetic model of red-ox reaction system. While his work considers isomer group ratios, a similar equilibration process may be taking place within the groups themselves as in our system. Such processes may be a function of the operating conditions and the type of feed. The type of feed being identical, i.e. PUF containing PBDPE, the combustion temperature is the parameter that is governing the isomerization reactions occurring in the system used in this study.

PAH Analysis:

"High Temperature" Experiments:

Phenanthrene, fluoranthene, pyrene, BaA and chrysene were

the PAHs quantified from the filter samples collected from the "high temperature" burn on November 5, 1991. Figures 3.15 and 3.16 illustrate the atmospheric stability of these compounds. Table 3.3 includes the results from linear regression analysis to test for the significance of the slopes of the curves shown in Figures 3.15 and 3.16.

TABLE 3.3
Significance of the Slopes of Concentration vs Time Plots

"High Temperature" Experiments					
	Phenan.	Fluor.	Pyrene	BaA	Chrys.
Slope	-1.219	1.6914	4.3429	-3.0819	-2.7695
P-value	0.9705	0.8293	0.6311	0.0552	0.4012

Examination of table 3.3 reveals that at a 10% level of significance only BaA has a significant negative slope. Assuming a first order rate constant for the decay of BaA yields a half-life of 7.7 h ($r^2=0.64$). Kamens et al. (1988, 1985) have found BaA as the one of the most reactive PAHs on atmospheric aerosols with half-lives ranging from 0.4 h to 7 h depending on solar intensity, humidity and temperature. Experiments conducted by Pitts et al. (1985), with PAHs adsorbed on GF and TIGF filters, show BaA as one of the most reactive PAHs. Behymer and Hites (1985) have found BaA as having the shortest half-life amongst phenanthrene, fluoranthene, pyrene and chrysene when these compounds were photolytically degraded adsorbed to silica gel or

FIGURE 3.15 BaA AND CHRYSENE CONCENTRATION VS CHAMBER AGING TIME

FIGURE 3.16 CONCENTRATION OF PHENANTHRENE, FLUORANTHENE AND PYRENE VS CHAMBER AGING TIME

alumina. However, a half-life value of 7.7 h, as in our experiment, is more an indicator of stability than of rapid decay. Lutes (1991) has also observed slower rates of degradation of PAHs generated from incineration of PUF as in our system. Keeping this in view, the stable behavior of PAHs resembles that of TBDF, PeBDF and TBDD emissions from "high temperature" experiments. The relative stability of PAHs can also be argued along the lines of particle formation and composition as in the case of PBDDs and PBDFs due to high temperature combustion.

"Low Temperature" Experiment:

PAHs quantified from "low temperature" experiments include phenanthrene, fluoranthene and pyrene. Unlike, the "high temperature" experiment BaA and chrysene were not detected and the concentrations of phenanthrene, fluoranthene and pyrene were lower. This observation underscores the importance of combustion conditions on the formation of PAHs. Commins (1969) has found that the optimum reaction temperature for PAH formation from wood combustion is around 800°C. This finding, therefore, supports the higher concentration of PAHs detected from particulate samples collected from the "high temperature" experiments. This fact can also account for the absence of BaA and chrysene in particulate samples from "low temperature" experiments.

Significant negative slopes were obtained for the PAHs quantified at a 10% level of significance. Figure 3.17 shows the behavior of PAHs with chamber aging time. The half-lives for

these compounds was calculated assuming a first-order decay constant. The half-lives values were as follows: phenanthrene 1.89 h ($r^2=0.93$), fluoranthene 1.44 h ($r^2=0.88$) and pyrene 1.55 h ($r^2=0.89$). The similar values of half-lives indicate that the degradation process may be independent of the type of compound and is dependent on the physical and chemical nature of the substrate. These half-life values are similar to those obtained for TBDD lending more support to the possibility of half-lives being independent of the chemical structure and more dependent on the physico-chemical interactions between the adsorbent and the substrate. This would also espouse the theory of different types of particles generated from "low temperature" and "high temperature" experiments.

Another point of contrast between "low temperature" and "high temperature" experiments is the ratio of fluoranthene/pyrene (FL/PY). In case of the former FL/PY is greater than unity averaging around 1.4 while it is less than with an average of around 0.8 for the latter. Schuetzle and Frazier (1986) have reported FL/PY ratios from various sources and have found that in case of light duty diesel engines this ratio is usually greater than one and is less than one for heavy duty diesel engines.

To further enhance our understanding of the differences in the particles a "low temperature" and a "high temperature" experiments were carried out on February 17, 1993 and filter samples from these experiments were analyzed for the fraction of

FIGURE 3.17 FLUORANTHENE, PYRENE AND PHENANTHRENE
CONCENTRATION VS CHAMBER AGING TIME

extractable particulate mass. It was believed that percent extractable mass from the particulate samples collected from "low temperature" burns would be higher than that from "high temperature" burns. A full scan analysis of these samples was also carried to ascertain any difference in the chemical composition of these particles. Soxhlet extraction for these samples was done in DCM at temperatures ranging from 50-55°C. This ensured that compounds having low volatility were not lost during the extraction process.

Comparison of Particle Characteristics:

Size Distribution:

Characterization of particle size distribution was done using two different instruments as mentioned before. Representative samples from "high temperature" experiment on November 5, 1991 and February 17, 1993 and "low temperature" experiments on May 21, 1992, October 3, 1992 and February 17, 1993 have been plotted on log probability paper and are shown in Figures 3.18, 3.19, 3.20 and 3.21. The size distribution in all cases can be described by a log-normal distribution with R-Square values exceeding 0.95. Relevant information from particle distribution data has been presented in Table 3.4.

TABLE 3.4

Particle Size Distributions & Specific Surface Areas

EXPT.	DEVICE	TPM (mg)	GMD (μm)	GSD	MMD (μm)	SMD (μm)	SSA (m^2/g)
Nov.5H	EAA	23.56	0.084	1.756	0.256	0.186	12.43
Nov.5H	LAS	23.56	0.230	1.448	0.372	0.324	12.26
May21L	EAA	234.52	0.095	1.708	0.259	0.194	13.06
May21L	LAS	234.52	0.215	1.398	0.319	0.285	15.03
Oct.3L	EAA	353.97	0.127	1.515	0.233	0.196	18.23
Feb.17H	EAA	103.24	0.067	1.845	0.250	0.172	11.33
Feb.17L	EAA	78.49	0.097	1.741	0.285	0.210	11.38

L: "Low temperature" Experiment
H: "High temperature" Experiment
TPM: Total Particulate Mass Present in the Chamber
GMD: Geometric Mean Diameter (d_g) = $\text{MMD}/\exp(3.5\ln^2\sigma_g)$
GSD: Geometric Standard Deviation (σ_g)
MMD: Mass Median Diameter
SMD: Surface Mean Diameter = $d_g\exp(2.5\ln^2\sigma_g)$
SSA: Specific Surface Area = Total Surface Area/TPM

HIGH TEMPERATURE BURN ON 11/05/92

EAA Data: MMD=0.256 μ m, σ_g =1.756

LAS Data: MMD=0.372 μ m, σ_g =1.448

FIGURE 3.18 CUMULATIVE LOG PROBABILITY GRAPH

LOW TEMPERATURE BURN ON 05/21/92

EAA Data: MMD=0.259 μ m, σ_g =1.708

LAS Data: MMD=0.319 μ m, σ_g =1.398

FIGURE 3.19 CUMULATIVE LOG PROBABILITY GRAPH

LOW TEMPERATURE BURN ON 10/03/92
EAA Data: MMD=0.233 μ m, σ_g =1.515

FIGURE 3.20 CUMULATIVE LOG PROBABILITY GRAPH

HIGH TEMPERATURE BURN ON 02/17/93

EAA Data: MMD=0.250 μ m, σ_g =1.845

LOW TEMPERATURE BURN ON 02/17/93

EAA Data: MMD=0.285 μ m, σ_g =1.741

FIGURE 3.21 CUMULATIVE LOG PROBABILITY GRAPH

From table 3.4 it is evident that the LAS measurements are consistently higher for observations related to particle size. This can be expected since the LAS sizes particles in the range $(0.09 - 3.0)\mu\text{m}$ while the EAA has a range from $(0.0075 - 0.75)\mu\text{m}$. Specific Surface Area (SSA) for each experiment has been calculated by assuming that particles are unit density spheres. Hence, the assumption that particle density is independent of the temperature of combustion. There is not a stark contrast between the SSA values from "high temperature" and "low temperature" experiments. This eliminates the possibility of higher SSA contributing towards faster degradation of PAHs and TBDD in "low temperature" experiments. Higher SSA has been cited as one of the reasons to explain different rates of photodegradation for PAHs adsorbed on surfaces like carbon black, fly ash, silica gel and alumina (Behymer and Hites, 1985). Significantly higher rates of degradation were observed for PAHs like BaA and BaP adsorbed on silica gel and alumina (< 5 hr) in contrast to fly ash (approximately 40 hr) and carbon black (> 500 hr). Silica gel and alumina have significantly higher specific areas than fly ash or carbon black. Higher surface area will facilitate more absorption of solar energy, hence, more scope for photodegradation.

Particle Morphology:

Filter samples collected on nucleopore filters and analyzed on the SEM gave an insight into particle morphology. Figures 3.22 and 3.23 show the photographs taken from the SEM.

SEM PHOTOGRAPHS

HIGH TEMPERATURE BURN ON 11/05/92

HIGH TEMPERATURE BURN ON 08/21/91

FIGURE 3.22

SEM PHOTOGRAPHS
LOW TEMPERATURE BURN ON 08/21/91

LOW TEMPERATURE BURN ON 08/21/91

FIGURE 3.23

Examination of these photographs indicates a different structure for particles generated from the two kinds of experiments. Particles from the "high temperature" experiments are characterized by presence of agglomerates, possibly a result of coagulation. Particles from "low temperature" experiments are predominantly composed of singular and spherical particles, probably, generated from condensation. Sethi and Biswas (1990) have studied the dynamics of particle formation in a flame incinerator. Figure 3.24 is a schematic of particle formation and growth mechanisms in a flame.

After examination of the photographs from the SEM it appears that particle formation and growth in "low temperature" experiments takes place in the decreasing temperature zone where the saturation ratio (SR) is greater than unity. Nucleation takes place in the saturated vapor conditions and once the particles are formed they scavenge the vapor by condensation. Thus the particles formed are singular and spherical. Condensation of species can also account for the organic layer around an aerosol core, the proposed model for a "low temperature" particle as discussed in Figure 3.8. Sethi and Biswas (1990) mention that under high temperature conditions particles may also be generated by chemical reaction and where further growth is controlled mostly by coagulation. Such a mechanism may explain the presence of agglomerates in the filter sample collected from the "high temperature" experiments. Higher temperatures will lead to a larger region with saturation ratio

FIGURE 3.24 SCHEMATIC OF THE BURNER SHOWING PARTICLE FORMATION AND GROWTH MECHANISMS

less than one and also more scope for particles to be generated from chemical reaction. Also, more complete combustion will lead to a lower concentration of volatile compounds in the vapor phase as oxidation will convert them into CO_2 . Hence there is a lesser possibility of vapor scavenging leading to a more "solid" particle with little organic layer around it.

The extent of combustion can also be gauged from the color of filter samples. "High temperature" experiments resulted in dark brown or black particles while "low temperature" experiments led to light brown shade. A more complete combustion will lead to darker particles due to elemental carbon or fly ash from the combustion process that cannot be easily oxidized. The lighter shade of the "low temperature" filter samples can also be associated with the condensation of organic species that can reflect light. Korfmacher et al. (1980) have mentioned the possibility that the color of the substrate can affect photolysis of compounds adsorbed on them. Darker substrates absorb more of the incident light which can reduce the rate of photolytic degradation of compounds adsorbed on the substrate.

Percent Extractable Analysis:

Filter samples were collected over time from a "low temperature" and a "high temperature" experiment carried out simultaneously on February 17, 1993. These filter samples were Soxhlet extracted in DCM and the extract was used for determination of percent extractable. A known amount from the extract (reduced to 1 ml) was spiked on pre-weighed filters and

the change in weight was measured. Variation in percent extractable over time is shown in Figure 3.25. It is evident from the Figure that percent extractable from the "low temperature" experiment filter samples are consistently higher than those from the "high temperature" experiment. The average percent extractable from the former being 46% and from the latter 30%. This is a significant observation as it serves to validate our explanations regarding behavioral differences in the stability of TBDD and PAHs generated from the two kinds of experiments. A higher percent extractable implies that there is more organic matter which can be related to the presence of a liquid organic layer surrounding the aerosol core, as shown in Figure 3.8. The observation regarding percent extractable and the presence of an organic layer can also be related to particle formation in "low temperature" and "high temperature" experiments. Condensation of vapor species on particles generated from nucleation or on fly ash can lead to the formation of an organic layer. It was proposed that particles generated from "low temperature" experiments may be the result of such a process. Figure 3.24 discusses the various particle formation mechanisms. It was also theorized that most particles formed from "high temperature" experiments are the result of coagulation of reaction products formed in the high temperature region of the flame and fly ash. Such a particle would corroborate to species adsorbed on a solid surface in the absence of an organic layer and the extractable portion in this case will represent the

□ "Low Temperature" Burn Average % Extractable = 46

+ "High Temperature" Burn Average % Extractable = 30

FIGURE 3.25 DATA ON PERCENT EXTRACTABLE MASS FOR
'LOW TEMPERATURE' & 'HIGH TEMPERATURE' BURNS

adsorbed species. Recapitulating, it was suggested that the presence of an organic layer can contribute to enhanced photodegradation by drawing analogy from experiments carried out by Buser (1988).

Full Scan Analysis:

Particulate samples extracted in DCM from the experiments carried out on February 17, 1993 were analyzed on full scan mode. The objective of this analysis was to arrive at a qualitative information regarding the chemical composition of the particles from the two kinds of experiments. Analysis was done on the HP 5890 Series II gas chromatograph interfaced to VG 70-SEQ mass spectrometer. The mass spectrometer was tuned to a resolution of 1,000. The temperature program used for this analysis was as follows: initial temperature at 90°C for 1 minute, increased at a rate of 6°/min to 300°C and held at 300°C for 10 minutes.

Chromatograms obtained from full scan analysis have been included in Appendix 1. The chromatograms in Appendix 1 are from the first filter samples collected from the two experiments. Examination of these chromatograms reveals the presence of more peaks in the filter sample from the "high temperature" experiment. Peaks eluting from the "low temperature" particulate sample are also present in the corresponding "high temperature" filter sample. Larger number of peaks present in the latter is symbolic of more chemical reactions taking place at the higher temperatures prevalent in "high temperature" burns. This would strengthen the proposed particle formation mechanism for

incineration at high temperatures. It was suggested particle formation at high temperatures takes place due to chemical reactions and growth is controlled by coagulation.

CONCLUSIONS

Chamber experiments have shown that incineration experiments with PUF containing PBDPE fire retardant at combustion temperatures ranging from 650-800°C ("high temperature" experiments) lead to emissions which are stable. Experiments conducted in the temperature range 400-500°C ("low temperature" experiments) yield particulate-bound emissions that have half-lives of the order of several hours. This difference has been attributed to the nature of particles generated from the two kinds of experiments. TBDF concentrations in "low temperature" experiments are characterized by isomerization reactions. The final distribution for TBDF resembles that obtained from "high temperature" experiments. This observation also suggests that the latter may yield more stable combustion products.

Observations suggest differences in physical and chemical properties of the particles formed from "low temperature" and "high temperature" experiments. The darker color of the particles from the latter may reduce the rate of photolytic degradation by absorbing more of the incident light. SEM photographs of nucleopore filter samples collected from "high temperature" combustion reveal coagulated masses of particles while "low temperature" combustion is characterized by singular, spherical particles. Percent extractable mass from the particulate samples collected from "low temperature" experiments is around 46% as opposed to 30% from the "high temperature" experiments. This difference can be related to the presence of

an organic layer around the particles. Therefore, photolysis in particles from "low temperature" experiments may be similar to solution-phase photoreactor experiments and behavior of emissions from "high temperature" experiments may be in congruence with solid-phase experiments. These observations suggest that particle formation and growth from nucleation and condensation mechanism may be more desirable as opposed to coagulation.

Chamber experiments show that under typical incinerator operating conditions, particulate-bound toxic emissions like PBDDs, PBDFs and PAHs are likely to be stable in the atmosphere. Operating temperatures around 500°C can lead to emissions that will degrade in the atmosphere. If dehalogenation is the mechanism for decay, then the products of photodegradation will be less toxic than their predecessors. Lower temperatures also imply lesser auxiliary fuel consumption by the incinerators. However, operation of incinerators at lower temperatures may not be desirable from certain other standpoints like the amount of fly ash and PICs formed.

RECOMMENDATIONS FOR ADDITIONAL RESEARCH

The effect of combustion temperature on the atmospheric stability of toxic emissions generated from incineration was an issue unaddressed thus far. This study has shown that operating incinerators at lower temperatures may lead to emissions that degrade in the atmosphere to possibly less toxic compounds. Validation of this theory into more general terms requires additional work to be performed. This study uses a very homogeneous feed for incineration. Therefore, the need arises to ascertain the atmospheric stability of emissions resulting from a more heterogeneous system as in a MWC. A similar study on other compounds like PCDDs and PCDFs will serve to validate the conclusions arrived upon by this study. Currently, work is being carried out in this direction in our research group. Characterization of the products of photolysis should also be done. This is important not only to determine whether the degradation products are less toxic but also to gain an understanding about the mechanism of photodegradation.

Particle formation and growth within the incinerator is an important consideration in the atmospheric behavior of the emissions. Conditions that lead to particle formation and growth due to nucleation and condensation should be investigated in more detail. We believe that such particles may have an organic layer surrounding them and toxic compounds dissolved in the layer are more prone to photodegradation than a solid particle resulting from coagulation.

REFERENCES

- Acharya, P.; DeCicco, S. G. and Novak, R. G. (1991) "Factors that can Influence and Control the Emissions of Dioxins and Furans from Hazardous Waste Incinerators" *J. Air Waste Manage. Assoc.* 41, 1605-15.
- Bacher, R.; Ballschmiter, K. (1991) "Patterns of Halogenated Dibenzodioxins and Dibenzofurans (Br, Cl=1-8) in Samples from Automobile Exhausts, Home Heating, Metal Reclaiming and in Samples with a Complex Input" *Proceedings of 11th International Symposium On Chlorinated Dioxins And Related Compounds*, Research Triangle Park, North Carolina, U.S.A.
- Behymer, T. and Hites, R. (1985) "Photolysis of Polycyclic Aromatic Hydrocarbons Adsorbed on Simulated Atmospheric Particulates" *Environ. Sci. Technol.* 19, 1004-6.
- Benefenati, E.; Gizzi, F.; Reginato, R.; Fanelli, R.; Lodi, M. and Tafliaferri, R. (1983) "Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans in Emissions from an Urban Incinerator. 2. Correlation Between Concentration of Micropollutants and Combustion Conditions" *Chemosphere* 12, 1151-7.
- Bidelman, T. F.; Billings, W. N. and Foreman, W. T. (1986) "Vapor-Particle Partitioning of Semivolatile Organic Compounds: Estimates from Field Collections" *Environ. Sci. Technol.* 20, 1038-43.
- Bidelman, T.F. and Foreman, W.T. (1987) Vapor-Particle Partitioning of Semivolatile Organic Compounds, in The Chemistry of Aquatic Pollutants (edited by R. A. Hites and S. J. Eisenrich), ACS Advances in Chemistry Series, ACS, New York.
- Bieniek, D.; Bahadir, M.; and Friedhelm K. (1989) "Formation of Heterocyclic Hazardous Compounds by Thermal Degradation of Organic Compounds" *Heterocycles* 28, 719-22.
- Buser, H.R. (1988) "Rapid Photolytic Decomposition of Brominated and Brominated/Chlorinated Dibenzodioxins and Dibenzofurans" *Chemosphere* 17, 889-903.
- Buser, H.R. (1987) "Brominated and Brominated/Chlorinated Dibenzodioxins and Dibenzofurans: Potential Environmental Contaminants" *Chemosphere* 16, 713-32.
- Buser, H.R. (1986) "Polybrominated Dibenzofurans and Dibenzo-p-Dioxins: Thermal Reaction Products of Polybrominated Diphenyl Ether Flame Retardants" *Enviro. Sci. Technol.* 20, 404-8.
- Choudhry, G. G.; Sundstorm, G.; Ruzzo, L.O. and Hutzinger, O.

Choudhry, G. G. and Webster, G. B. R. (1989) "Environmental Photochemistry of PCDDs. 2. Quantum Yields of the Direct Phototransformation of 1,2,3,7,-Tetra-, 1,3,6,8-Tetra-, 1,2,3,4,6,7,8-Hepta and 1,2,3,4,5,6,7,8,9- Octachlorodibenzo-p-Dioxin in Aqueous Acetonitrile and their Sunlight Half-Lives" *J. Agric. Food Chem.* 37, 254-61.

Commings, B. T. (1969) "Formation of Polycyclic Aromatic Hydrocarbons during Pyrolysis and Combustion of Hydrocarbons" *Atmos. Environ.* 3, 565-72.

Crosby, D. G.; Wong, A. S.; Plimmer, J. R. and Woolson, E. A. (1971) "Photodecomposition of Chlorinated Dibenzo-p-Dioxins" *Science* 173, 748-9.

Czuczwa, J. W. and Hites, R. A. (1984) "Environmental Fate of Combustion-Generated Polychlorinated Dioxins and Furans" *Environ. Sci. Technol.* 18, 444-50.

Daisey, J. M.; Cheney, J. L. and Liou, P. J. (1986) "Profiles of Organic Particulate Emissions from Air Pollution Sources: Status and Needs for Receptor Source Apportionment Modeling" *J. Air Poll. Control Assoc.* 36, 17-33.

Dulin, D.; Drossman, H. and Mill, T. (1986) "Products and Quantum Yields for Photolysis of Chloroaromatics in Water" *Environ. Sci. Technol.* 20, 72-77.

Hawthorne, S. B.; Krieger, M. S.; Miller, D. J. and Mathiason, M. B. (1989) "Collection and Quantitation of Methyloxyated Phenol Tracers for Atmospheric Pollution from Residential Wood Stoves" *Environ. Sci. Technol.* 23, 470-5.

Hiraoka, M.; Takizawa, Y.; Masuda, Y.; Takeshita, R.; Yagome, K.; Taaka, M.; Watanabe, Y. and Morikawa, K. (1987) "Investigation of Generation of Dioxins and Related Compounds from Municipal Incinerators in Japan" *Chemosphere* 16, 1943-8.

Hosoya, K.; Kimata, K.; Funkunishi, K.; Araki, T and Tanaka, N. (1993) "Photodecomposition of 1,2,3,4-Tetrachlorodibenzo-p-dioxin in Water-Alcohol Media on a Solid Support" (in press)

Japar, S. M.; Szkarlat, A. C.; Gorse, R. A.; Heyerdahl, E. K.; Johnson, R. L.; Rau, J. A. and Huntzicker, J. J. (1984) "Comparison of Solvent Extraction and Thermo-Optical Analysis Methods: Applications to Diesel Exhaust" *Environ. Sci. Technol.* 18, 231-4.

Jeffries, H. E.; Sexton, K. G.; Arnold, J.; McDow, S. and Fister, T. (1990) Progress Report for EPA Cooperative Agreement. Development of a Standard Chamber Data Base and Protocol for Evaluating Oxidant Mechanisms for Urban and Regional Models

Junge, C. E. (1977) in Fate of Pollutants in the Air and Water Environment, (Edited by I. H. Suffet) Wiley Interscience: New York, 7-25.

Kamens, R. M.; Guo, Z.; Fulcher, J. N. and Bell, D. A. (1988) "Influence of Humidity, Sunlight and Temperature on the Daytime Decay of Polyaromatic Hydrocarbons on Atmospheric Soot Particles" *Enviro. Sci. Technol.* 22, 103-8.

Kamens, R. M.; Perry, J. M.; Saucy, D. A.; Bell, D. A.; Newton, D. L. and Brand, B. (1985) "Factors which Influence Polycyclic Aromatic Hydrocarbon Decomposition on Wood Smoke Particles" *Enviro. Int.* 12, 131-6.

Kieatiwong, S.; Nguyen, L. V.; Herbert, V. R.; Hackett, M.; Miller, G. C.; Mille, M. J. and Mitzel, R. (1990) "Photolysis of Chlorinated Dioxins in Organic Solvents and on Soils" *Enviro. Sci. Technol.* 24, 1575-80.

Korfmacher, W. A.; Wehry, E. L.; Mamantov, G. and Natusch, D. F. S. (1980) "Resistance to Photochemical Decomposition of Polycyclic Aromatic Hydrocarbons Vapor-Adsorbed on Coal Fly Ash" *Enviro. Sci. Technol.* 14, 1094-9.

Liberti, A.; Brocco, D.; Allegrini, I.; Cecinato, A. and Possanzini, M. (1978) "Solar and UV Photodecomposition of 2,3,7,8-Tetrachloro Dibenzo-p-dioxin in the Environment" *The Science of the Total Environment* 10, 97-104.

Lindahl, R.; Rappe, C. and Buser, H. R. (1980) "Formation of Polychlorinated Dibenzofurans and Polychlorinated Dibenzo-p-dioxins from the Pyrolysis of Polychlorinated Diphenyl Ethers" *Chemosphere* 9, 351-61.

Lutes, C. C.; Charles, J. M.; Odum, J. R. and Kamens, R. M. (1992) "Chamber Aging Studies on the Atmospheric Stability of Polybrominated Dibenzo-p-dioxins and Dibenzofurans" *Enviro. Sci. Technol.* 26, 991-998.

Lutes, C. C. (1991) Master's Technical Report, University of North Carolina at Chapel Hill, Department of Environmental Sciences and Engineering.

Mason, G. M.; Denomme, A.; Safe, L. and Safe, S. (1987) "Polybrominated and Chlorinated Dibenzo-p-dioxins: Synthesis Biologic and Toxic Effects and Structure-Activity Relationships" *Chemosphere* 16, 1729-31.

McDow, S. R.; Sun, Q. R.; Vartiainen, M.; Hong, Y. S.; Yao, Y. L.; Hayes, E. A. and Kamens, R. M. (1992) "Photodegradation of Polycyclic Aromatic Hydrocarbons in Hexadecane and Methoxyphenols" *Polycyclic Aromatic Compounds*, in press.

McDow, S. R.; Sun, Q. R.; Vartiainen, M.; Hong, Y. S.; Yao, Y. L.; Hayes, E. A. and Kamens, R. M. (1991) "Factors Influencing Photodegradation of Polycyclic Aromatic Hydrocarbons in Liquid Organic Media" in *Measurement of Toxic and Related Air Pollutants*, AWMA, Pittsburgh, 140-6.

Moore, J. A.; McConnell, E. E.; Dalgard, D. W. and Harris, M. W. (1979) "Comparative Toxicity of Three Halogenated Dibenzofurans in Guinea Pigs, Mice and Rhesus Monkeys" *Ann. of the New York Acad. of Sciences* 320, 151-63.

Muto, H.; Shinada, M. and Takizawa, Y. (1991) "Heterogeneous Photolysis of Polychlorinated Dibenzo-p-dioxins on Fly Ash in Water-Acetonitrile Solution in Relation to the Reaction with Ozone" *Enviro. Sci. Technol.* 25, 316-22.

Nestrick, T. J.; Lamparski, L. L. and Townsend, D. I. (1980) "Identification of Tetrachloro-p-dioxin at the 1 ng Level by Photolytic Degradation and Pattern Recognition Techniques" *Anal. Chem.* 52, 1865-74.

Norstrom, A.; Andersson, K. and Rappe, C. (1976) "Formation of Chlorodibenzofurans by Irradiation of Chlorinated Diphenyl Ethers" *Chemosphere* 1, 21-24.

Ozvacic, V.; Wong, G.; Tosine, H.; Clement, R. E. and Osborne, J. (1985) "Emissions of Chlorinated Organics from Two Municipal Incinerators in Ontario" *J. Air Poll. Control Assoc.* 35, 849-55.

Pankow, J. F. (1987) "Review and Comparative Analysis of the Theories on Partitioning between the Gas and Aerosol Particulate Phases in the Atmosphere" *Atmos. Environ.* 21, 2275-83.

Pitts, J. N.; Jr.; Sweetman, J. A.; Zielinska, B.; Winer, A. M.; Atkinson, R.; and Harger, W. P. (1986) "Factors Influencing the Reactivity of Polycyclic Aromatic Hydrocarbons Adsorbed on Model Substrates and in Ambient POM with Ambient Levels of Ozone" *Chemosphere* 15, 675-85.

Podoll, T. R.; Jaber, H. M. and Mill, T. (1986) "Tetrachlorodibenzodioxin: Rates of Volatilization and Photolysis in the Environment" *Enviro. Sci. Technol.* 20, 490-2.

Ramalingam, R.; Mazer, T.; Wagel, D. J.; Malloy, C. M.; Taylor, M. L.; Tiernan, T. O.; Garrett, J. H. and Rifkind A. B. (1986) "Synthesis and Characterization of Polybromo and Polybromochloro-Dibenzo-p-dioxin and Dibenzofurans" in Chlorinated Dioxins and Dibenzofurans in Perspective (edited by C. Rappe, G. Choudhry and L. H. Keith), Lewis Publishers Inc., Chelsea, MI.

Rappe, C. (1983) "Chlorinated Dioxins and Furans in the Environment" *Enviro. Sci. Technol.* 17, 124-130.

Rau, J. A. (1989) "Composition and Size Distribution of Residential Wood Smoke Particles" *Aerosol Sci. Technol.* 10, 181-192.

Schafer, W. and Ballschmiter, K. (1986) "Monobromo-Polychloro-Derivatives of Benzene, Biphenyl, Dibenzofurane and Dibenzodioxine in Chemical-Waste Burning" *Chemosphere* 15, 755-63.

Schmidt, K. F. (1992) "Dioxin's Other Face: Potrait of an "Environmental Hormone"" *Sci. News* 141, 24-27.

Schuelitze, D.; Lee, F. S. C.; Prater, T. J. and Tejada, S. B. (1981) "The Identification of Polynuclear Aromatic Hydrocarbon Derivatives in Mutagenic Fractions of Diesel Particulate Extracts" *Int. J. Environ. Anal. Chem.* 9, 93-7.

Schuelitze, D. and Frazier, J. A. (1986) "Factors Influencing the Emission of Vapor and Particulate Phase Components from Diesel Engines" in Carcinogenic and Mutagenic Effects of Diesel Engine Exhaust (edited by N. Ishinishi, A. Koizumi, R. O. McClellan and W. Stober), Elsevier Science Publishers.

Sethi, V. and Biswas, P. (1990) "Modeling of Particle Formation and Dynamics in a Flame Incinerator" *J. Air Waste Manage. Assoc.* 40, 42-46.

Shaub, W. M. and Tsang, W. "Overview of Dioxin Formation in Gas and Solid Phases under Municipal Incinerator Conditions" in Chlorinated Dibenzodioxins and Dibenzofurans in the Total Environment II (edited by G. Choudhry, L. H. Keith and C. Rappe), Stoneham, MA.

Shaub, W. M. and Tsang, W. "Dioxin Formation in Incinerators" *Environ. Sci. Technol.* 17, 721-30.

Smith, L. M.; Stalling, D. L. and Johnson, J. L. (1984) "Determination of Parts-per-Trillion Levels of Polychlorinated Dibenzofurans and Dioxins in Environmental Samples" *Anal. Chem.* 56, 1830-42.

Stanley, J. S. and Sack, T. M. (1986) Protocol for the Analysis of 2,3,7,8-Tetrachlorodibenzo-p-dioxin by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry EPA/600/4-86/004.

Tiernan, T. O.; Taylor, M. L.; Garrett, J. H.; VanNess, G. F.; Solch, J. G.; Deis, D. A. and Wagel, D. J. (1983) "Chlorodibenzodioxins, Chlorodibenzofurans and Related Compounds in the Effluents from Combustion Processes" *Chemosphere* 16, 1943-8.

Townsend, D. I. (1983) "Change of Isomer Ratio and Fate of

Polychlorinated-*p*-dioxins in the Environment" *Chemosphere* 12, 637-43.

Townsend, D. I. (1980) "The Use of Isomer Group Ratios to Identify Sources and Define Background Levels of Dioxins in the Environment" *J. Environ. Sci. Health B15*(5), 571-609.

Visalli, J. R. (1987) "A Comparison of Dioxin, Furan and Combustion Gas Data from Test Programs at Three MSW Incinerators" *J. Air Poll. Control Assoc.* 37, 1451-63.

Watanabe, I. and Tatsukawa, R. (1987) "Formation of Brominated Dibenzofurans from the Photolysis of Decabromobiphenyl Ether in Hexane Solution by UV and Sun Light" *Bull. Environ. Contam. Toxicol.* 39, 953-9.

Watson, J. G. (1979) Ph. D. Thesis, Oregon Graduate Center, Beaverton, Oregon.

Wingerter, E. J. (1989) "Are Landfills and Incinerators Part of the Answer? Three Viewpoints" *EPA J.* 15, 22-23.

Yu, M. L. and Hites R. A. (1981) "Identification of Organic Compounds on Diesel Engine Soot" *Anal. Chem.* 53, 951-4.

APPENDIX 1

File:V4050 Scans:1-1800 Acquired: 3-MAR-93 13:36:52 Ionization:EI+ Function:Magnet 70SEQ Inlet:»
 TIC (+RP) Experiment:GC_MS
 File Text:W1_0217 "HIGH TEMPERATURE" EXPERIMENT CHROMATOGRAM

File:V4051 Scans:1-1366 Acquired: 3-MAR-93 14:24:25 Ionization:EI+ Function:Magnet 70SEQ Inlet:»
 TIC (+RP) Experiment:GC_MS
 File Text:E1_0217 "LOW TEMPERATURE" EXPERIMENT CHROMATOGRAM

File:V4050 Scans:1-1800 Acquired: 3-MAR-93 13:36:52 Ionization:EI+ Function:Magnet 70SEQ Inlet:»
TIC (+RP) Experiment:GC_MS
File Text:W1_0217

File:V4051 Scans:1-1432 Acquired: 3-MAR-93 14:24:25 Ionization:EI+ Function:Magnet 70SEQ Inlet:»
TIC (+RP) Experiment:GC_MS
File Text:E1_0217

File:V4050 Scans:1-1800 Acquired: 3-MAR-93 13:36:52 Ionization:EI+ Function:Magnet 70SEQ Inlet:»
TIC (+RP) Experiment:GC_MS
File Text:W1_0217

File:V4051 Scans:1-1466 Acquired: 3-MAR-93 14:24:25 Ionization:EI+ Function:Magnet 70SEQ Inlet:»
TIC (+RP) Experiment:GC_MS
File Text:E1_0217

File:V4050 Scans:1-1800 Acquired: 3-MAR-93 13:36:52 Ionization:EI+ Function:Magnet 70SEQ Inlet:»
TIC (+RP) Experiment:GC_MS
File Text:W1_0217

File:V4051 Scans:1-1550 Acquired: 3-MAR-93 14:24:25 Ionization:EI+ Function:Magnet 70SEQ Inlet:»
TIC (+RP) Experiment:GC_MS
File Text:E1_0217

File:V4050 Scans:1-1800 Acquired: 3-MAR-93 13:36:52 Ionization:EI+ Function:Magnet 70SEQ Inlet:»
TIC (+RP) Experiment:GC_MS
File Text:W1_0217

File:V4051 Scans:1-1576 Acquired: 3-MAR-93 14:24:25 Ionization:EI+ Function:Magnet 70SEQ Inlet:»
TIC (+RP) Experiment:GC_MS
File Text:E1_0217

File:V4050 Scans:1-1800 Acquired: 3-MAR-93 13:36:52 Ionization:EI+ Function:Magnet 70SEQ Inlet:»
TIC (+RP) Experiment:GC_MS
File Text:W1_0217

File:V4051 Scans:1-1603 Acquired: 3-MAR-93 14:24:25 Ionization:EI+ Function:Magnet 70SEQ Inlet:»
TIC (+RP) Experiment:GC_MS
File Text:E1_0217