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Combustion Emissions from Hazardous Waste Incinerators, Boilers and Industrial Furnaces, and Municipal Solid Waste Incinerators—Results from Five Star Grants and Research Needs

December 2006



**Combustion Emissions from Hazardous Waste
Incinerators, Boilers and Industrial Furnaces,
and Municipal Solid Waste Incinerators –
Results from Five STAR Grants and Research Needs**

December 2006

U.S. Environmental Protection Agency
Office of Research and Development
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DISCLAIMER

The research described in this document has been funded wholly by the United States Environmental Protection Agency (EPA) under the Science to Achieve Results (STAR) grants program. The information presented in this report is intended to provide the reader with insights about the progress and scientific achievements of STAR research grants within a broader context. This report could be used for decision-making about future investment in combustion research. Readers who are interested in obtaining more specific information about any of the individual projects described herein should read the peer-reviewed publications produced by those STAR grants. Mention of trade names or commercial products does not constitute endorsement or recommendation by EPA for use.

This report has undergone external peer review.

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EXECUTIVE SUMMARY

This report presents the results of five competitively awarded research grants on combustion emissions from hazardous waste incinerators, industrial furnaces and boilers, and municipal solid waste incinerators. These grants were awarded in response to a Request for Applications (RFA) that was issued by EPA's Office of Research and Development (ORD) in 1999 under the National Center for Environmental Research's (NCER) Science to Achieve Results (STAR) Program. The RFA was developed in consultation with EPA program offices and other parts of ORD. The grants were awarded in 2000 and completed in 2004-2005. The total investment in the five grants was \$1,685,000. Information about these and other STAR grants can be obtained at: <http://www.epa.gov/ncer>.

The recent completion of the grants and the preparation of this report offer the opportunity to review where the combustion sources addressed by the RFA fall within the universe of combustion emission sources that comprises, among other sources, smokestack industries, mobile sources, and open burning. They permit putting this research in the context of other research conducted in support of the Resource Conservation and Recovery Act (RCRA) and of the Clean Air Act (CAA). The report also provides a basis for identifying combustion-related research needs.

Mechanisms of Formation of Chemical Compounds in Combustion Systems

Three of the five grants addressed developing a better understanding of certain compounds that are formed and the physical and chemical processes by which they are formed as a result of the combustion that takes place in these sources.

A project by Taylor (University of Dayton) developed fundamental data and models that will contribute to the infrastructure of knowledge of reactions of chlorinated hydrocarbons and their impact on the environment. Results of this research project provide important inputs in the development of a comprehensive gas-phase model of the transformation of polychlorinated p-dibenzo dioxins (PCDDs) under a wide range of conditions. This model can be used to manage risk by preventing and controlling formation and emissions of PCDDs through combustion modification or other emission abatement techniques. The model can also be applied to site-specific risk assessment for combustion sources. There is, however, no published kinetic model incorporating these rate coefficients.

A project by Dellinger and Lomnicki (Louisiana State University) developed a unified mechanism and understanding of polychlorinated p-dibenzo dioxin/furan (PCDD/F) formation in the post-combustion, cool-zone of combustors that will greatly facilitate the development of improved risk management and risk assessment strategies for combustion systems. Gas-phase reactions and kinetics impact the formation of PCDD/F in combustion systems, but the effect is primarily indirect through destruction of gas-phase PCDD/Fs and homogeneous gas-phase formation of some precursors. The principal source of PCDD/F in combustion systems is in all likelihood surface-mediated by fine and ultrafine particles. Understanding of these mechanisms could be applied to the development of emissions abatement strategies for combustion systems.

General strategies include:

- Modifying post-combustion time-temperature profiles to mitigate PCDD/F formation.
- Controlling the content of catalytic metals in the combustor feed.
- Modifying combustion conditions to minimize formation of catalytic, fine and ultrafine particles.
- Blending of fuels and wastes to avoid the optimum compositions for PCDD/F formation.

A project by Senkan (University of California - Los Angeles) generated data concerning major, minor, and trace species concentration profiles and soot and temperature profiles that will be useful for the development and validation of detailed chemical kinetic mechanisms (DCKM) describing the combustion of hydrocarbons and intermediates which were found from brominated hydrocarbons in flames. In fact, the development of DCKM for hydrocarbons was determined to be an important prerequisite to develop insights into the formation of toxic products of incomplete combustion (PICs) in the combustion of halogenated hydrocarbons.

The development of DCKM will result in improved predictions regarding the conditions under which polycyclic aromatic hydrocarbons (PAHs) and dioxins form in incinerators. The detailed mechanisms developed can subsequently be combined with fluid dynamic models to simulate, design, and develop optimum strategies for practical incinerators such that their operations would result in emissions of lowest possible levels of PICs, thereby reducing possible risk to public health.

The three grants provide improved characterization of the mechanisms of formation of components of air emissions from combustion systems. They identify dioxin and furan precursor compounds and halogenated dioxin and furan species and provide insight into the formation and transformation mechanisms in combustion systems.

Specifically, Taylor has characterized chlorinated dioxins and provided OH radical reaction rate measurements that have not previously been investigated. Dellinger and Lomnicki investigated the effects of metals on catalysis of formation of chlorinated dioxins and furans in combustion systems and identified a correlation between the amount of dibenzo dioxin and the amount of highly chlorinated dioxin products formed as well as the effect of temperature on this mechanism. These results also identify dioxin and furan formation issues related to combustion of hazardous waste and provide data relevant to the identification of surrogate compounds to correlate to emissions of more highly chlorinated dioxins and furans. Senkan provided information concerning mechanisms of formation of PAHs and soot. These results are also relevant to formation issues related to combustion of hazardous waste and to identification of surrogate compounds.

Monitoring and Analytical Methods for Chemical Compounds in Combustion Systems

Two of the five grants addressed developing monitoring and analysis methods that will permit better characterization of all the compounds that are created as a result of combustion in the sources that are the subject of this report, including the chemicals and the number, size, and composition of particles that are emitted.

A project by Rubey, Striebich, and Taylor (University of Dayton) shows that multi-dimensional gas chromatography-mass spectrometry (MDGC-MS) has significant potential in its ability to identify specific components of complex chemical mixtures sampled from municipal solid waste and hazardous waste incinerators. This technique also possesses the capability of quantifying separated substances that occur over a wide range of concentrations. It is hoped that use of advanced chromatographic techniques (e.g., a thermal gradient programmed GC) along with a faster MS system will allow more comprehensive characterization of both toxic and non-toxic PICs to be performed in a rapid (i.e., real-time or near real-time) fashion, thereby reducing uncertainties associated with site-specific risk assessments.

A project by Smith and Boudries (Massachusetts Institute of Technology in collaboration with Aerodyne Research, Inc.) deployed a state-of-the-art aerosol mass spectrometer (AMS) at three municipal waste incinerators to measure the real-time chemical and size distribution of sub-micron particulate emissions from incinerators. Overall, the data collected within the framework of this project show the development of new and promising techniques for real-time chemical analysis and measurement of size-resolved ambient aerosols.

Although the AMS was initially developed to characterize non-refractory species, further development and improvements were performed during this project to include the measurement of refractory species, such as metals. This new technique offers the simultaneous real-time measurement of a variety of chemical species present in/on aerosols and their corresponding size distribution in a rapid manner with respect to individual species for a variety of combustion systems. These species include organics, sulfate, nitrate, ammonium, chloride and metals. Through this research, a mobile commercial instrument with the capability of performing the size distribution and mass loading concentration measurements in real-time will be available to the research and regulatory communities.

The results from these two projects can be directly applied to design and application of sampling and analysis systems to further characterize emissions from combustion systems, in particular focusing on identification of potentially toxic constituents that have not been previously characterized in combustion system exhaust gas and fine particulate. Such real-time or near real-time monitoring systems and the data provided by them could be applied directly to preparation of site-specific risk assessments for combustion systems as well as to development, design, and implementation of emission control systems.

Research Needs

Research needs were identified by consulting the Principal Investigators of these grants, interviewing experts in the field of combustion, and holding research needs discussions as part of

an Annual EPA-Air and Waste Management Association (AWMA) Information Exchange and an American Flame Research Committee meeting. The latter discussions were the first times that EPA in-house and extramural academic researchers, experts from industry, and consulting engineers met for this purpose. There was agreement among the participants that interactions such as these would be desirable at least yearly.

The research needs identified during the preparation of this report fell into the following categories: (a) improving understanding of the mechanisms of formation of chemical compounds in combustion systems, which can be used to develop new control technologies and operating parameters to limit emissions of pollutants and ultimately reduce risk; (b) developing better monitoring, sampling, and analysis methods to more accurately characterize combustion emissions; (c) identifying toxic fractions of combustion-related emissions to more accurately characterize risks; (d) improving knowledge related to the fate and transport of combustion-related emissions to better assess potential impacts of these materials on human health and the environment; and (e) improving understanding of mechanisms of toxicity and potential health effects associated with combustion emissions, particularly for those compounds for which little or no information is available.

Some of the combustion researchers and experts felt that new environmental problems not directly related to combustion currently have and perhaps should have greater priority in terms of research needs. Nevertheless, this peer-reviewed report offers the basis for identifying combustion-related research that may be needed in developing and implementing future rule-makings and in meeting any changes that the nation may wish to make in the types of combustion systems it thinks best meet its economic and human health and environmental quality objectives.

1. INTRODUCTION

In 1999, the U.S. Environmental Protection Agency's (EPA) National Center for Environmental Research (NCER) published a Request for Applications (RFA) (entitled "Combustion Emissions") for research grants under its Science to Achieve Results (STAR) program to explore the risks posed from emissions of contaminants from hazardous waste incinerators, furnaces and boilers, and municipal incinerators. Five grants were awarded based on this RFA. The total amount awarded was \$1,685,000. The work performed under these five grants has recently concluded.

The purpose of this report is to summarize the important scientific findings from this research, place these findings in the context of past and on-going research on combustion emissions, and identify research needs on this topic. The intended audiences for this report are primarily EPA program and research offices, but also outside experts in the combustion field and people who may review EPA's need for additional research on combustion from these sources and other sources as well.

Further information regarding the STAR program is available at: <http://www.epa.gov/ncer>. This website contains a search function that allows for searching for information on these and other NCER grants by principal investigator (PI) name, institution, grant number, and key words.

1.1 OVERVIEW OF TYPES OF COMBUSTION SOURCES

Combustion emissions are generated by burning material for energy, waste reduction/disposal, or both. The major types of stationary and mobile combustion sources in the United States are:

- Power plants.
- Process heaters and industrial processes.
- Mobile sources.
- Open burning and residential heating.
- Incinerators and boilers and industrial furnaces.

Power plants There are about 1,300 coal-fired generation units in about 500 coal-fired power plants representing about 305 GW of generation capacity. There were 309 oil-fired units at 137 plants in 1998 and 104 units at 74 plants in 2003. The number has likely declined since 2003. Power plants are generally considered to have the most overall pollutant emissions among combustion sources, including emissions of several criteria pollutants (e.g., particulate matter, nitrogen oxides, sulfur oxides) as well as a number of air toxics (e.g., mercury). For 2001, it is estimated that coal- and oil-burning power plants generated 45 percent (339,976 tons) of the 755,502 tons of air toxics released in North America (CEC 2004). Emissions from individual facilities vary based on fuel throughput; the size, design features, level of maintenance, and operating characteristics of the facility; and the fuel (e.g., natural gas, oil, coal).

Process heaters It is estimated that there are 15,248 process heaters: 13,481 gas-fired, 353 distillate oil-fired, 674 residual oil-fired, 0 coal-fired, and 42 wood-fired. Process heaters are enclosed devices using a controlled flame designed to transfer heat as part of an industrial process. Process heaters are commonly used in petroleum refining and iron and steel production, as well as in a number of other industrial applications. The majority of process heaters burn gaseous fuels (e.g., natural gas) or fuel oils. The gas-fired heaters are believed to have low air toxics emissions, often near emission test method detection limits (EPA 2002). For oil-fired heaters poor maintenance of the burners, low-quality fuel, and lack of air pollution control devices can result in significant emissions of NO_x , SO_2 , SO_3 , PM and $\text{PM}_{2.5}$, and a spectrum of polynuclear hydrocarbons and heavy metals.

Industrial processes that involve combustion include furnaces and kilns, such as blast furnaces used in iron and steel production and rotary kilns used in cement and lightweight aggregate production, where the flame directly contacts the industrial process raw material. These sources may combust metallurgical coke (made from coal), petroleum coke (made from oil), coal, oil, natural gas or a combination of fuels. Furnaces and kilns emit criteria pollutants (e.g., particulate matter, nitrogen oxides, sulfur oxides) and air toxics (e.g., dioxins). Some types of industrial process sources, in particular cement and lightweight aggregate kilns, may also burn solid or liquid wastes. Such waste-burning industrial sources are categorized by EPA regulations as “industrial furnaces” and are subject to additional emissions limitations for air toxics when incinerating hazardous waste.

Mobile sources are generally divided into two categories: on-road and non-road sources. On-road sources include highway vehicles such as cars and light trucks, heavy trucks, buses, and motorcycles. Emissions from individual on-road sources are generally low, relative to smokestack plumes that many people associate with air pollution. However, in numerous cities across the country, the on-road sources are the single greatest pollution category, as emissions from millions of vehicles on the road add up. Non-road mobile sources include outdoor power equipment, recreational equipment, farm equipment, construction equipment, lawn and garden equipment, marine vessels, locomotives, and aircraft. In some areas of the country, emissions from non-road sources represent a third of the total emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOCs) from all mobile sources, including cars and trucks, and over two-thirds of emissions of particulate matter from all mobile sources (EPA 2005a).

Open burning and residential heating are also significant sources of combustion emissions. These sources are similar to mobile sources in that the emissions from an individual source are generally low but, due to their number, the total emissions from these types of sources can be significant. Open burning is defined as “the burning of any matter in such a manner that products of combustion resulting from the burning are emitted directly into the ambient air without passing through an adequate stack, duct, or chimney.” This includes activities such as burning yard waste, campfires, and land clearing fires. Emissions from residential heating are generated by the combustion of wood, natural gas, propane, or other fuel for the purpose of heating residences. The quantity and composition of emissions from these types of sources vary depending on the design, operating, and maintenance characteristics of the combustors; the composition of the fuel; and the amount of fuel burned.

Incinerators and waste-burning boilers and industrial furnaces Municipal solid waste incinerators are known as Municipal Waste Combustors (MWC). There are 167 large (unit capacity greater than or equal to 250 tons per day) MWC units at 66 facilities, 84 small (unit capacity greater than or equal to 35 tons per day and less than 250 tons per day) MWC units at 39 facilities, and 12 very small (unit capacity less than 35 tons per day) MWC units at 12 facilities. Incinerators, boilers, and furnaces can emit a range of air pollutants, including criteria pollutants and air toxics.

Hazardous waste is combusted at four main types of facilities: commercial incinerators, on-site incinerators, waste burning kilns (cement kilns and light weight aggregate kilns), and industrial boilers. Commercial incinerators are generally larger in size and designed to manage virtually all types of solids, as well as liquid wastes. On-site incinerators are more often designed as liquid-injection systems that handle liquids and pumpable solids. Waste burning kilns and boilers generally burn hazardous wastes to generate heat and power for their manufacturing processes.

There are 267 hazardous waste burning sources (systems) in operation in the U.S. Liquid fuel-boilers account for 104 sources, followed by on-site incinerators at 92 sources. Cement kilns, hydrochloric acid production furnaces, and commercial incinerators account for 25, 10, and 15 sources, respectively. Solid fuel boilers and lightweight aggregate kilns make up the remainder, at 12 and nine systems, respectively. These 267 sources are operated at a total of 145 different facilities. Combustion systems operating at chemical manufacturing facilities were found to account for about 70 percent of the total number of facilities and manage 58 percent of all hazardous waste burned in 2003. (70 FR at 59531, October 12, 2005)

Generally, incinerators are used to reduce waste volumes and toxicity, furnaces are used to reclaim reusable products and/or heat value from wastes, and boilers that burn waste materials are used to recover energy from wastes. Industrial furnaces include cement kilns and lightweight aggregate kilns that burn waste for energy recovery and to reduce the overall net energy cost from the low cost per unit of heat content in comparison with fossil fuels and/or income from waste disposal fees. The emissions from these facilities are significant in a number of areas of the United States and are often complex mixtures of pollutants that can be difficult to identify and quantify.

The research conducted under the five grants summarized in this report focused on emissions from hazardous waste incinerators, boilers and industrial furnaces, and municipal solid waste incinerators. Several of the projects are also relevant to air emissions from other types of stationary combustion sources and mobile sources. These sources are described in more detail in the following sections.

1.2 OVERVIEW OF HAZARDOUS WASTE AND MUNICIPAL SOLID WASTE COMBUSTION

For over one hundred years, the combustion of hazardous waste and municipal solid waste has been used in the United States to both generate energy and reduce waste volumes, with energy recovery from incineration of municipal solid waste beginning in New York City in 1898

(EIA 2005). It is estimated that 80 to 85 percent of the 3.6 million tons of hazardous waste combusted annually is burned in hazardous waste incinerators, cement kilns, and lightweight aggregate kilns, with the remaining hazardous waste burned in industrial boilers and other types of industrial furnaces. Currently, hazardous waste combustion occurs at approximately 244 facilities in 30 states, with the majority of the facilities located in southern states, primarily Texas and Louisiana (EPA 2004b).

Municipal solid waste is also commonly incinerated to reduce the volume of the waste and to generate energy. Approximately 14.7 percent (34 million tons) of 230 million tons of municipal solid waste generated annually in the United States is combusted (EPA 2003a). An additional four million tons of hazardous waste (two percent of all hazardous waste) are destroyed annually in hazardous waste incinerators (EPA 2005b). Furthermore, sewage sludge incinerators burn about 25 percent of the sewage sludge generated annually in the U.S. (Werther and Ogada 1999). Combustion of municipal solid waste increased steadily from the 1960s through the 1980s and has declined slightly since its peak in the 1980s. The majority of combustion of municipal solid waste in the United States incorporates recovery of the energy produced; these facilities are referred to as “waste-to-energy” facilities. In 2001, there were 97 waste-to-energy facilities in the United States, with 40 facilities in the Northeast, 30 in the Southeast, 19 in the Midwest, and eight in the West (EPA 2003a).

The composition of the uncontrolled emissions generated from the combustion of hazardous and municipal solid waste varies depending on combustor design and operating characteristics and on the composition of the waste and may include the following pollutants of potential concern:

- Particulate matter (PM).
- Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, known collectively as dioxins and furans.
- Organic compounds (volatile, semivolatile, and nonvolatile) other than dioxins and furans, often referred to as products of incomplete combustion (PICs).
- Metals that are potentially toxic to human or ecological receptors (e.g., mercury, lead, cadmium).
- Acid gases (e.g., hydrogen halides [HBr, HF, and HCl]), NO_x, and sulfur oxides (SO₂ and SO₃).

Table 1-1 provides an overview of the known human health effects of pollutants in each of these categories.

Human and ecological exposure to emissions of these pollutants can occur via a number of pathways. The pathways of primary concern can vary by pollutant. Most combustion emissions are released to the air. Human and ecological receptors can be exposed to these pollutants through inhalation. The pollutants can include PM, hydrogen chloride, and carbon

monoxide. Other pollutants generated by combustion, such as NO_x, can undergo chemical reactions in the atmosphere with other compounds to form secondary pollutants, such as tropospheric ozone, for which inhalation exposure is a concern.

In addition, some of these pollutants, such as dioxins and furans, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and metals, are persistent in that they do not quickly (or ever) degrade in the environment and have a tendency to bioaccumulate. Human and ecological exposure to these pollutants can occur through ingestion of soil or biota that have been impacted by emissions of these pollutants. For example, dioxin compounds released to the air could deposit to the surface of a plant, this plant could be consumed by a cow, which in turn is consumed by a human being, resulting in human exposure to the released dioxin compounds.

It is also important to note that emissions from incinerators and other industrial combustion processes are one of the primary sources of endocrine disrupting compounds (EDCs) in the environment. Evidence suggests that environmental exposure to some anthropogenic EDCs may result in disruption of endocrine systems in both human and wildlife populations. Because of the potential global scope of the EDC problem, the possibility of serious effects in humans and wildlife, and the persistence of some suspected EDCs in the environment, research on EDCs is a high priority in EPA's Office of Research and Development (ORD) (EPA 2005c).

1.3 REGULATION OF HAZARDOUS WASTE AND MUNICIPAL SOLID WASTE COMBUSTION

Combustion of hazardous and municipal solid waste has the potential to adversely affect human health and the environment and it is therefore subject to state and federal regulation. As a result, the burning of hazardous and municipal solid waste in incinerators, boilers, and industrial furnaces is regulated through stack emission limitations and unit operating requirements. The regulatory standards for hazardous waste combustion and municipal solid waste combustion are described separately below.

1.3.1 Hazardous Waste Combustion

Hazardous waste combustion is subject to standards under the Resource Conservation and Recovery Act (RCRA); and maximum achievable control technology (MACT) standards (i.e., National Emission Standards for Hazardous Air Pollutants) under section 112 of the Clean Air Act Amendments of 1990 (CAAA). Under RCRA, EPA's Office of Solid Waste (OSW) is responsible for ensuring that combustion units that burn hazardous waste (1) meet performance standards, including a demonstration of the unit's destruction and removal efficiency (DRE) for certain principal organic hazardous constituents (POHCs), and (2) meet emission standards for hydrogen chloride, chlorine gas, metals, and particulate matter.

Table 1-1 Known Health Effects of Constituents of Combustion Pollutant Emissions

Pollutant Category	Known Health Effects
Dioxins and Furans	Short-term (acute) exposure of humans to high levels may result in skin lesions and altered liver function. Long-term (chronic) exposure is linked to impairment of the immune system, the developing nervous system, the endocrine system, and reproductive functions. Identified as probable endocrine disrupting compounds (EDCs). Classified by EPA as a “known human carcinogen.” (WHO 1999; EPA 2004c) The contribution of combustors to EDCs in the environment is not known, hence the identified need for research.
Other PICs	Varies widely across chemicals. Some PICs are classified by EPA as “probable human carcinogens” or “known human carcinogens” and are linked to a range of non-cancer effects, such as impairment of the immune system and altered liver function. (EPA 2005d)
Metals	Linked to both chronic and acute health effects, although effects vary widely across chemicals. Metals emitted can include mercury, which is linked to birth defects, immune system damage, and nervous system disorders; lead, which is linked to nervous system disorders; and cadmium, which is linked to kidney failure, hypertension, and genetic damage.
Acid Gases	Acid gases are linked to acute and chronic respiratory effects. (EPA 2005d; WDNR 2003)
Particulate Matter	Particulate matter (PM) is linked to acute and chronic cardiopulmonary effects, including premature mortality. Scientific studies have linked particulate matter, especially fine particles (alone or in combination with other air pollutants), with a series of significant health problems, including: premature death; respiratory related hospital admissions; aggravated asthma; chronic bronchitis; and acute respiratory symptoms. (EPA 1997a)
Polychlorinated Biphenyls	PCBs have been shown to cause cancer in animals. PCBs have also been shown to cause a number of serious non-cancer health effects in animals, including effects on the immune system, reproductive system, nervous system, endocrine system and other health effects. Studies in humans provide supportive evidence for potential carcinogenic and non-carcinogenic effects of PCBs. (EPA 2004d)

To ensure the performance and emissions standards are met, the combustion unit’s RCRA permit sets operating requirements that specify allowable ranges for, and requires continuous monitoring of, certain critical parameters intended to ensure compliance with the performance and emission standards. Because hazardous waste combustion units are a type of treatment, storage, and disposal facility (TSDF), hazardous waste combustion units are also subject to the general TSDF standards under RCRA (EPA 2003b).

Under the CAAA, EPA’s OSW is responsible for developing MACT standards that limit emissions of hazardous air pollutants (HAP) from hazardous waste combustors (HWCs). The

EPA's Office of Enforcement and Compliance Assurance (OECA) is responsible for enforcing these standards. The MACT standards for HWCs were developed and implemented in two phases. The Phase 1 standards include federal emission limitations for dioxins and furans, mercury, semi-volatile and low volatile metals, particulate matter, carbon monoxide, hydrocarbons, DRE, and total chlorine for three categories of sources: hazardous waste incinerators, cement kilns, and lightweight aggregate kilns.

The Phase 1 standards were first promulgated in 1999 and then replaced with interim standards in 2002. EPA proposed replacement standards for the Phase 1 interim standards on April 20, 2004, and these replacement standards on October 14, 2005. The Phase 2 MACT standards for HWCs include federal emission limitations for boilers and hydrochloric acid production furnaces for the same set of pollutants as the Phase 1 standards. The Phase 2 standards were first proposed on April 20, 2004, and were also finalized on October 14, 2005 (EPA 2005e).

It is expected that the proposed Phase 1 and Phase 2 MACT standards will reduce emissions of hazardous air pollutants by approximately 3,300 tons per year, which equates to a 25 percent reduction in national annual HAP emissions from 1990 levels. This reduction in emissions may result in fewer premature deaths, fewer multiple organ cancers and endocrine and reproductive effects, fewer cases of chronic bronchitis, and reduced hospital admissions for pneumonia, asthma, and cardiovascular problems (EPA 2004b).

Upon implementation of the MACT standards, once a facility has demonstrated compliance with the MACT standards, it will no longer be subject to the RCRA emission requirements, with few exceptions. Existing RCRA permitted facilities, however, must continue to comply with their permitted emissions requirements until they obtain modifications to their RCRA permits to remove any duplicative emissions conditions (EPA 2003b).

1.3.2 Municipal Solid Waste Combustion

Air emissions are the principal environmental concern associated with the combustion of municipal solid waste. Thus, EPA's OAR is primarily responsible for regulating municipal solid waste combustors (MWC). These MWCs are regulated by OAR under Section 129 of the Clean Air Act, which specifies that New Source Performance Standards (NSPS) must be developed to apply to all newly constructed units while emission guidelines must be developed for existing units. The NSPS are direct federal regulations that apply to new sources. The emission guidelines for existing sources do not directly regulate MWCs; instead they establish requirements for State MWC Plans which are the vehicles by which states implement the emission guidelines. Once approved, these State Plans become federally enforceable. Both the NSPS for new MWCs and the guidelines for existing MWCs are MACT-based. The MWC regulations were adopted and implemented in two phases. In the first phase, MACT regulations for large MWCs were developed and in the second phase MACT regulations for small MWCs were developed. The large MWC regulations were adopted in 1995 and fully implemented by 2000. The small MWC regulations were adopted in 2000 and were fully implemented by the end of 2005.

The regulations for both new and existing sources require control of the following criteria and toxic pollutants: dioxins and furans, cadmium, lead, mercury, particulate matter, hydrogen chloride, sulfur dioxide, nitrogen oxides, and carbon monoxide. State MWC Plans include source and emission inventories, emission limits, and testing, monitoring, and reporting requirements, as well as generic or site-specific compliance schedules including increments of progress. Implementation of the MWC emission guidelines through the State MWC Plans have reduced toxic air pollutant emissions by 87,000 tons per year from 1990 levels for the following pollutants of concern: dioxin, metals, lead, mercury, particulate matter, acid gases, and nitrogen oxides. EPA is presently collecting MACT compliance data from small MWCs and will calculate emission reductions achieved. However, the calculations have not been completed. EPA expects the small MWC regulations to reduce emissions by more than 33,000 tons per year. In combination, emissions from large and small MWCs will have been reduced by 120,000 tons per year by these two MACT regulations. Specifically, the regulatory standards for large MWCs have reduced dioxin and furan emissions by more than 99 percent, and have reduced mercury emissions by more than 90 percent from 1990 levels (EPA 2005f). The same levels of reduction are expected for small MWCs.

1.4 OVERVIEW OF RELEVANT EPA RESEARCH

The combustion research that is the subject of this synthesis report is but a small part of the ORD research devoted to combustion over the past several years. It is in turn completely dwarfed by ORD's investment in PM research over the past several years which has ranged between \$53 million and \$68 million per year. Most of this latter research has been devoted to better understanding the impacts of PM on human health.

1.4.1 Overview of the ORD Particulate Matter Research Program

Over the last decade, a wealth of studies has underscored that anthropogenic air pollution—notably PM—can adversely impact human health and welfare, despite clear evidence that overall air quality has improved.¹ The White House Office of Management and Budget (OMB) has estimated an annual savings of \$120 to \$183 billion in hospitalization and emergency room visits, lost workdays, and premature deaths between 1992 and 2002 that can be attributed to air pollution regulations—again most notably PM (OMB 2003).

Reducing the uncertainties regarding the source-associated attributes of PM responsible for these impacts and the biological factors that underlie susceptibility would further increase these benefits. The goal is obtain information on critical combustion related factors that would lead to the development of cost-effective strategies to environmental regulation and control. Identifying individuals who may be at greatest risk would further refine assessment of associated risks.

¹ These data are summarized in the recently released *Air Quality Criteria Document for PM* (EPA 2004e) and *Air Quality Criteria for Ozone and Related Photochemical Oxidants (Draft)* (EPA 2005g). Trends in air quality and emissions can be found at the EPA Office of Air Quality, Planning, and Standards website <http://epa.gov/air/oaqps/cheanair.html>.

By 1997, the scientific evidence, although still controversial, was sufficient for EPA to conclude that respirable ambient levels of PM presented significant risks to public health. Therefore, the existent National Ambient Air Quality Standard (NAAQS) for particulate matter with a diameter of less than 10 microns (PM₁₀) was revised and an additional, new NAAQS for particulate less than 2.5 microns in diameter (PM_{2.5}) was established. Congress chose to augment the President's recommended EPA budget to accelerate investigations of the role of PM in air pollution-associated health outcomes, and to implement health risk reductions via scientifically defensible regulatory analysis.

Congress also mandated the formation of a committee of air pollution experts via the National Academy of Sciences' National Research Council (NAS/NRC) to assist in this national effort. This NRC Committee met initially to define the scope of the issue and subsequently produced a series of documents (most recently in Vol. IV published in April 2004), that evaluated ongoing scientific and administrative progress which reduced uncertainties associated with the PM issue and made recommendations regarding direction and implementation of the program. Following the release of a related NRC report in 2004 entitled *Air Quality Management in the United States* (NRC 2003), a subgroup of the Clean Air Act Advisory Committee (CAAAC) developed parallel recommendations for improvements to air quality management.

The intervening years of intensive research activity since the initial NRC research Priorities Report in 1998, have yielded significant advances in the understanding of health, exposure and atmospheric PM science. In February 2004, ORD released *Particulate Matter Research Program: Five Years of Progress* (EPA 2004f), which summarized the achievements of EPA's research program in advancing understanding of both health/exposure and air quality issues. Advances were summarized into three broad areas: (a) the credibility and extent of PM-associated health effects and the complex roles of PM attributes and human host factors that contribute to the health outcomes; (b) the factors determining public and individual exposures, including characterization of the sources and atmospheric processes needed to aid implementation of the NAAQS; and (c) the development and implementation of 'tools' and state-of-the-art technologies needed by the EPA regions, states, and tribes to implement the NAAQS and achieve EPA's Strategic Air Quality Goal to "protect and improve the air so it is healthy to breathe and risks to human health and the environment are reduced" (EPA 2003c).

The PM Program has provided essential information for the reassessment of the PM NAAQS which is expected to be promulgated in December 2006. Meanwhile, essential tools for attainment assessments and the development of State Implementation Plans have been released, and these processes are well underway. The research program continues to work in the area of characterizing the health impacts of PM and refining implementation tools and data to assist local regulators in meeting the NAAQS. The evolution of "PM science" has moved the research to addressing questions regarding the hazardous components or attributes of PM as key to reducing risk. The complex nature of this approach is such that the research has focused more on profiling sources of PM modes in an effort to move to controlling key and essential contributing sources to the atmospheric PM-complex.

Initially, this effort has focused on primary fossil fuel combustion sources (coal, oil, diesel gasoline and natural gas) emitting a broad spectrum of suspect components, including organics, metals, sulfates, and related compounds. Of these, animal inhalation studies have been conducted to date on oil and coal emissions and diluted diesel exhaust. Specifically, studies are manipulating the chemical composition of these combustion atmospheres in an effort to alter subsequent toxicity. In addition, susceptible animal models are being used to learn more about potential risk. Similarly, human studies of diesel emissions are also conducted with a focus on both the health outcomes and potential its gene-environment interactions. Field epidemiology studies are being integrated (e.g. Detroit) with exposure and observational studies in human, with a goal of determining associations with specific sources. Emission surveys are being done in the field with new advanced technologies; and atmospheric models are being refined along with specific methods to measure PM models likely to be regulated (fine and coarse PM). Other PM sources (e.g., automobile, wood smoke, and potential specialized emitters) and secondary transformation PM products are planned for study.

The fundamental goal of the research program is to better understand the multiple aspects of air quality, exposure and health from a multipollutant perspective. This would be achieved by linking health outcomes with pollutant sources through the complexities of atmospheric transformation. Among this complexity is determining who is at greatest risk (susceptible subgroups—children, elderly, and health compromised). In the end, a more comprehensive understanding of air pollution and strategic approach to effective and efficient control can be established.

1.4.2 Overview of the Resource Conservation and Recovery Act (RCRA) and ORD's RCRA Research

Since 1976, active industrial facilities and generators, handlers, and disposers of hazardous waste have managed their facilities and operations to reduce the improper disposition of hazardous materials.

The Resource Conservation and Recovery Act of 1976 (RCRA), and subsequent acts to amend and supplement it, seeks to ensure proper management of large volumes of industrial and municipal waste. RCRA originally framed waste management options hierarchically, with reducing waste generation as the most preferred option, and effective waste disposal as the least preferred, albeit most widely used approach.

For nearly three decades RCRA implementation by EPA, and by states with delegated authority, focused foremost on defining wastes, defining acceptable management practices and acceptable treatment and disposal methods, and ensuring corrective action where hazards were not effectively controlled. Over the last decade, there has been an increasing focus on the conservation component of RCRA, with multiple efforts to reduce municipal solid waste, commercial and industrial solid wastes, and hazardous wastes.

More recently OSW issued the Resource Conservation Challenge (EPA 2005h), which focuses on four areas:

- Municipal Solid Waste Recycling.
- Reusing and Recycling Industrial Materials.
- Priority and Toxic Chemical Reductions.
- Green Initiatives Electronics.

Research to support RCRA has paralleled program development over the years. Early work focused on assessing risks from solid waste and identifying wastes that should be designated as hazardous; developing and demonstrating effective methods for waste treatment; developing and demonstrating effective waste containment in landfills and the materials used to isolate the waste; and evaluating approaches for reducing the stream of municipal solid waste destined for landfills. For the past several years, the research program has placed additional focus on waste minimization and resource conservation.

The research program, with total resources of \$11.6 million in fiscal year 2006 and \$10.6 million requested in the President's Budget for fiscal year 2007, is focused on multimedia decision making and various options for managing wastes and materials.

The multimedia decision making component of the research program has developed a model framework, technical modules, and underlying science to support national level decisions on waste management. The work was favorably reviewed by a panel of the Science Advisory Board (see *EPA's Multimedia, Multipathway, and Multireceptor Risk Assessment [3MRA] Modeling System: A Review by the 3MRA Review Panel of the EPA Science Advisory Board [EPA 2004g]*). As the research continues, the emphasis will be on the broader question of materials management, which can encompass not only waste management decisions, but decisions related to beneficial use of waste and material selections to reduce the use of toxic constituents, prevent pollution, and move toward sustainability.

The waste and materials management component of the program has covered three themes: landfills, hard-to-treat wastes and leaching tests, and combustion. Resource reductions in recent years may not allow research in all three areas to be sustained.

Landfills are still widely used for municipal solid waste and hazardous wastes. Ongoing research addresses both conventional containment materials and landfill bioreactor operation. The concept of a bioreactor is to operate the landfill in such a way that organic wastes are rapidly degraded, yielding recovered landfill capacity and offering the possibility of generating higher methane volumes early in the landfill life that can be captured for energy value. Research needs to determine favorable operating conditions, suitable monitoring requirements, and ways to ensure that fugitive gas emissions are controlled. Ongoing research investigates the properties and performance of conventional liner and cover materials because we rely on these materials to permanently segregate waste and its hazardous constituents from people and the environment.

The small research effort on hard-to-treat wastes has focused on wastes containing species like mercury and arsenic, which have complex chemistry that is not amenable to

conventional treatment processes. Leaching test research is related to waste treatment in that the test is trying to estimate the degree to which treatment will be successful in preventing the spread of hazardous constituents. Having reliable, well-understood leach tests becomes even more important as recycling and beneficial use of materials that were formerly disposed of in landfills becomes more widespread. Multiple tests are being evaluated to address some deficiencies noted by the Science Advisory Board in commentaries on the subject.

Combustion research is important because many thermal units have to be permitted under RCRA, generally by states with delegated authority. The research needs for complying with RCRA and with air pollution control requirements overlap, and the research planning is coordinated to avoid duplication of effort. RCRA research is focused on understanding organic compound transformations in the combustion process and on monitoring organic and metals in combustor emissions. The purpose of both efforts is to guide and optimize combustor operation to minimize formation and emission of toxic constituents including chlorinated dioxins and furans and metals. Monitoring research investigates advanced sensors that can detect one or more constituents of concern or surrogates that are easier to analyze. The regulatory authorities can then stipulate operating conditions and monitoring controls that reduce risks to people and the environment.

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2. BACKGROUND AND APPROACH

2.1 DESCRIPTION OF REQUEST FOR APPLICATIONS

On February 17, 1999, EPA's NCER published a Request for Application (RFA) soliciting research proposals on topics that will supplement current understanding of risks posed by the emission of contaminants from hazardous waste incinerators, boilers and industrial furnaces, and municipal solid waste incinerators. The RFA explicitly excluded from consideration research on medical waste incinerators or any research being solicited under other EPA programs (e.g., mercury research). The RFA emphasized the need for an improved understanding of indirect exposure pathways, including the transport, transformation, and environmental fate, of combustion products, particularly for combustion products not already receiving priority attention (e.g., co-planar PCBs, brominated aromatic hydrocarbons, and metals such as arsenic).

2.2 OVERVIEW OF RESEARCH CONDUCTED UNDER COMBUSTION RESEARCH GRANTS

NCER identified in the 1999 RFA the need to (1) improve understanding of indirect (i.e., non-inhalation) exposure pathways, particularly for pollutants not already receiving priority attention, and (2) determine which pollutants are of most potential concern. EPA awarded five grants under the STAR program in 2000 to address these issues. The total investment in these grants was \$1,685,000. They were completed in 2004-2005. These five grants and their Principal Investigators (PIs) are listed in Table 2-1.

The overall objective of Taylor's research project (R828189) was to determine the rates and mechanisms of hydroxyl (OH) radical reactions with dioxin and selected congeners in waste combustion systems over an extended temperature range. The gas-phase transformation of dioxins under high-temperature incineration conditions is not well understood, but studies have shown that OH radical reactions are among the most important elementary steps in dioxin formation under these reaction conditions.

Senkan's (R828193) research goal was to develop insights into the formation and control of potentially toxic PICs in the incineration of brominated and other halogenated hydrocarbons. Because some of these PICs are known or suspected carcinogens, a better understanding of their origins and formation mechanisms is important in assessing potential control mechanisms for the continued use of incineration as a waste minimization technology. The presence of brominated flame retardants in consumer electronics goods and other products are of concern, both from a PIC standpoint, but also because BFRs have been implicated as potential EDCs.

Dellinger and Lomnicki (R828191) studied the mechanism of the formation of dioxins and furans on metal oxide surfaces. Previous field studies have suggested that dioxins and furans are formed in the post-combustion, cool-zone of combustors by surface-mediated/catalyzed pathways, rather than in the primary combustion chamber. The objective of Dellinger and Lomnicki's grant was to reveal the chemical mechanism of this formation.

There is an overall need for improved analytical techniques to identify and quantify chemical compounds in combustion systems in a rapid manner. To help address this need, Rubey, Striebich, and Taylor (R828190) developed, tested, and applied advanced multi-dimensional gas chromatography (MDGC) instrumentation, capable of achieving high resolution separations, to examine combustion effluents and residues. Their goal was to conduct separations and characterization of individual constituents of combustion effluents and residues in a two column gas chromatography system, in such a way that the second column was operating fast enough to keep up with the first column analysis. Rubey, Striebich, and Taylor applied the MDGC method to various types of combustion emissions, including emissions from incineration, open burning, and mobile sources.

Smith and Boudries (R828192) recognized the critical need for real-time (i.e., fast enough as to seem instantaneous) quantification of pollutants associated with fine particulates in the exhaust gas of waste and sewage sludge incinerators. Fine particulates (i.e., those particulates smaller than 2.5 microns in diameter) are able to penetrate deeper into the human lungs and, if deposited there, may be an efficient vehicle for exposure to many different chemicals (Wilson and Spengler, 1996). Several previous studies also showed that incinerator emissions are enriched in particulate matter sized 0.10 to 2 μm due to decreased efficiency in particulate control for this size range (Saxena and Jotshi 1996; Ruth 1998).

These particulates tend to be enriched in condensable organics and toxic metals such as arsenic, cadmium, and lead (Ruth 1998; Linak and Wendt 1993; Niessen and Porter 1991). This enrichment occurs because the amount of condensation of a given species during exhaust cooling is proportional to the particle surface area, thus favoring fine particles over coarse ones. Thus, there is a need to better quantify the amount, chemical composition, and toxics content of these particles. The objective of their research project was to perform a real-time analysis and quantification of fine particulate emissions in the exhaust of waste incinerators, as well as develop instrumentation for this type of analysis, promote real time monitoring, and better characterize combustion emissions.

2.3 OBJECTIVES OF THIS REPORT

This synthesis report was developed with the following five objectives:

- (1) Summarize the important scientific findings of each of the five research projects that resulted from this RFA.
- (2) Place these findings in the context of past and on-going research on combustion emissions in general (briefly) and combustion emissions from hazardous waste and municipal solid waste combustion (in greater detail).
- (3) Identify the contributions of these projects to achieving the goals and objectives of EPA ORD's RCRA Multi-Year Plan (EPA 2004a).

Table 2-1 Grants Awarded Under the Combustion Emissions Solicitation*

Grant Number	Principal Investigator(s)	Institution	Title of Project
R828189	Phillip H. Taylor	University of Dayton	<i>Mechanistic Studies of the Transformation of Polychlorinated Dibenzo-p-Dioxins via Hydroxyl Radical Attack</i>
R828191	Barry Dellinger, Slawomir Lomnicki	Louisiana State University - Baton Rouge	<i>Toward the Development of a Detailed Mechanism of Transition Metal Catalyzed Formation of PCDD/F from Combustion Generated Hydrocarbons</i>
R828193	Selim M. Senkan	University of California – Los Angeles	<i>Products of Incomplete Combustion in the Incineration of Brominated Hydrocarbons</i>
R828190	Wayne A. Rubey, Richard Striebich, Philip H. Taylor	University of Dayton	<i>Trace-level Measurement of Complex Combustion Effluents and Residues using Multi-dimensional Gas Chromatography-Mass Spectrometry (MDGC-MS)</i>
R828192	Kenneth A. Smith, Hacene Boudries, Xuefeng Zhang, Douglas R. Worsnop	Massachusetts Institute of Technology, Aerodyne Research Inc.	<i>Characterization and Minimization of Fine Particulate Emissions from Waste Incinerators by Real-Time Monitoring of Size-Resolved Mass and Chemical Composition</i>

* Further information regarding the STAR grants program and these grants in particular is available at <http://www.epa.gov/ncer>.

- (4) Identify research needs related to the topic areas of these projects and the RFA in general.
- (5) Provide a summary of research needs.

2.4 METHODOLOGY

This section describes the methodology used to generate this report, particularly the information sources and how each was used, and summarizes the quality assurance plan and review process used to ensure that the report is accurate and meets the stated objectives.

2.4.1 Information Sources

This report was developed using a number of different sources, including:

- Reports, publications, and presentation materials provided by the PIs.

- Notes taken at the December 2003 EPA-AWMA Information Exchange, an annual two-day event with an audience of EPA staff, industry representatives, academia, and environmental consultants, which included at the end of the second day a panel of PIs and an ORD laboratory representative presenting EPA extramural and in-house combustion research with a guided discussion of research needs after the presentations.
- Notes taken at the April 2005 American Flame Research Committee meeting, which included presentations by several ORD in-house researchers, presentations by the PIs, and a consultant's presentation of a draft of this synthesis report, followed by a discussion of criteria for setting priorities for combustion research.
- Interviews with experts in the field of combustion research (see Appendix A).
- Limited literature review of past and ongoing combustion research.

Descriptions of the methodologies and results of the five grants were developed using annual status reports, final technical reports, publications, presentations and presentation materials, and discussions with and written comments provided by the PIs.

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3. RESULTS AND CONTRIBUTIONS OF THE RESEARCH

3.1 MECHANISMS OF FORMATION OF CHEMICAL COMPOUNDS IN COMBUSTION SYSTEMS

Research into the mechanisms of formation of chemical compounds in combustion systems is a broad theme of the EPA RCRA Multi-Year Plan (EPA 2004a). Research by Taylor and by Dellinger and Lomnicki described in this section both relate to improving the understanding of mechanisms of formation of chlorinated dioxins and furans in combustion systems. The research conducted by Senkan described in this section relates to incineration of brominated compounds and formation of halogenated dioxins and furans and polycyclic aromatic hydrocarbons.

These three projects identify dioxin and furan precursor compounds and support development of a comprehensive model of the formation and transformation of halogenated dioxins and furans under various combustion conditions for various types of wastes, and also support site-specific risk assessment for combustion systems. Results of these studies are also applicable to the development of risk management strategies and emissions abatement strategies for combustion systems.

3.1.1 Mechanistic Studies of the Transformation of Polychlorinated Dibenzo-p-Dioxins via Hydroxyl Radical Attack, Philip H. Taylor, University of Dayton

3.1.1.1 Background

Polychlorinated dibenzo-p-dioxins (PCDD) are considered among the most toxic organic chemicals associated with our industrial society. The gas-phase formation and transformation of these chemicals under high-temperature incineration conditions are not well understood. Previous studies have shown that OH radical reactions are among the most important elementary steps in dioxin transformation under these reaction conditions. Prior determinations of OH radical rate coefficients with dioxins in combustion systems do not exist. Prior bench-scale experiments on formation of dioxins in combustion systems have measured the formation of dibenzo-p-dioxin (DD), 1-chlorodibenzo-p-dioxin, 2,7-dichlorodibenzo-p-dioxin (2,7-DCDD), and 1,2,3,4-tetrachlorodibenzo-p-dioxin (TCDD) at low temperatures (< 500 K) relevant to atmospheric conditions. A review of the literature demonstrates that knowledge of the rate of reaction of OH with DD and PCDD is limited to three low temperature experimental studies and to inference from estimates of room-temperature reactivity. The mechanism of reaction is completely uncharacterized and is addressed as part of this research project.

3.1.1.2 Objectives

The overall objective of this research project was to determine the rates and mechanisms of OH radical reactions with DD and selected PCDD compounds over an extended temperature range. The specific objectives of this research project were identified as follows:

- (1) Obtain first absolute rate measurements of the reaction of OH radicals with DD (**k1**); 2-chloro dibenzo-p-dioxin (2-CDD) (**k2**); 2,3-dichlorinated dibenzo-p-dioxins (2,3-DCDD) (**k3**); 2,7-DCDD (**k4**); 2,8-DCDD (**k5**); TCDD (**k6**); and octachloro dibenzo-p-dioxin (OCDD) (**k7**) over an extended temperature range (including temperatures approaching post-combustion conditions) with determination of accurate Arrhenius or modified Arrhenius parameters.
- (2) Verify previous low temperature rate measurements for DD, 2,7-DCDD, and 1,2,3,4-TCDD.
- (3) Investigate mechanisms of the reaction by examining the relative importance of the following pathways through limited theoretical analyses: OH addition, OH addition followed by Cl elimination, and H-atom abstraction.

3.1.1.3 Methodology

OH radicals were produced by three methods:

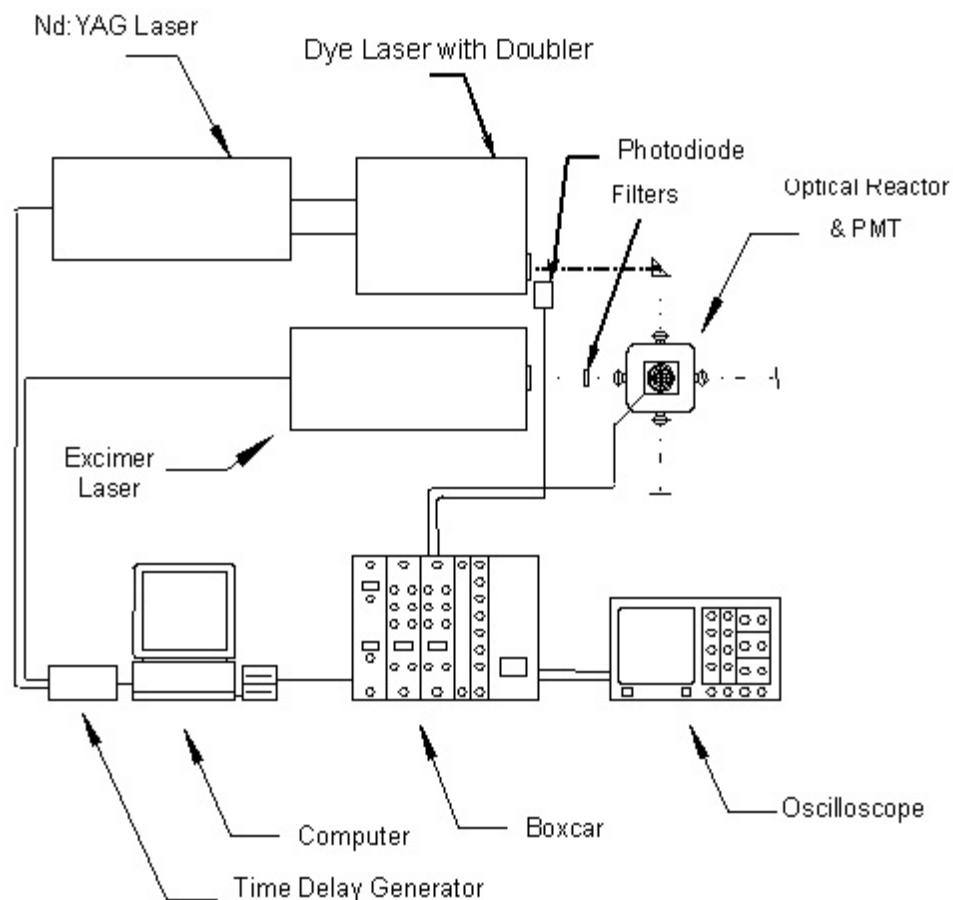
- Photodissociation of nitrous oxide/water vapor mixtures (wavelength = 193 nm).
- Photodissociation of hydrogen peroxide (wavelength = 248 nm).
- Photodissociation of nitrous acid (wavelength = 351 nm) using an excimer laser.

Measurements at lower temperatures were conducted with hydrogen peroxide and nitrous acid to investigate the effect of photolysis wavelength on the rate measurements. The nitrous oxide precursor system was used predominantly at elevated temperatures. Experiments were conducted at low photolysis energies to minimize photolysis of the substrates. Detection of OH radicals was achieved by laser-induced fluorescence (LIF), exciting the OH band at 282.2 nm with LIF observed at 306 nm. A schematic of the experimental apparatus is shown in Figure 3-1, and a schematic of the optical reactor is shown in Figure 3-2.

Gas-phase dioxin was introduced as follows:

1. Solid substrates (typically 4 to 5 mg of sample) were loosely packed into quartz tubing and set in place using quartz wool. The dioxin and chlorinated dioxin substrates were 98+ percent pure and were used as received.
2. Helium or argon carrier gas was passed through a sample probe and delivered a known amount of dioxin vapor to the reactor.
3. Desired dioxin concentration was obtained by controlling sample temperature, measured by a thermocouple.
4. Concentrations of DD, 2-CDD, and 1,2,3,4-TCDD in the gas stream were comparable to recent vapor pressure measurements for these substrates as reported in the literature.

Figure 3-1 Schematic of Overall Reactor System for Taylor's Grant



- Concentration was controlled by changing the carrier gas flow rate through the sample inlet at a constant temperature.

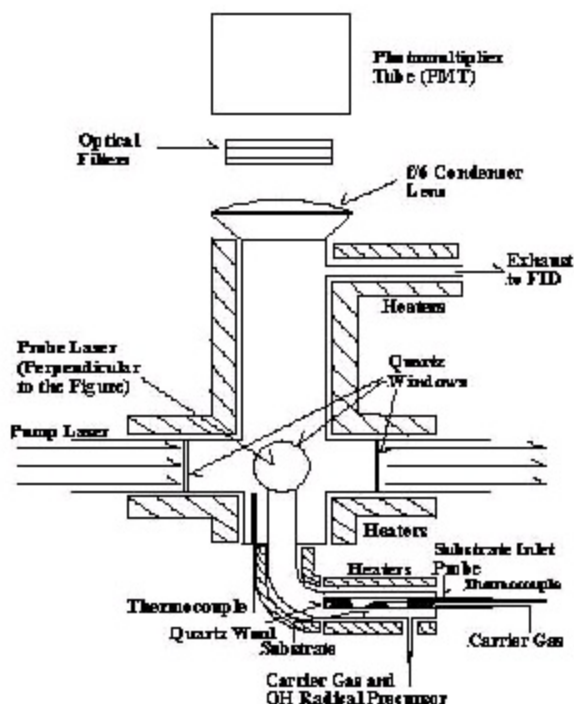
The buildup of reaction products was minimized by conducting experiments under slow flow conditions. Total gas flows ranged from 220 to 775 ml per minute; linear gas velocities ranged from 12.9 to 37.6 cm per second. Experiments were performed at a total pressure of 740 ± 10 torr. All experiments were performed under pseudo-first order conditions. Pseudo-first order exponential OH decays were observed, confirming that the substrate concentration was in large excess of OH. The individual bimolecular rate constants were determined from:

$$k' = k_{bi}[\text{substrate}] + k_d$$

where:

k' = pseudo-first order rate constant;

Figure 3-2 Blow-Up Schematic of Optical Reactor for Taylor's Grant



k_{bi} = bimolecular rate constant, which is the slope of the least-squares fit of k' versus substrate concentration; and

k_d = first-order decay constant due to diffusion and reaction with the OH precursor.

First absolute rate measurements were acquired using Laser Photolysis/Laser Induced Fluorescence (LP/LIF) technique.

3.1.1.4 Results and Discussion

Experimental Results

Absolute rate measurements were reported for OH reaction with DD, 2-CDD, 2,3-DCDD, 2,7-DCDD, 2,8-DCDD, 1,2,3,4-TCDD, and OCDD (**k1-k7**). Rate measurements were obtained over a temperature range of approximately 300 to 400 K (27 to 127°C) to approximately 900 K (627°C). Measurements at lower temperatures were not possible because of the inability to establish pseudo first-order conditions in the reactor because of the low substrate vapor pressures. The upper limit temperature for the experiments performed was 1,000 K, due to thermal dissociation of the OH radical precursor (nitrous oxide, N_2O). The dioxin substrates may also begin to dissociate at this temperature, although measurements to 1,100 to 1,200 K may be possible using a different OH radical precursor or through modification of the optical reactor (a

reduction of the residence time at temperature of the N₂O precursor would minimize its dissociation and permit measurements to slightly higher temperatures).

Changes in carrier gas (helium or argon) had no impact on the rate measurements within statistical uncertainties. Variation in photolysis wavelength (193 and 248 nm, and 351 nm for DD and 2-CDD), photolysis energy, total flow rate, substrate concentration, and initial OH concentration also had no impact on the rate measurements within statistical uncertainties. The major source of error in these measurements was the uncertainty in the substrate concentration. Overall, uncertainties ranged from +/- a factor of 2 (DD, 2-CDD, 2,3-DCDD, 2,7-DCDD, and 2,8-DCDD) to +/- a factor of 4 for 1,2,3,4-TCDD and OCDD.

An Arrhenius fit of the extended temperature data for k1 to k7 yielded the following expressions (in units of cm³/molecule-second; error bars are 1 σ):

$$\begin{aligned} \mathbf{k1} \text{ (326-907 K)} &= (1.70 \pm 0.22) \times 10^{-12} \exp(979 \pm 55)/T, \\ \mathbf{k2} \text{ (346-905 K)} &= (2.79 \pm 0.27) \times 10^{-12} \exp(784 \pm 54)/T, \\ \mathbf{k3} \text{ (400-927 K)} &= (1.83 \pm 0.19) \times 10^{-12} \exp(742 \pm 67)/T, \\ \mathbf{k4} \text{ (390-769 K)} &= (1.10 \pm 0.10) \times 10^{-12} \exp(569 \pm 53)/T, \\ \mathbf{k5} \text{ (379-931 K)} &= (1.02 \pm 0.10) \times 10^{-12} \exp(580 \pm 68)/T, \\ \mathbf{k6} \text{ (409-936 K)} &= (1.66 \pm 0.38) \times 10^{-12} \exp(713 \pm 114)/T, \\ \mathbf{k7} \text{ (514-928 K)} &= (3.18 \pm 0.54) \times 10^{-11} \exp(-667 \pm 115)/T. \end{aligned}$$

Comparison of the absolute rate measurements for DD, 2,7-DCDD, and 1,2,3,4-TCDD with previous relative rate measurements generally were within combined experimental uncertainties of the respective measurements.

In most cases, the likely reaction mechanism for the chlorinated dioxin congeners is OH addition to form a stabilized hydroxycyclohexadienyl-type radical. The magnitude and negative temperature dependence of rate measurements are consistent with this mechanism. The reaction rate and temperature dependence of the OH + OCDD reaction was different from all other chlorinated dioxin congeners examined in this study. OCDD exhibited a slower reaction rate and *positive* temperature dependence throughout the temperature range studied. OH addition at the Cl-substituted carbon site was the dominant pathway for the OH + OCDD reaction at all temperatures. OH addition followed by Cl elimination is not significant for the other chlorinated dioxin congeners because of the much faster OH addition to the non-chlorinated carbon sites.

At elevated temperatures (500 to 1,000 K [227 to 727°C]) relevant to combustion and post-combustion conditions, there was no evidence for a change in reaction mechanism from the formation of a stabilized OH addition to H atom abstraction. However, at higher temperatures (> 1,000 K [727°C]), H atom abstraction is likely the dominant reaction mechanism for most if not all dioxins (excluding OCDD).

Peer-Reviewed Publication

- Taylor, P.H., T. Yamada, and A. Neuforth. Kinetics of OH radical reactions with dibenzodioxin and selected chlorinated dibenzo-p-dioxins. *Chemosphere* 58(3): 243-252.

3.1.1.5 Utilization of Research Results

The fundamental data and models developed in this study will contribute to the infrastructure of knowledge of reactions of chlorinated hydrocarbons and their impact on the environment. Results of this research project provide important inputs in the development of a comprehensive gas-phase model of the transformation of PCDDs under a wide range of conditions. This model can be used to manage risk by preventing and controlling formation and emissions of PCDDs through combustion modification or other emission abatement techniques. The model can also be applied to site-specific risk assessment for combustion sources. There is, however, no published kinetic model incorporating these rate coefficients.

3.1.1.6 Research Needs

Project-Related Research Needs

The PI identified the following research needs related to the above project:

- Dioxin atmospheric fate data are needed for source attribution studies.
- The understanding of the fate of dioxins in the atmosphere needs to be improved. This requires ambient temperature kinetic data versus the high temperature chemistry data obtained in this study.
- Results of this study should be compared with those results generated from different techniques.
- Extension of the work to other CDD species, especially 2,3,7,8 TCDD.
- Collection and analysis of experimental data to follow the degradation reaction scheme for CDD species after OH addition to track changes (up or down) in the environmental significance of downstream species (PICs).
- A comprehensive model for dioxin formation in incinerators should be developed, but not if there are insufficient funds to validate the full-scale model.

3.1.2 Toward the Development of a Detailed Mechanism of Transition Metal Catalyzed Formation of PCDD/F from Combustion Generated Hydrocarbons, Barry Dellinger and Slawomir Lomnicki, Louisiana State University - Baton Rouge

3.1.2.1 Background

The formation of dioxins and furans in combustion sources is a significant environmental issue. Field studies suggest that they are formed in the post-combustion, cool-zone of combustors by surface-mediated/catalyzed pathways. Laboratory studies have demonstrated that some transition metals, incorporated into silica-based fly ash, can catalyze dioxin formation in the 250 to 500°C (523 to 773 K) range. However, the exact mechanism has not been determined and is the subject of this research project.

3.1.2.2 Objectives

The objective of this research project was to reveal the mechanism of the formation of dioxins and furans on metal oxide surfaces based on the following assumptions:

- Dioxins can be formed by surface condensation of dioxin precursor compounds (e.g., chlorophenols, chlorobenzenes).
- Light hydrocarbons (containing less than 6 carbon atoms) present in the combustion system exhaust gas stream can undergo metal catalyzed growth and aromatization to form dioxin precursors.

3.1.2.3 Methodology

Experimental studies were conducted using a high-temperature flow reactor equipped with an in-line GC-MS for chemical analysis of the reactor effluent. The system is designed so that solid, liquid, or gaseous reactants, as pure compounds or mixtures, can be introduced at a constant feed rate. The injection region of the system has a separate temperature control to facilitate introduction of reactants. The system is designed for interchangeable reactors. The gas-phase reactor can be operated from room temperature to 1,100°C and gas-phase residence times of 0.25 to 6.0 s. The solid phase reactor can be operated over the same temperature range but the gas-phase residence time is typically < 2.0 s within the packed-bed.

The GC-MS is connected to the outlet of the reactor by a heated transfer line. The temperature of all transfer lines is maintained at a temperature that allows reactant and products to be transported without thermal degradation. Because the reactor effluent is directly transported to the GC without intermediate trapping, very low levels (20 pg) of products can be detected. The GC column is cryogenically cooled with liquid nitrogen, which traps and focuses the products at the head of the GC column. Once the temperature program of the GC is activated, normal separation of products and GC-MS analysis is performed.

For the purposes of this research project, catalytic tests were performed under both oxygen-free and oxidative conditions. Experiments were set up as follows:

- A five percent copper oxide/silica catalyst system was prepared.
- Experiments were carried out under two conditions: pyrolytic (helium only) and oxidative (20 percent O₂ in helium).
- Studies were performed over a 200 to 500°C (473 to 773 K) temperature range, using 1 mg and 3 mg of the catalyst.
- 2-chlorophenol was introduced to a fixed bed flow reactor. The gas-phase concentration of 2-chlorophenol ranged from 30 to 180 parts per million (ppm).
- A reactant flow rate of 5.5 cm³ per minute was used.

Figure 3-3 depicts a flow diagram of research activities associated with Dellinger and Lomnicki's project. The block at the top labeled chlorophenol and copper oxide processes refers to the reaction of chlorinated phenols over a copper oxide catalyst bed. PCDD/F as well as non-PCDD/F (PICs, or products of incomplete combustion) were identified in the flow reactor studies (middle path in the diagram). Separate NSF-funded studies addressed chemisorption of PCDD/F precursors and formation of surface-associated, persistent free radicals (left-hand path). Assessment of reaction and rate constants led to the development of reaction kinetic models of PCDD/F formation (right-hand pathway).

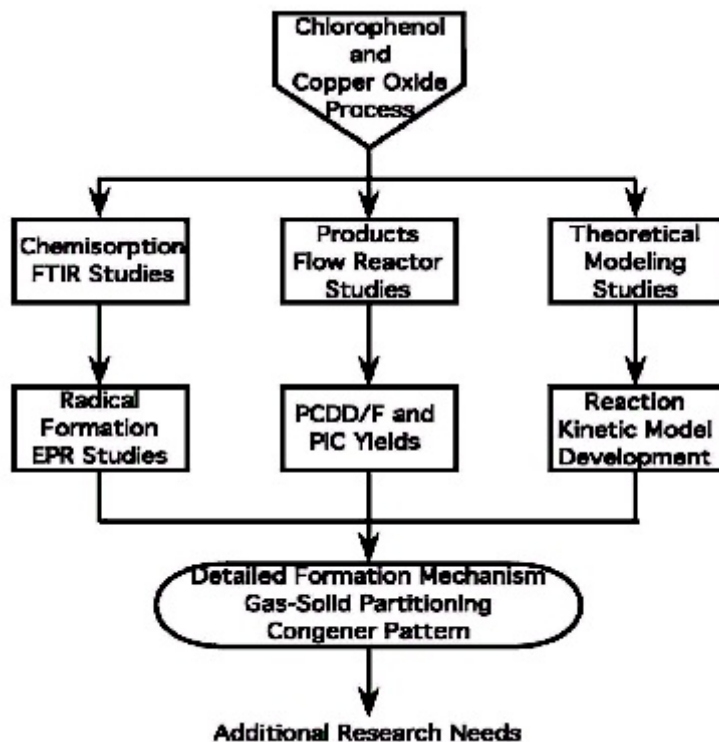
3.1.2.4 Results and Discussion

Experimental Results

Catalytic Test (Pyrolytic Conditions):

- The direct condensation reaction of 2-chlorophenol formed a limited number of PCDD/F congeners as follows: dibenzo-p-dioxin (DD), 1-monochlorodibenzo-p-dioxin (MCDD), and 4,6-dichlorodibenzofuran (DCDF).
- For the surface mediated reaction, the maximum PCDD/F formation occurred at temperatures around 400 to 450°C (673 to 723 K).
- For the gas-phase reaction, the maximum PCDD/F formation occurred at temperatures around 550 to 600°C (823 to 873 K).
- 0.28 percent of the 2-chlorophenol introduced was converted to one or more of the three congeners.
- The highest overall conversion occurred for DD; at low temperatures (200 to 350°C [473 to 623 K]), DCDF yield was highest.

Figure 3-3 Flow Diagram of Research Activities of Dellinger and Lomnicki's Project



- Similar trends were observed using 1 mg and 3 mg of catalyst. The amount of catalyst *did not* affect conversion of 2-chlorophenol to DD and MCDD, but *did* affect DCDF conversion. Conversion to DCDF increased from 0.11 percent for 3 mg catalyst to 0.15 percent for 1 mg of catalyst. The smaller the amount of catalyst, the higher the yield of DCDF.
- There was a sharp decline in PCDD/F formation above 475°C (748 K) due to the oxidation of PCDD/Fs or its surface precursors. The surface of the copper oxide was the source of the oxygen for this oxidation process.
- More than 95 percent of 2-chlorophenol was oxidized at temperatures above 350°C (623 K).
- As a result of the 2-chlorophenol reaction over the catalyst, higher chlorinated congeners of dioxins were found in the reaction products. Almost all PCDD congeners were detected; however, at temperatures of 350°C (623 K) and above, polychlorinated dioxins disappeared from the products and only DD and MCDD were formed. No higher chlorinated furans were detected in reaction products over the entire temperature range.
- A correlation between the amount of DD formed and the amount of highly chlorinated dioxin reaction products was observed. DD stays adsorbed to the surface immediately

after its own formation at low temperature (200 to 350°C [473 to 623 K]). It is believed that highly-chlorinated dioxins result from the chlorination of adsorbed DD. When temperature increases (in this case at 350°C [623 K] and above), the desorption rate of DD increases, the amount of dioxin formed increases, and polychlorinated dioxins disappear.

Catalytic Test (Oxidative Conditions):

Similar experiments were performed under oxidative conditions, results of which are discussed below.

- At 3 mg of catalyst, no PCDD/Fs were detected at temperatures above 250°C (523 K). Below 250°C (523 K), only MCDD was detected. However, its maximum yield was only at the detection limit. Therefore, other PCDD/Fs may have been formed, but below detection limits.
- At 1 mg of catalyst, MCDD yield was highest (~0.28 percent), an order of magnitude higher than the MCDD yielded under pyrolytic conditions. This highest yield occurred at 350 to 375°C (623 to 648 K). Because MCDD is desorbed after its formation, it is not subject to extensive surface oxidation by the copper oxide.
- Yield of DCDF appeared to be unaffected by the presence of oxygen. Therefore, oxygen does not appear to be a limiting factor in DCDF formation.
- Yield of DD dropped by one half in the presence of gas-phase oxygen. It was hypothesized that, with the presence of oxygen, more of the surface-adsorbed DD is being oxidized, resulting in an overall decrease in DD yields.
- More highly chlorinated PCDDs were formed as reaction products under oxidative conditions versus pyrolytic conditions. Under oxidative conditions, the rate of DD chlorination (to form the highly chlorinated PCDDs) was greater than the rate of DD adsorption.

As mentioned earlier, the chlorination process and formation of highly chlorinated PCDDs was suppressed under pyrolytic conditions at temperatures of 350°C (623 K) and above; however, under oxidative conditions, the chlorination process was more effective above 350°C (623 K) and the concentrations of highly chlorinated PCDDs were higher.

Reaction Rates for DD, MCDD, and DCDF Formation:

- Rate orders of the three congeners were determined at 250°C (523 K) under oxidative conditions.
- DD and MCDD exhibited similar positive reaction rates of 0.6 and 0.7, respectively.

- The slightly higher reaction rate for MCDD compared to DD indicates a weaker adsorption factor for MCDD.
- DCDF formation exhibited a negative rate order (-0.6).
- DCDF is likely formed by a Langmuir-Hinshelwood mechanism; DD and MCDD are formed according to the Eley-Rideal mechanism. Langmuir-Hinshelwood assumes that both reacting molecules adsorb on the surface, react on the surface, and then reaction products desorb from the surface. Eley-Rideal assumes that only one of the reacting molecules is adsorbed on the surface, while the other reacts from the gas phase.

Peer-Reviewed Publication

- Lomnicki, S. and B. Dellinger. 2003. A detailed mechanism of the surface-mediated formation of PCDD/F from the oxidation of 2-chlorophenol on a CuO/silica surface. *Journal of Physical Chemistry A* 107(22): 4387-4395.

3.1.2.5 Utilization of Research Results

The development of a unified mechanism and understanding of PCDD/F formation in the post-combustion, cool-zone of combustors will greatly facilitate the development of improved risk management and risk assessment strategies for combustion systems. Gas-phase reactions and kinetics impact the formation of PCDD/F in combustion systems, but the effect is primarily indirect through destruction of gas-phase PCDD/Fs and homogeneous gas-phase formation of some precursors. The principal source of PCDD/F in combustion systems is in all likelihood surface-mediated by fine and ultrafine particles. Understanding of these mechanisms could be applied to the development of emissions abatement strategies for combustion systems.

General strategies include:

- Modifying post-combustion time-temperature profiles to mitigate PCDD/F formation.
- Controlling the content of catalytic metals in the combustor feed.
- Modifying combustion conditions to minimize formation of catalytic, fine and ultrafine particles.
- Blending of fuels and wastes to avoid the optimum compositions for PCDD/F formation.

3.1.2.6 Research Needs

Project-Related Research Needs

According to the PIs, the above work also has implications for the possible involvement of other species, such as chlorinated benzenes, in the formation of PCDD/Fs. The exhaust of incinerators contains higher concentrations of chlorinated benzenes than chlorinated phenols. Based on the proposed mechanism of formation, this suggests significant consequences with respect to the formation of dioxins and furans; therefore, chlorinated benzenes (and their role in the formation of PCDD/Fs) deserve further study.

Additional Research Needs

The following research recommendations related to combustion emissions were also identified by the PIs:

- Study the role of chlorobenzenes in the surface-mediated mechanisms of PCDD/F formation.
- Examine the role of combustion-generated nanoparticles in pollutant formation in all chlorine-containing combustion systems. This is an important area as PCDD/F-forming reactions may occur on nanoparticles prior to their concentration being reduced by aggregation and agglomeration.
- Determine the origin and nature of gas-phase and particle-associated persistent free radicals.
- Develop improved techniques for the study of high temperature surface reactions for time scales on the order of seconds.
- Examine elementary reactions of chlorinated phenoxy and phenyl radicals.
- Investigate photothermal reactions in flares and plumes.
- Characterize emissions from on-site “thermal treatment” systems used for site remediation and compare the emission profiles for these systems to the emission profiles for high temperature systems. There is an unfortunate trend to use lower-temperature thermal desorbers and non-flame, thermal treatment systems as on-site remediation devices to avoid being labeled as an “incinerator.” These lower temperature systems may enhance formation of PCDD/F and other PICs in an effort to avoid incinerator regulations and negative public opinion.
- Characterize the sources of bromine in combustion systems that emit brominated hydrocarbons.

3.1.3 Products of Incomplete Combustion in the Incineration of Brominated Hydrocarbons, Selim M. Senkan, University of California - Los Angeles

3.1.3.1 Background

Incineration is used as a treatment method for the disposal of organic hazardous wastes, including wastes that contain halogenated hydrocarbons. However, the combustion of halogenated hydrocarbons is associated with the formation of trace levels of toxic products of incomplete combustion (PICs), such as aromatics and polycyclic aromatic hydrocarbons (PAHs), halogenated dibenzo-furans (HDFs), bi-phenyls, and pyrenes. Because some of these PICs are known or suspected carcinogens, the development of a better understanding of their origins and fate is important for the continued use of incineration as a waste minimization technology. The fact that these pollutants are formed at trace levels, i.e., parts per billion (ppb) to parts per trillion, means that incineration and combustion chemistries must be quantified at the ppb and parts per trillion levels.

3.1.3.2 Objectives

Initial objectives of this research project were to develop detailed insights into the formation and control of potentially toxic PICs in the incineration of brominated and related halogenated hydrocarbons. Initial experiments, however, showed the production of excessive amounts of soot, which prevented sampling of the flames of brominated hydrocarbons. These initial tests also revealed the production of hydrocarbon intermediates such as acetylene, 1,3-butadiene and n-heptane in the combustion of brominated hydrocarbons. Because these intermediates were also reported in the combustion of unhalogenated hydrocarbons, efforts were directed towards developing detailed insights into the combustion of these hydrocarbon intermediates. Such an effort will be crucial for the development of detailed chemical kinetic mechanisms (DCKM) describing the formation and destruction of PICs in the combustion of halogenated and unhalogenated hydrocarbons.

The specific objectives of this research project were as follows:

- (1) To determine the absolute concentration profiles of major, minor, and trace PIC species, as well as temperature and soot profiles in the laminar pre-mixed and diffusion flames of acetylene, 1,3-butadiene, and n-heptane, that were produced as significant intermediates in the flames of brominated hydrocarbons (BHCs).
- (2) To establish detailed mechanisms for the combustion of acetylene, 1,3-butadiene, and n-heptane that allow quantitative predictions of the formation of PIC in combustion and incineration processes. These DCKM will also be useful in developing better insights into the role halogens play in combustion, i.e., how they promote soot, polycyclic aromatic hydrocarbon (PAH), and dioxin formation.

3.1.3.3 Methodology

The first objective was accomplished by employing the following methodology:

- Species concentration profiles were determined by withdrawing samples from within flames using heated micro-probes followed by gas analysis by an online high-resolution gas chromatography/quadrupole mass spectrometry (GC/QMS).
- Temperature measurements were taken with thermocouples using the rapid insertion thermocouple technique to prevent excessive soot accumulation on thermocouple beads.

Throughout the duration of the project, a number of premixed and diffusion flame experiments were performed. A brief description of each is provided below.

- Experiment 1: Evaluated combustion of pure CH_3Br in O_2/Ar using an opposed jet diffusion flame system.
- Experiment 2: Evaluated the effects of equivalence ratio on species and soot formation using premixed n-heptane flames in O_2/Ar . After considering the O_2 requirements for hydrogen to water and carbon to carbon dioxide, the resulting mix had carbon to oxygen (C/O) atom ratios of 0.63 and 0.67. A heated quartz microprobe coupled to an online GC/MS (HP 5890 Series II/HP 5972) was used to identify and determine absolute concentrations of stable major, minor, and trace species using direct analysis of samples withdrawn from the flames. Soot-particle diameters, number densities, and volume fractions were determined using classical light scattering and extinction measurements.
- Experiment 2a: Evaluated the effects of three oxygenate additives (methanol, ethanol, and methyl tertiary butyl ether) on the formation of PAHs and soot in laminar, premixed, atmospheric-pressure, and fuel-rich flames of n-heptane at an equivalence ratio of 2.10. These runs were performed in order to assess how oxygenated species decrease PAH and soot formation, which is equivalent to studying flames with lower C/O ratios. In oxygenated species there is less need for O_2 .
- Experiment 3: Studied soot formation in premixed flames of methane, ethane, propane, and butane at three different equivalence ratios. Soot-particle sizes, number densities, and volume fractions were determined using classical light scattering measurement techniques.
- Experiment 4: Studied the effects of three percent O_2 addition on PAH formation, using a 1,3-butadiene counter-flow diffusion flame. Effects were investigated using heated microprobe sampling and online GC/MS. Centerline gas temperature and species mole fraction profiles were measured both with and without oxygen on the fuel side. The rapid thermocouple insertion method was used to obtain the flame temperature profiles.

- Experiment 5: Performed kinetic modeling of counter flow diffusion flames of butadiene and mixing effect. A comprehensive, semi-detailed kinetic scheme was used to simulate the chemical structures of counter-flow diffusion and fuel-rich premixed 1,3-butadiene flames to better understand PAH formation.
- Experiment 6: Acetylene, a ubiquitous combustion intermediate, is believed to be a major hydrocarbon intermediate product responsible for the production of aromatics, polyaromatics, dioxins, furans, PAHs, and soot in hydrocarbon and halogenated hydrocarbon flames. Despite its important role as a flame intermediate, however, the detailed chemical structures of pure acetylene diffusion flames have not been studied. PAHs in counter-flow diffusion flames of acetylene were studied as a function of carbon density. Rapid insertion thermocouple techniques were used for temperature measurements.

Figure 3-4 is a schematic diagram of the counter flow diffusion flame setup used in Senkan's experiments 1, 4, 5, and 6. Pre-mixed, McKenna-type burners were used for experiments 2 and 3.

3.1.3.4 Results and Discussion

Experimental Results

- Experiment 1 (CH₃Br): Flames produced significant levels of acetylene and 1,3-butadiene and excessive amounts soot. That is, the levels were so high that the sampling probe was rapidly plugged. Soot plugged the sampling probes within 100 milliseconds and representative flame samples could not be obtained. It is believed that acetylene and 1,3-butadiene are major hydrocarbon intermediates in flames responsible for the production of aromatics, polyaromatics, dioxins, furans, PAHs, and ultimately soot, as discussed in the publications listed below..
- Experiment 2 (n-heptane): The aromatic compound detected in most abundance was benzene. The largest molecular weight PAHs detected were in the C₁₈H₁₀ fraction that includes cyclopenta[cd]pyrene and benzo[ghi]fluoranthene. Peak concentrations of these PAHs were 8 ppm and 6 ppm, respectively. The largest soot-particle diameter measured was about 18 nm, and the soot- volume fraction reached the amount of 4.9×10^7 .
- Experiment 2a (n-heptane and oxygenated additives): All of the oxygenate additives studied reduced the mole fractions of aromatic and PAH species by generally in the range of 20 to 40 percent. Depending on conditions, this is probably not enough to represent a control technology. Soot formation was also reduced by about 10 to 40 percent by all oxygenate additives in a comparable manner.
- Experiment 3 (premixed hydrocarbon flame): Results of this experiment revealed that the soot properties were sensitive to fuel type and the combustion parameter equivalence ratio. An increase in the equivalence ratio increased the amount of soot

formed for each fuel. In addition, methane flames showed larger particle diameters at higher distances above the burner surface followed by propane, ethane, and butane, respectively.

- **Experiment 4 (PAH formation and oxygen addition):** The addition of oxygen to the fuel side did not significantly change the shape and peak values of the temperature profiles; however, species mole fraction profiles were altered significantly due to oxygen addition in the fuel. The presence of oxygen in the fuel led to decreased peak mole fractions of the aromatic and two-ring PAHs. In contrast, the peak mole fractions of PAHs having three or more rings *increased* significantly in the presence of oxygen on the fuel side.
- **Experiment 5 (PAH formation in 1,3-butadiene flames):** The pathways characterizing the pollutant formation are very different in the premixed and counter-flow flames, confirming the need to verify and refine the detailed mechanisms for premixed conditions when they are extrapolated and used in diffusion flames. Reaction path analysis for PAH formation in the counter-flow flame showed that the hydrogen-abstraction/ carbon-addition mechanism and the resonantly stabilized radicals are important for the growth of PAHs.
- **Experiment 6 (Carbon density and PAH formation in acetylene diffusion flames):** Butadiene was the most abundant pyrolysis product in the acetylene flames followed by vinylacetylene (1-buten-3-yne). The aromatic compound detected most was benzene followed by phenylacetylene (ethynylbenzene). As particular characteristics of acetylene flames, acenaphthylene was more abundant than naphthalene. Paraffins such as methane, ethane propane, butane, and heavier compounds were not detected. The largest PAHs detected were in the $C_{18}H_{10}$ fraction that includes cyclopenta[cd]pyrene and benzo[ghi]fluoranthene.

Peer-reviewed Publications

- Olten, N. and S. Senkan. 2001. Effect of oxygen addition on polycyclic aromatic hydrocarbon formation in 1,3 butadiene counter-flow diffusion flames. *Combustion and Flame* 125(1-2): 1032-1039.
- Inal, F. and S. Senkan. 2002. Effects of equivalence ratio on species and soot concentrations in premixed N-heptane flames. *Combustion and Flame* 131(1-2): 16-28.
- Inal, F. and S. Senkan. 2002. Effects of oxygenate additives on polycyclic aromatic hydrocarbons (PAHs) and soot formation. *Combustion Science and Technology* 174(9): 1-19.
- Inal, F., G. Tayfur, and S. Senkan. 2003. Experimental and artificial neural network modeling study on soot formation in premixed hydrocarbon flames. *Fuel* 82(12): 1477-1490.

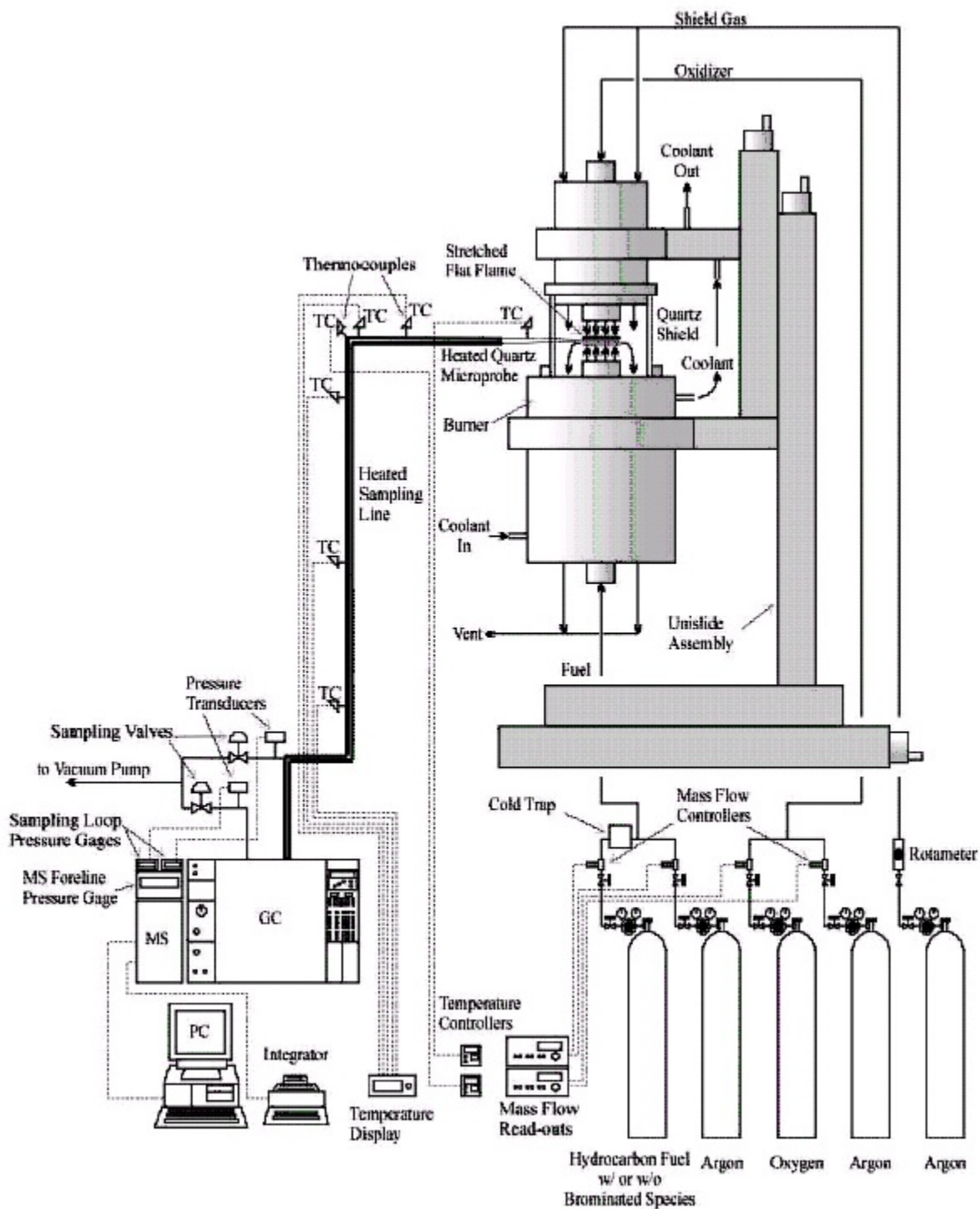
- Granata, S., T. Faravelli, E. Ranzi, N. Olten, and S. Senkan. 2002. Kinetic modeling of counterflow diffusion flames of butadiene. *Combustion and Flame* 131(3): 273-284.
- Yamamoto, M. and S. Senkan. The effect of strain rate on polycyclic aromatic hydrocarbons (PAH) formation in acetylene diffusion flames. Accepted for publication as of January 2006.

3.1.3.5 Utilization of Research Results

According to the PI, the results of this research project may be useful to the combustion/incineration community in the following ways.

- Generating these data concerning major, minor, and trace species concentration profiles and soot and temperature profiles will provide valuable new information. These data are useful for the development and validation of DCKM describing the combustion of hydrocarbons and intermediates which were found from brominated hydrocarbons in flames. In fact, the development of DCKM for hydrocarbons was determined to be an important prerequisite to develop insights into the formation of toxic PICs in the combustion of halogenated hydrocarbons.

Figure 3-4 Counter Flow Diffusion Flame Setup from Senkan's Project



The development of DCKM will result in improved predictions regarding the conditions under which PAHs and dioxins form in incinerators.

- The detailed mechanisms developed can subsequently be combined with fluid dynamic models to simulate, design, and develop optimum strategies for practical incinerators such that their operations would result in emissions of lowest possible levels of PICs, thereby reducing possible risk to public health.

3.1.3.6 Research Needs

Project-Related Research Needs

In relation to Experiment 1, the PI identified the need to conduct experiments where CH_3Br represents a small fraction of the fuel combusted. However, under these conditions it is difficult to unambiguously establish the role halogens play in combustion and incineration processes because the hydrocarbon fuel dominates the reaction process. In relation to Experiment 4, the PI suggested the need to invoke new reaction mechanisms describing the formation and destruction of PAHs in hydrocarbon combustion, including steps describing the formation of soot. The PI also identified the need to study brominated hydrocarbon combustion in flameless, flow reactors in order to facilitate control the temperature time history and be able to acquire species concentration data before the onset of soot formation.

In addition, the PI noted that the existing kinetic models (Experiment 5) were unsuccessful in predicting the increased reactivity in O_2 -doped diffusion flames and indicated the need for improved models and the opportunity for new experiments of butadiene oxidation in the intermediate temperature region. With regard to Experiment 6, the PI noted the need to revise the DCKM in order to properly account for significant increases observed in the formation of aromatics and polyaromatics in lower strain rate flames of acetylene.

Additional Research Needs

The PI noted that followup research should focus on the development and validation of detailed chemical kinetic mechanisms describing the formation and destruction of trace PICs associated with combustion and incineration processes. These studies should involve the use of experimental data generated by the PI, which are the most comprehensive in the open literature. These modeling studies will result in the identification of the most influential elementary reactions, which can then be studied by research groups as described elsewhere in this report.

3.1.4 Summary of the Overall Contributions of These Three Projects to the RCRA Multi-Year Plan and Its Broad Theme of “Mechanisms of Formation”

The RCRA Multi-Year Plan identifies the following three Waste Management Science Questions (EPA 2004a).

- What easily monitored components of emissions can be used to predict more difficult-to-measure components (e.g., PCDD/PCDF)?
- How can complex mixtures of organic compounds in the stack gases be characterized with respect to risk assessment needs?
- What PCDD/PCDF formation issues exist during combustion of hazardous wastes?

The three grants described in the preceding sections directly address these questions through improved characterization of the mechanisms of formation of components of air emissions from combustion systems. These three research projects identify dioxin and furan precursor compounds and halogenated dioxin and furan species and provide insight into the formation and transformation mechanisms in combustion systems.

Specifically, Taylor has characterized chlorinated dioxins and provided OH radical reaction rate measurements that have not previously been investigated. Dellinger and Lomnicki investigated the effects of metals on catalysis of formation of chlorinated dioxins and furans in combustion systems and identified a correlation between the amount of dibenzo dioxin and the amount of highly-chlorinated dioxin products formed as well as the effect of temperature on this mechanism. These results also identify dioxin and furan formation issues related to combustion of hazardous waste and provide data relevant to the identification of surrogate compounds to correlate to emissions of more highly chlorinated dioxins and furans. Senkan provided information concerning mechanisms of formation of PAHs and soot. These results are also relevant to formation issues related to combustion of hazardous waste and to identification of surrogate compounds.

3.2 MONITORING AND ANALYTICAL METHODS FOR CHEMICAL COMPOUNDS IN COMBUSTION SYSTEMS

Research into the monitoring and analytical methods for chemical compounds in combustion systems is a broad theme of the EPA RCRA Multi-Year Plan (EPA 2004a). Research by Striebich et al. and Smith et al. described in this section relate to improving analytical methods for measurement of halogenated dioxins and furans and metals in combustion systems. The research conducted by Rubey, Striebich, and Taylor described in this section relates to development of advanced chromatographic techniques to enable separation and characterization of complex mixtures of emissions from combustion systems in a rapid manner. The research conducted by Smith and Boudries relates to development of advanced techniques to collect fine particulate emissions from combustion systems and characterize individual species in the fine particulate emissions. Data generated by such advanced sampling and analysis systems would enable identification of specific toxic compounds in the emissions from combustion systems and support site-specific risk assessment for combustion systems. Results of these studies are also applicable to the development of risk management strategies and emissions abatement strategies for combustion systems.

3.2.1 Trace-Level Measurement of Complex Combustion Effluents and Residues Using Multidimensional Gas Chromatography-Mass Spectrometry (MDGC-MS), Wayne A. Rubey, Richard C. Striebich, and Philip H. Taylor, University of Dayton

3.2.1.1 Background

Effluents from hazardous waste incinerators, municipal solid waste incinerators, and other combustion sources can be very complex. Although most combustion systems are capable of destroying the organic feedstocks that come into direct contact with the flame, the great majority of compounds observed in combustion effluents (i.e., PICs) may be formed in reactions occurring outside of the flame zone. Due to the wide range of potential PIC formation conditions and extreme variation in the composition of wastes, highly complex combustion emissions and residues are probable.

Organic emissions and organic compounds extracted from particulate matter (PM) are more complex than standard gas chromatography-mass spectrometry (GC-MS)-based instrumentation can currently measure. The ability to correctly identify and quantify components of complex combustion emissions is critical to determine the toxicity and risk associated with combustion sources. Therefore, more advanced instrumentation is needed to better characterize these complex organic compounds and PM extracts from combustion emissions sources. The greater number of analytes accounted for by advanced techniques, the less uncertainty may be associated with site-specific risk assessments.

Conventional GC-MS uses a single primary separation technique (i.e., a one-dimensional chromatographic analysis) and may be adequate for simpler mixtures and for identifying compounds of known toxicity that are currently regulated. However, with regard to many of the complex combustion effluents and residues, use of a single gas chromatography system results in separations with a substantial amount of superpositioning of analyte zones. This co-elution restricts the mass spectral analysis of individual constituents and prohibits accurate quantization of many solutes. In particular, low, small concentration peaks are lost. Complete separation of complex mixtures requires increased peak capacity beyond that which a conventional GC can provide. With conventional GC-MS, users may only identify a modest number of the major chemical components and some prominent target species in effluent samples.

The large number of compounds in these various fractions requires enhanced analytical separation techniques, such as that available with multi-dimensional gas chromatography (MDGC). MDGC combines one-dimensional techniques to achieve multidimensional separation. Systems currently in use are capable of achieving excellent chromatographic separation for complex mixtures associated with combustion effluents and residues.

3.2.1.2 Objectives

The primary purpose of the first phase of this research project was to demonstrate that MDGC-MS significantly improves chromatographic separation for complex mixtures, such as

those emitted from hazardous and municipal solid waste incinerators. In addition, there is a continuing need to conduct these analyses in a rapid fashion without losing the separation power in the chromatographic step. Therefore, the purpose of the second phase of this project was to enhance the speed of separations using this multidimensional system.

Based on this need for improved analytical techniques for identifying and quantifying chemical compounds in combustion systems in a rapid manner, the overall objectives of this research project were as follows:

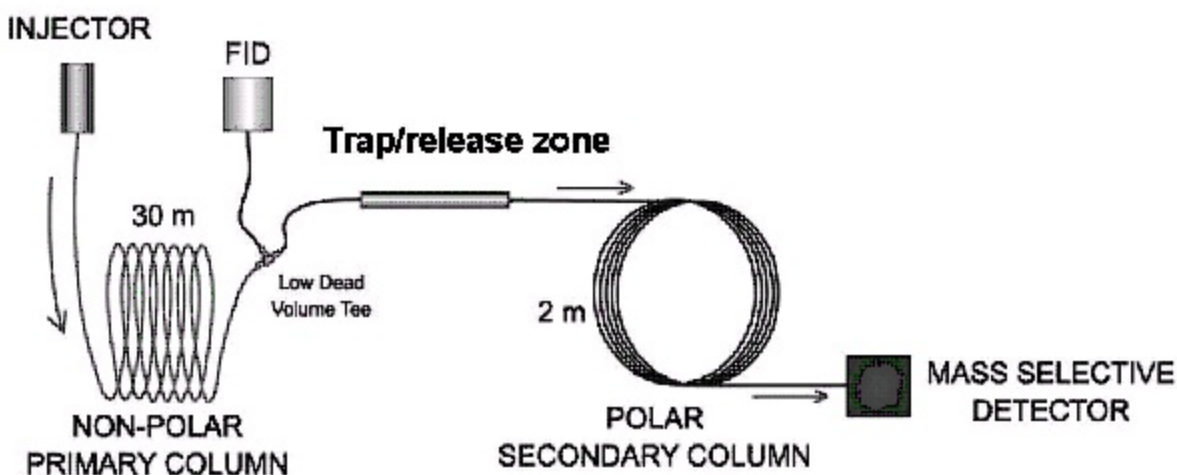
- To develop, test, and use advanced MDGC instrumentation capable of achieving high resolution separations to examine combustion effluents and residues. Higher resolution would result in more precise identification and quantization of these compounds and higher confidence mass spectral analyses.
- To couple the MDGC system with an MS for the identification of uncharacterized compounds.
- To conduct separations and characterization of combustion effluents and residues in a rapid fashion such that secondary column separations can keep up with the primary column separations.

3.2.1.3 Methodology

Figure 3-5 shows a schematic of the MDGC-MS system. The MDGC-MS system designed for the purposes of this research project consisted of two capillary chromatography columns (i.e., a non-polar primary column and a polar secondary column) connected with a cryogenic refocusing trap. A mass selective detector (i.e., mass spectrometer) was added for component identification. Additional components of the MDGC-MS system included the flame ionization detector (FID) used to measure the effluent from the primary column and monitor the one-dimensional separation. Solute zones passed into the secondary column via the cryogenic trap, where they were refocused into a narrow band of solute, eliminating component dispersion. (Dispersion in chromatography can cause the separation of components and make peak identification and quantification difficult.) The secondary column was designed for fast chromatography. This column eases the identification of components by separating major compound classes based on polarity. After secondary separation, components of the sample were detected using the mass selective detector.

Samples of several complex mixtures related to combustion processes, including diesel engine exhaust, hazardous waste incinerator effluent, and open burning of household wastes, were tested using this system. Mixtures were tested on both the MDGC-MS system and a conventional GC-MS system and chromatographic separations were compared. All research publications used a GC-MS of some kind, either a GC with Agilent MS or currently GC-TOFMS. The FID was used for the primary detection but not for the secondary detection.

Figure 3-5 Schematic of a MDGC System Used in Rubey, Striebich, and Taylor's Project



The research project now uses a very fast mass spectrometer to take the MDGC data to accommodate the shorter, faster secondary columns, and has a TOFMS and an associated data station which can sample at 500 Hz compared to 10-20 Hz for conventional mass spectrometers.

During the final year of this research project, a new trap and release system, specifically a thermal gradient programmed GC (TGPGC), was tested to enhance the speed of separations in the secondary column of the MDGC-MS system. In using this optimized secondary separation, it was determined that the current MS was neither fast enough nor sensitive enough to perform these fast analyses. Therefore, use of a time of flight mass spectrometer (TOFMS) as detector for the TGPGC system is planned for future experiments (but was not employed as part of this grant). The research project now uses a very fast mass spectrometer to take the MDGC data to accommodate the shorter, faster secondary columns, and also uses a TOFMS and an associated data station which can sample at 500 Hz compared to 10-20 Hz for conventional mass spectrometers.

3.2.1.4 Results and Discussion

Experimental Results

For the purposes of this research project, the PIs designed, built, and tested a MDGC-MS system for the analysis of several combustion mixtures that are more complex than conventional GC-MS systems can analyze (i.e., diesel exhaust, hazardous waste incinerator effluent, and open burning of household wastes). The design and construction of this system was accomplished during the first 14 to 18 months of the project.

Tests of this system showed that it was capable of comprehensive analysis of all of the tested mixtures. Researchers demonstrated that using the MDGC-MS system significantly improved chromatographic separation for complex combustion-related mixtures. Using this

system, the PIs were able to identify new compounds in combustion samples not previously identified using conventional GC-MS systems due to the fact that they are in low concentration, not regulated (i.e., no one routinely looks for them), and obscured within complex mixtures not easily separated by conventional techniques. Most notable is that the MDGC-MS detected bromine compounds, oxy-PAH, and other oxygenates that the conventional GC did not detect. Additional details regarding results using the MDGC-MS system are provided below (by mixture).

Hazardous Waste Incineration Mixture

- PICs, difficult to analyze by conventional techniques, were identified by MDGC-MS.
- Most of the compounds detected in the hazardous waste sample contained chlorine or bromine atoms, an indication that the compounds may be of interest for future studies.

Diesel Exhaust Emissions from Automobile Engines

- Concentrations of compounds were low (one to five ppm); MDGC-MS enabled researchers to separate these low concentration oxygenated PAHs from high concentration compounds.
- Compounds were accurately identified; concentrations and emission rates were also determined.

Diesel Truck Exhaust

- Many alkene and alkane components were separated by MDGC in the secondary column and revealed potentially toxic compounds in combustion emissions that were not identified using conventional GC-MS techniques.
- With this technology, non-target compounds (e.g., oxygenated PAHs) were readily observed.

Open Burning of Household Waste

- Represented the most complex mixture examined; the multi-dimensional chromatogram contained hundreds of peaks, the majority of which were separated with the high resolution MDGC-MS system.
- Component concentrations were determined.
- Brominated compounds were identified in the combustion sample.

- Compounds such as bisphenol A (BPA; a potential endocrine disruptor) were found using MDGC-MS.

Based on the results of these tests, key advantages of MDGC-MS over conventional GC-MS may be summarized as follows:

- **Improved separation and component resolution.** With enhanced separation power, co-elution was greatly reduced. Low concentration compounds were detected and correctly identified.
- **Improved peak identification.** MDGC-MS can provide more reliable mass spectral patterns and the ability to identify those compounds which may be toxic or are of unknown toxicity that are not regulated and are therefore typically ignored.
- **Enhanced peak capacity.** MDGC-MS can provide more accuracy in quantifying the amount of particular compounds in a mixture.

Overall, MDGC-MS worked better for characterizing complex mixtures associated with combustion effluents and residues than conventional GC-MS techniques. It is important to note, however, that not every sample requires MDGC-MS analysis. Conventional techniques are still appropriate for particular, less complex mixtures.

For the purposes of this research project, MDGC-MS was successful, although it did not separate *all* complex components completely and run times were long (3 hours or more). Due to the long run times, the MDGC system was recreated using a more advanced secondary separation technique (TGPGC) to increase the speed of analysis as well as to decrease peak width of individual solute profiles and increase peak detectability. Using TGPGC optimized secondary separation and resulted in 15-second secondary separations, versus 45-second secondary analysis using MDGC-MS.

In using the enhanced TGPGC system, the peaks are produced from the secondary column faster and are made narrower in time. A narrower peak means a higher and more detectable peak. Therefore, faster scanning speeds are needed to obtain the identification of the peak. The next step is to incorporate the TOFMS, a faster MS for detecting peaks of interest, into the TGPGC to obtain a more effective analysis system. With incorporation of TOFMS, it should be possible to provide a 45-minute primary analysis with 15-second secondary analysis to obtain the highest resolution chromatograms, even for the most complex samples.

For this research effort, PIs were not yet able to incorporate TOFMS into the TGPGC system since the TOFMS instrument was not available to them at the time. It is expected that the additional work to combine these systems will be done under different funding.

Peer-Reviewed Publications

- Sidhu, S., B. Gullett, R. Striebich, J. Klosterman, J. Contreras, and M. DeVito. 2005. Endocrine disrupting chemical emissions from combustion sources: Diesel particulate emissions and domestic waste open burn emissions. *Atmospheric Environment* 39(5): 801-811.
- Striebich R., W. Rubey, and J. Klosterman. 2002. Trace-level measurement of complex combustion effluents and residues using multidimensional gas chromatography-mass spectrometry (MDGC-MS). *Waste Management* 22(4): 413-420.

3.2.1.5 Utilization of Research Results

This research shows that MDGC-MS has significant potential in its ability to identify specific components of complex chemical mixtures sampled from municipal solid waste and hazardous waste incinerators. This technique also possesses the capability of quantifying separated substances that occur over a wide range of concentrations. It is hoped that use of advanced chromatographic techniques (e.g., TGPGC) along with a faster MS system will allow more comprehensive characterization of both toxic and non-toxic PICs to be performed in a rapid (i.e., real-time or near real-time) fashion, thereby reducing uncertainties associated with site-specific risk assessments.

3.2.1.6 Research Needs

Project-Related Research Needs

As a result of this research project, new instrumentation was developed and tested and several studies were conducted to better characterize complex combustion by-products. However, the ultimate analytical system intended by the PIs has not been completed. The ultimate analytical system will be a combination of the TGPGC and TOFMS to obtain a more effective analysis system for characterizing PICs associated with combustion in a rapid, real-time or near real-time fashion. Once development of this more advanced system is complete, thorough testing will be needed to support its use in characterizing complex combustion effluents and in conducting site specific risk assessments.

Additional Research Needs

Additional research needs for combustion emissions were also identified by the PIs. These are summarized below.

- There is a tremendous difference in the emissions produced by efficient engines and combustion systems as compared to inefficient and uncontrolled sources. Considering that rural refuse incineration, fireplaces, cooking products, flares, forest

fires, agricultural burning, and other open burning situations may provide a significant fraction of combustion emissions compared to the larger operations involving efficient combustion engines and devices, further study is needed to more fully understand the compounds released from these and other inefficient and uncontrolled sources.

- There is a need to study difficult to incinerate materials or materials that will be increasingly found in the municipal solid waste stream (e.g., electronic wastes, Teflon materials). Some of these materials are highly brominated (flame retardant) and reactions will be catalyzed by a mixture of metals.
- Assays which identify toxicity in fractions are needed, followed by routine and non-routine analysis by a technique which can identify the compounds of interest.

3.2.2 Characterization and Minimization of Fine Particulate Emissions from Waste Incinerators by Real-Time Monitoring of Size-Resolved Mass and Chemical Composition, Kenneth A. Smith, Hacene Boudries, Douglas R. Worsnop, and Xuefeng Zhang, Massachusetts Institute of Technology

3.2.2.1 Background

Incineration is a common method of waste disposal/minimization. Concerns about toxic air pollutants that may be emitted from incinerators remain a major obstacle to public acceptance of these systems. To date, concerns have focused on dioxins/furans, toxic metals, and acidic gases. Little attention has been devoted to particulate emissions resulting from incineration, partially because most of the particulate mass leaving the combustion chamber is efficiently captured in modern baghouses. However, most of the captured mass is associated with coarse particles because the coarse fraction of PM accounts for most of the uncontrolled particle mass. Incinerator emissions are enriched in fine particles because control systems in incinerators are least efficient for this size range. Fine particulates (i.e., those particulates smaller than 2.5 microns) are able to penetrate deeply into the human lungs and, if deposited there, may be an efficient vehicle for exposure to many different chemicals. Therefore, there is a need to better quantify the amounts, chemical composition, and toxicity of these fine particles.

There is also a critical need for real-time quantification of pollutants associated with fine particulates in the exhaust gases of waste and sewage sludge incinerators. At the national level, incineration processes generate relatively little PM. However, for the evaluation of local risk, monitoring individual incineration units to ensure there are not releases of hazardous materials is essential. Further, real-time characterization of PM emissions followed by correlation of emissions to waste composition and hardware design and operating parameters offers the potential to identify means to reduce emissions. Such means could include new hardware or automatic operating control systems that adjust process parameters to control emissions in the same way, for example, that lime dosage is modulated in municipal refuse combustion systems to limit acid gas emission rates. The particulate control systems currently used in waste incinerators

are generally least efficient for those fine particle sizes for which the health effects are largest, though well-designed and operated systems are more efficient at capturing fine particles. These particulates tend to be enriched in condensable toxic organic compounds, acid salts, and metals such as arsenic, cadmium, and lead.

3.2.2.2 Objectives

The objective of this research project was to perform a real-time analysis and quantification of the size-resolved chemical composition of fine particulate emissions in the exhaust gases of municipal waste incinerators. All the pollutants that were proposed to be measured were known to be either toxic or carcinogenic. As part of this task, substantial efforts were implemented within the framework of this project to advance the suitability of the instrument for field sampling of PM and analysis of incinerator exhaust.

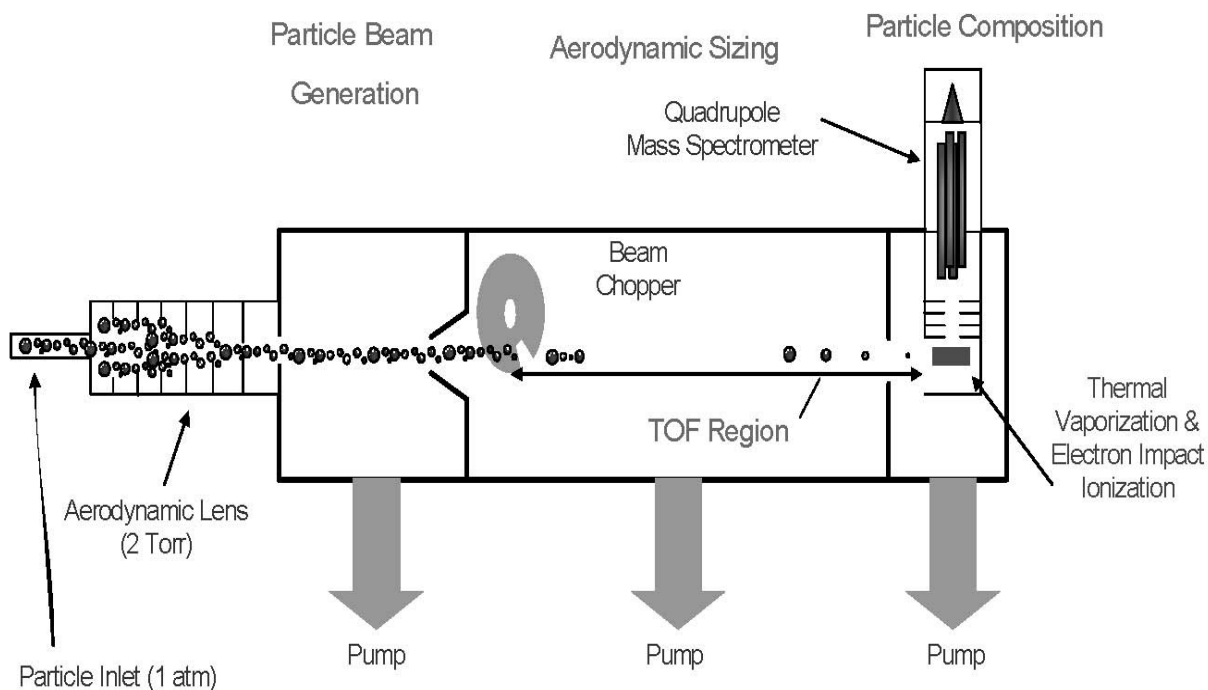
3.2.2.3 Methodology

This project involved the use of two instruments: an Aerosol Mass Spectrometer (AMS) from Aerodyne Research, Inc. (ARI) for monitoring volatiles, semi-volatiles, and refractory species, and a resonance enhanced multiphoton ionization (REMPI) time-of-flight (TOF) AMS for selective and sensitive detection of toxic organics (specifically, chlorinated PAHs). The ARI AMS and REMPI-TOFAMS were used to monitor, in real time, the chemical and physical composition of aerosols emitted from two test sewage sludge incinerators and a municipal solid waste incinerator (MSWI). The REMPI-TOFAMS, originally developed under a previous EPA grant, was modified for the purposes of this project.

For aerosols containing volatile and semi-volatile species, the ARI AMS can provide quantitative information on chemical composition as a function of particle size in real time. As shown in Figure 3-6, submicron aerosols emitted by the municipal incinerators were sampled by the AMS through a 100 mm critical orifice, then focused by the aerodynamic lens. The aerodynamic inlet delivered a particle beam from which the vacuum aerodynamic particle diameter was determined via particle time-of-flight. The particles were then directed toward a heated tungsten surface vaporizer maintained between 500°C and 1,200°C (773 and 1,473 K).

The chemical composition was measured by flash evaporation of the particle followed by electron impact ionization and positive ion detection with a quadrupole mass spectrometer (QMS). Based on current laboratory calibrations, the detection limit (DL) is calculated automatically by the AMS and estimated at 0.10 µg per m³ for sulfates, nitrate, chloride, and ammonium compounds, and 1 µg per m³ for organic compounds and metals. A mass spectrum was obtained every two seconds and averaged over 25 seconds. The size distribution of aerosols with a vacuum aerodynamic diameter between 30 nm and 2.5 µm was measured each second and averaged over 35 seconds. Detailed information about the AMS, including its operation, is well documented elsewhere (Jayne et al. 2000; Allan et al. 2003; Jimenez et al. 2003).

Figure 3-6 Schematic of the Aerosol Mass Spectrometer (AMS) for Smith and Boudries' Project

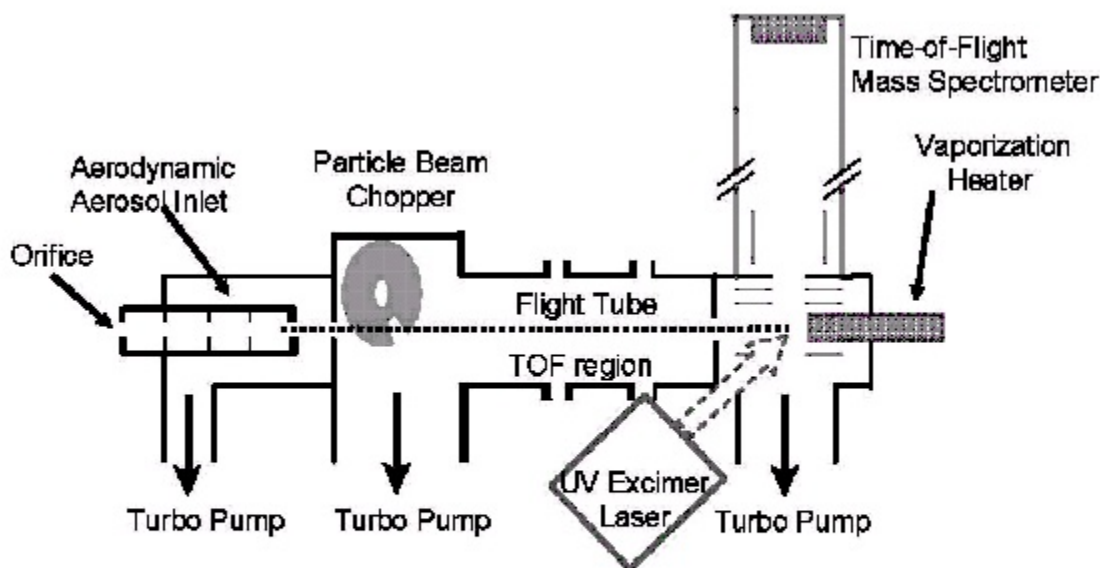


Aerodynamic particle size is determined from a particle time-of-flight (TOF) measurement. Size-resolved composition is measured via flash vaporization on a heated surface, electron impact ionization, and detection with a quadrupole mass spectrometer.

In order to enhance the sensitivity and selectivity of the instrument for PAHs and chlorinated aromatics, the AMS was coupled with the REMPI-TOFAMS system. A DL as low as 10 parts per trillion for the particle mass for PAHs and chlorinated aromatics may be achievable with REMPI-TOFAMS. The schematic diagram of the REMPI-TOFAMS is shown in Figure 3-7. Ambient aerosols are sampled into vacuum using an aerodynamic lens. Aerodynamic particle size is determined from a particle time-of-flight (TOF) measurement. Size resolved composition is measured by a TOF mass spectrometers following particle flash vaporization on a resistively heated surface and laser ionization of the vaporized species.

All particulate sampling was performed in the stack just before being emitted into the atmosphere. A sampling line (copper tube, 1/2 inch o.d., 5 m long) and a cyclone were used to sample aerosol particles below 2.5 mm at a flow rate of 10 L min⁻¹. Both the sampling line and the cyclone were heated to the temperature of the gas inside the stack in order to avoid water vapor condensation in the sampling line. The sampling line was also kept as short as possible by sampling very close to the stack. Both Aerosol Mass Spectrometers were connected to iso-kinetically sample through the sampling line. During this experiment, the REMPI-AMS and AMS were set to sample at 0.1 L min⁻¹.

Figure 3-7 Schematic of Resonance Enhanced Multiphoton Ionization Time of Flight Aerosol Mass Spectrometer for Smith and Boudries' Project



Resonance Enhanced Multiphoton Ionization Time-of-Flight Aerosol Mass Spectrometer (REMPI-TOFAMS) used for size and composition analysis of sub-micron aerosol.

Experiments were carried out at four incinerators during the specified time frames:

- Pilot incinerator at the New Jersey Institute of Technology (NJIT) (10/29/01 - 11/02/01).
- Sewage Sludge Incinerator - Fluidized Bed Incinerator (08/12/02 - 08/19/02).
- Municipal Solid Waste Incinerator - Special Boiler (06/03).
- Sewage Sludge Incinerator - Multi-Hearth Sludge Incinerator (09/03).

Size-resolved particulate mass and chemical composition measurements were performed while sampling exhaust gas from these systems. Particulate-bound inorganics (e.g., sulfate and nitrate), PAHs, and chlorinated aromatics were detected in the stack exhaust. The effect of operating parameters, including start-ups, shutdowns, and setpoint changes, on aerosol chemical and physical composition were not conducted during this project due to difficulty in obtaining authorization to conduct such tests at the incinerators.

3.2.2.4 Results and Discussion

Experimental Results

Pilot Incinerator at NJIT

Technology of the Pilot Incinerator at NJIT

- The NJIT incinerator consists of four different components, the primary combustion chamber, the secondary combustion chamber, the heat exchanger, and finally the baghouse (Thipse 2001a).
- The NJIT incinerator is a unique facility and was constructed to work at conditions similar to those found in a large-scale incinerator.
- Synthetic fuel, composed of paper (35 weight %), yard trimmings (14.3%), wood (7.1%), plastics (9.1%), metals (7.6%), food wastes (6.7%), glass (6.2%), textiles (3.6%), rubber and leather (2.9%), miscellaneous inorganic wastes (1.5%), and others (1.7%), was used during this experiment.
- Synthetic fuel is fed to the Primary Combustion Chamber (PCC) at a rate necessary to maintain the temperature in the PCC in the range from 300 to 650°C.

Results for the Pilot Incinerator

- A well-defined fuel was prepared at NJIT (Thipse 2001a; Thipse et al. 2001b) to provide a composition with thermal characteristics (moisture, heat content) comparable to Municipal Solid Waste (EPA 1997b).
- Major aerosol components for prepared fuel burned between 300°C and 600°C (573 and 873 K) were measured at the exit of the primary combustion chamber by both the AMS and REMPI-TOFAMS.
- REMPI-TOFAMS data indicated that particulate PAH emissions sampled after the baghouse were inversely correlated with the combustion chamber temperature (emissions were low at 600°C [873 K] and higher at 300°C [573 K]).
- For low combustion temperatures (300 to 480°C [573 to 753 K]), the total mass loadings were found to be in the range of 20 to 8,900 µg per m³ with an average concentration of 2,400 µg per m³.
- For high combustion temperatures (530 to 600°C [803 to 873 K]), the total mass loadings were found to be in the range of 40 to 105 µg per m³ with an average concentration of 80 µg per m³.

- Individual PAH concentrations were found to be in the range of 0.15 to 150 ng per m³.
- Total PAHs emissions are usually in the range of 0.1 to 300 µg m⁻³ depending on the feed rate and combustion status (start-up, burning, burnout).
- ARI AMS results show the presence of five different groups of compounds: chlorides, ammonium, water, PAHs, and organics. Nitrates and sulfates were not observed.
- The organic fraction is dominant when operating the incinerator at low temperatures (~300°C [573 K]).
- At high primary combustion chamber temperatures (600°C [873 K]), results show that particulate ammonium is the dominant species.
- Aerosols were internally mixed (i.e., all of the chemical species are present in every particle) with average vacuum aerodynamic diameters of 200 nm.

Fluidized Bed Sewage Sludge Incinerator (SSI)

Technology of the SSI

- The SSI has a sand bed, which sludge is fed into, which is maintained at approximately 750°C (1,023 K).
- Materials are rapidly evaporated and volatile matter in the sludge is combusted.
- Exhaust is cooled to 560°C (833 K) using heat exchange to the incoming combustion air and a Venturi scrubber reduces particulate emissions.
- An impingement tray scrubber introduces water to cool the exhaust to ~43°C (316 K).
- A caustic solution is used to remove acidic gases.
- Exhaust gas is emitted into the atmosphere through a stack.

Results for the SSI

- All data were obtained from the gases leaving the heat exchanger using the ARI AMS equipped with a QMS. The PAH concentration was well below the Detection Limit of the REMPI-TOFAMS.
- The majority of aerosol mass was associated with ammonium sulfate.
- Chlorides, organics, and nitrates were also present.

- Combustion chamber temperature and auxiliary fuel feeding rates represented potential operating conditions that affected emitted aerosol mass loadings.
- Mercury and mercury dichloride were observed in incinerator exhaust.
- Mass concentrations of total mercury were detected up to 0.4 $\mu\text{g per m}^3$.
- Total aerosol mass loadings ranged from 10 to 380 $\mu\text{g per m}^3$.
- Vacuum aerodynamic diameters of particles ranged from 140 to 220 nm.
- Aerosols were found to be externally mixed (i.e., different particles contain different chemical species) and to consist of ammonium sulfate, organic compounds, chlorinated organic compounds, and nitrates.

Municipal Solid Waste Incinerator (MSWI)—Shred-and-Burn Technology, Special Boiler

Technology of the MSWI

- Designed to provide disposal and recycling of 5,000 tons per day of municipal solid waste.
- The first stage consists of shredding the waste, which is followed by magnetic separation to remove most ferrous materials. The processed waste is then blown into the boilers above the grate.
- The municipal solid waste is converted to a processed refuse fuel via a single shredding stage, reducing its particle size to about six inches followed by a single magnetic separation stage (Zakaria and Sutin 1994).
- Combustion gases are passed through a dry scrubber and sprayed with a lime reagent to remove acidic gas constituents.
- Electrostatic precipitators capture particulates.
- Exhaust gas is emitted into the atmosphere through a 300-foot stack.

Results for the MSWI

- Data were obtained from the ARI AMS equipped with a QMS that sampled gases in the duct between the combustion chamber/boiler and the dry scrubber. Only pyrene was detected with the REMPI-TOFAMS during this experiment.

- The ARI AMS was operated with a vaporization temperature between 550 and 1,200°C (823 and 1,473 K) in order to quantify both refractory and non-refractory species.
- Detailed analysis of mass spectra identified the presence of chlorinated hydrocarbons, other organics, and inorganic nitrates. The majority of aerosol mass was comprised of the inorganic sulfate, transition metals, and chlorine-containing compounds.
- Increasing the AMS vaporization temperature (from 550 to 1,200°C [823 to 1,473 K]) helped identify refractory compounds such as transition metals.
- Transition metals, including lead, zinc, manganese, iron, antimony, nickel, copper, chromium, and cadmium were present.
- Total mass loadings were positively correlated with vaporization temperature, indicating that the composition of aerosols from this incinerator was composed mostly of refractory compounds (e.g., lead).
- A large fraction of the transition metals were believed to be fine particulates (less than 1 µm).
- Transition metals represent the dominant fraction with a contribution of 43 percent of total mass loadings.
- Total mass loadings ranged from 20 to 141 µg per m³, with an average concentration of 80 µg per m³.
- Aerosols were found to be internally mixed (i.e., all of the chemical species are present in every particle) with average vacuum aerodynamic diameters of 600 to 700 nm.

Sewage Sludge Incinerator - Multiple-Hearth Sludge Incinerator

Technology of the Multiple Hearth Sludge Incinerator:

- The multiple-hearth incinerator consists of a vertical cylindrical shell containing 11 firebrick hearths.
- The sludge (22 to 32% solids) enters at the top of the furnace (hearth # 3, maintained at a temperature of 450°C [723 K]) and moves toward the bottom of the furnace (hearth # 11, maintained at a temperature of about 540°C [813 K]).
- Combustion exhaust exits the furnace at a temperature of about 650°C [923 K] on the upper hearth, which serves as an afterburner.

- The exhaust gases are cooled down to between 16 and 27°C [289 and 300K] in the Venturi scrubber. PM is also reduced in the Venturi.
- The exhaust gas, with PM reduced by the Venturi and cooled to a temperature varying between 15 and 21°C (288 and 294 K), is emitted into the atmosphere through an exhaust stack.

Results of the Multiple Hearth Sludge Incinerator

- The AMS vaporization temperature was operated between 550 and 1,200°C [823 and 1,473 K].
- No increase in total concentration was observed when the AMS vaporization temperature was raised above its normal operation temperature of about 600°C [873 K].
- Results indicate that refractory species are very low and represent less than two percent of total mass loadings.
- The total mass loadings were found in a range of 14 to 4,983 $\mu\text{g per m}^3$, with an average concentration of 1,153 $\mu\text{g per m}^3$.
- Exhaust particles consisted primarily of ammonium sulfate.
- The aerosol compositions were dominated by sulfates and ammonium, representing about 73 percent and 22 percent, respectively.
- Chlorides, organics, and nitrates were also present but at very low concentrations.
- Aerosols were found to be internally mixed with average vacuum aerodynamic diameters of particles averaged 200 nm.

3.2.2.5 Utilization of Research Results

During this project, Massachusetts Institute of Technology in collaboration with Aerodyne Research, Inc. deployed a state-of-the-art Aerodyne Aerosol Mass Spectrometer (AMS) to three municipal waste incinerators to measure the real-time chemical and size distribution of sub-micron particulate emissions from incinerators. Overall, the data collected within the framework of this project show the development of new and promising techniques for real-time chemical analysis and measurement of size-resolved ambient aerosols. Although the AMS was initially developed to characterize non-refractory species, further development and improvements were performed during this project to include the measurement of refractory species, such as metals. This new technique offers the simultaneous real-time measurement of a variety of chemical species present in/on aerosols and their corresponding size distribution in a rapid manner with respect to individual species for a variety of combustion systems. These

species include organics, sulfate, nitrate, ammonium, chloride and metals. Through this research, a mobile commercial instrument with the capability of performing the size distribution and mass loading concentration measurements in real-time will be available to the research and regulatory communities.

3.2.2.6 Research Needs

Project-Related Research Needs

Two research needs related to the above project were identified by the PIs. These are discussed below.

(1) Develop real-time in-field monitoring systems to detect toxic species.

Previous studies have shown significant variations in incinerator emissions with levels exceeding what is allowed by permit in some cases. Analytical instruments capable of continuous monitoring could sound an alarm or provide input to a process control system when toxic emissions exceed standards and trigger intervention to prevent further emission from the stack. However, current instrumentation is either not sensitive enough or not fast enough for real time measurement. Thus, the development of an accurate and sensitive real-time monitoring system for organic compounds and metals present on fine, and especially sub-micron aerosol particles ($PM_{2.5}$ and/or $PM_{1.0}$) emitted by combustion sources is very important.

The goal of further research is to develop analytical systems to:

- Provide real-time measurement for fine, and especially sub-micron, aerosols.
- Supplement current analytical methods for particulate organic compounds and metals measurement.
- Provide quantitative measurement of individual organic compounds and metals.
- Offer a value-added instrument which is easily deployed into the field and which requires no post-measurement laboratory analysis.

(2) Perform intensive field experiments to determine the composition of particulate and gas phase species.

Commercial instruments that can provide high levels of sensitivity and resolution and do so in real time and at low cost, would be used to improve understanding of the processes that control the composition of particulate and gas phase species produced from combustion sources and their chemical evolution in the atmosphere. The following areas are of particular interest:

1. Carbonaceous Particles From Diesel Combustion

Particulate emissions from diesel combustion engines represent a significant source of fine, non-fugitive, carbonaceous PM. They contribute more than four percent of the total $PM_{2.5}$ inventory. $PM_{2.5}$ emission rates from mobile diesel engines and non-road and stationary diesel engines should be studied.

2. Particulate Emissions From Incinerators

Most of the previous measurements were conducted to characterize the composition and quantity of the exhaust aerosol from the stack. Studies should also include sampling at multiple ports in order to better characterize the evolution of particulate composition and chemical and size evolution in the system prior to emission into the atmosphere.

3. Comparison Exercise

A study of various analytical instruments should be initiated in order to evaluate the performance of the new analytical instruments and study the possibility of using these new analytical instruments for defining new EPA methods (for instance, comparing the results of the ARI AMS with EPA Method 29 for measurement of total particulate metals).

Additional Research Needs

Further research is required for a better understanding of the chemical and physical processes controlling the composition of chemical species present in/on particles before emission into the atmosphere, including:

- Sampling at several sampling ports between the boiler and emission into the atmosphere.
- Systematic experiments to draw firm conclusions about the particulate emissions as functions of combustion temperature, fuel types and air/fuel equivalent ratio.
- Investigation into the effect of stack temperature, excess air, and feed rate on aerosol mass loading.
- Accurate measurement of the size-dependent chemical composition of atmospheric and laboratory aerosols having significant implications for climate, air quality and human health.

3.2.3 Summary of the Overall Contributions of These Two Projects to the RCRA MYP and Its Broad Theme of “Monitoring and Analytical Methods”

The RCRA MYP identifies Potential Additions to the Research Program with respect to Improved Approaches to Sampling and Analysis (EPA 2004a). These include improved speciation of products of incomplete combustion. This objective is directly supported by research conducted by both Rubey, Striebich, and Taylor’s grant and Smith and Boudries’ grant. The results of this research can be directly applied to design and application of sampling and analysis systems to further characterize emissions from combustion systems, in particular focusing on identification of potentially toxic constituents that have not been previously characterized in combustion system exhaust gas and fine particulate. Such sampling and analysis systems and the data provided by them could be applied directly to preparation of site-specific risk assessments for combustion systems.

3.3 EPA–AWMA INFORMATION EXCHANGE

3.3.1 Summary

The 28th Annual Environmental Protection Agency-Air and Waste Management Association (AWMA) Information Exchange was held in Research Triangle Park, North Carolina on December 2-3, 2003. This annual forum provides an opportunity for EPA and other interested parties to exchange information across and within the various areas of research pertaining to air and waste management. The audience of approximately 70+ consisted of EPA staff, industry representatives, academia, and environmental consultants.

EPA staff presented talks on the following topics:

- Mercury.
- Multi-pollutant control technologies.
- Coal combustion residues
- New Source Review reform.
- Homeland security.
- Ozone implementation.
- Animal waste and ammonia emissions.
- Fine particulate matter.
- Carpet and electronic waste incineration.
- Open burning.
- Indoor air mold.
- Combustion research.

On Day 2 of the Information Exchange, four of the five the combustion emissions PIs reported on the progress of their research. In addition, Clyde Owens, representing the National Risk Management Research Laboratory (NRMRL), provided an overview of ORD’s in-house combustion research.

In 1999, EPA identified combustion emissions as a critical human health and environmental problem requiring further scientific and technical research. As the combustion emissions research grants come to an end, EPA was interested in understanding how the current research has addressed this problem and identifying any additional short- and long-term research needs. Furthermore, a rule making is expected to come out in the near future covering emissions from these sources.

As a result, a more thorough understanding of the sources, pollutants, and potential health concerns is essential at this time. For these reasons, an update on the status of the STAR recipients' research was of particular interest. The PIs from four of the five STAR grants participated in the conference. Their topics are listed below.

- *Mechanistic Studies of the Transformation of Polychlorinated Dibenzo-p-Dioxins via Hydroxyl Radical Attack*, Phillip H. Taylor, University of Dayton.
- *Trace-level Measurement of Complex Combustion Effluents and Residues using Multi-dimensional Gas Chromatography-Mass Spectrometry (MDGC-MS)*, Richard Striebich, University of Dayton.
- *Characterization and Minimization of Fine Particulate Emissions from Waste Incinerators by Real-Time Monitoring of Size-Resolved Mass and Chemical Composition*, Hacene Boudries, Massachusetts Institute of Technology and Aerodyne Research, Inc.
- *Toward the Development of a Detailed Mechanism of Transition Metal Catalyzed Formation of PCDD/F from Combustion Generated Hydrocarbons*, Barry Dellinger, Louisiana State University - Baton Rouge.

The fifth PI, Selim M. Senkan, who examined the products of incomplete combustion, was not in attendance. Earlier versions of PIs presentations, including that of Dr. Senkan, were given at the AWMA National Meeting in Anaheim, CA, in June 2003. In addition, Clyde Owens of NRMRL presented the ORD in-house research findings in the presentation *Endocrine Disruptors from Combustion and Vehicular Emissions: Identification and Source Nomination*.

At the conclusion of the presentations, PIs and other experts were invited to participate in an open discussion of research needs related to combustion emissions. A summary of the research needs identified by members of the discussion panel is provided in Section 3.3.3.

3.3.2 Presentations

The research that resulted from these five grants is discussed in Section 3.1 and 3.2 and is not repeated here.

Clyde Owens (NRMRL) presented the results and findings of ORD's in-house research focused on investigation of endocrine disrupting chemicals (EDCs) from combustion and

vehicular emissions. EDCs are linked to breast and prostate cancer, which rank second in cancer deaths for women and men, respectively. The purpose of this project was to determine whether EDCs are emitted from various combustion sources, including domestic waste burning, fireplaces/wood stoves, and forest fires, and if so, in what quantities.

Owens sampled and analyzed exhaust from both combustion and vehicular sources to confirm the presence of EDCs. Combustion sources were evaluated for potential EDCs using bioassays, sample fractionation to isolate the target compounds, and gas chromatography-mass spectroscopy (GC-MS) for identification of each compound once isolated. The research identified potential EDCs in diesel exhaust and pine, oak, and artificial wood. Compounds released from wood burns and in diesel exhaust were labeled as possibly androgenic.

3.3.3 Research Needs Identified During Panel Discussion

Participants in the panel discussion included the PIs and ORD/NRMRL researchers. Discussion was also open to session attendees. The research needs identified during the discussion are summarized below by topic; the name of the commenter(s) follows in parentheses.

Chemical Compounds in Combustion Systems:

- Nanoparticle fractions. These fractions are sites of increased activity (compared to micron-size particles) and much of the chemistry occurs at this level² (Dellinger).
- Chlorobenzenes and their role in dioxin formation (Dellinger).
- Brominated and oxygenated compounds in combustion emissions (Dellinger, Lemieux).
- Combustion by-products formed in the post-flame combustion zone. Radicals that may be formed in the “hot zone” are critical in the “cool zone” (Dellinger, Smith).
- Gas-phase and surface reactions in combustion emissions (Taylor).
- Chlorinated by-products that are persistent in the environment. Specifically, whether they are products of combustion or from other sources (Taylor).
- Toxicity information for many of the combustion by-products (e.g., poly-brominated compounds) for risk assessment purposes (Owens).
- Toxicity information for the constituents of diesel emissions (Owens).

² Atmospheric nanoparticles or ultrafine particles is defined as particles smaller than 100 nm in diameter (Friedlander and Pui 2003).

- Toxicity of chemical mixtures. Specifically, determine what is toxic in these mixtures (Striebich).
- Evaluate the biomass of sugar cane that is burned and the quantity and composition of the emissions (Owens).

Monitoring and Analytical Methods for Combustion Systems:

- Develop instrument to study high temperature surface reactions on the order of seconds (Dellinger).
- Improve instrumentation for conducting routine, in-field real time measurements (Smith, Striebich, Lemieux).
- Develop more robust measurement techniques (Smith).
- New techniques to study larger intermediate molecules for gas-phase reactions (Taylor).
- Further study of multi-dimensional gas chromatography (Lemieux).
- Develop better, cheaper, more reliable lasers (Lemieux).

General Research Improvement:

- Better coupling of theory and experimental results (Taylor).
- There are many tools available that are not consistent with EPA methods. More outreach and flexibility to use these other methods is needed (Session attendee).
- Coal combustion should be one of the priority sources of study (Lemieux).
- Grants should be more focused on data/knowledge gaps instead of regulatory needs (Smith).
- Increase funding for combustion emissions research (Owens).
- More discussion and information exchange between researchers who characterize emissions and fate and transport experts (Taylor, Lemieux).
- Increased interaction among PIs, EPA, the academic community, equipment/facility designers and operators, and other researchers (Lemieux).

- Improve emissions data and emissions factors and the connection between research and modeling. Develop a forum for researchers and modelers to exchange information/ideas (Session attendee).

Some participants said at the end of the discussion that this was the first time that academic, ORD in-house, and industry researchers came together to discuss research needs in combustion research. They wanted to know how soon another such session could take place.

3.4 AMERICAN FLAME RESEARCH COMMITTEE SPRING MEETING

The Spring Meeting of the American Flame Research Committee (AFRC) was hosted by EPA and held in the EPA facility in Research Triangle Park, NC, on April 27 and 28, 2005.

3.4.1 Topics and Speakers

Most of the presenters were EPA ORD in-house researchers, primarily from the ORD National Risk Management Research Laboratory (NRMRL). Among the presenters was Clyde Owens from NRMRL, who had participated on the combustion emissions panels at the two AWMA meetings. The topics and speakers during the first day and a half included the following:

1. *Formation and Mitigation of Visible Acid Aerosol Plumes from Coal-fired Power Plants*, Andy Miller, NRMRL.
2. *ORD PM Research Program*, Andy Miller, NRMRL.
3. *Combustion Generated Fine Particles, Trace Metal Speciation, and Health Effects*, Bill Linak, NRMRL.
4. *PCDD and PCDF Formation and Monitoring of Combustion Sources*, Shawn Ryan, EPA.
5. *PCDD/F Emissions from Open Burning Simulations*, Brian Gullett, ORD.
6. *Control of Mercury Emissions from Coal-Fired Power Plants*, Ravi Srivastava, NRMRL.

There were on the afternoon of the second day presentations on three of the five grants —by Taylor, Smith and Boudries, and Striebich. They were followed by a presentation by Mark Lee of ICF Consulting on the status of this synthesis report. After that, Bob Hall of ORD/NRMRL and Paul Shapiro of ORD/NCER led a discussion of research needs.

The topics of these speakers were:

1. *Endocrine Disruptors from the Combustion of Electronic Waste*. Clyde Owens, NRMRL.
2. *Kinetic Studies of Hazardous Air Pollutants Under Post-Combustion Conditions*, Phillip Taylor, University of Dayton.
3. *Real-Time Chemical and Physical Characteristics of Fine Particulate Emissions from Waste Incinerators by the Aerodyne Aerosol Mass Spectrometer*, Kenneth Smith, MIT, and Hacene Boudries, Aerodyne.
4. *Multidimensional Gas Chromatography: Time of Flight Mass Spectrometry for Identification of Combustion Products and Residues*, Richard Striebich, University of Dayton.
5. *Synthesis of Hazardous Waste Combustion Research and Research Needs*, Mark Lee, ICF Consulting.

3.4.2 Discussion and Prioritization of Combustion Research Needs

The AFRC meeting continued with a the identification and prioritization of combustion research needs. The meeting participants identified possible criteria for ranking research needs. The criteria were:

- (1) Potential for risk reduction.
- (2) Widespread applicability.
- (3) Filling significant gap.
- (4) Importance for regulatory needs.
- (5) Cost-effective investment.
- (6) Likelihood of success.
- (7) Complementary to government and industry research.
- (8) Quality of researchers available.
- (9) Pressing national need.
- (10) Balance to research portfolio.
- (11) Inter- or multi-disciplinary.
- (12) Focus is on current and future, not past issues.

In discussing how to identify and prioritize research needs as related to the criteria participants made the following points:

- (1) Potential for risk reduction and (6) Likelihood of success are MUCH more important than others.

- All criteria need to be considered and the whole of the proposal must be considered when making decisions.
- For exploratory research, cost should not play as big a role; as technology matures, cost should be considered more heavily. For example, in the 1980s NO_x burners were seen as more cost-effective than Selective Catalytic Reduction (SCR) so investment was not made at that time in SCR.
- EPA needs to balance “exploratory” with “application-oriented” research.
- Risk communication is needed.

The participants then identified what they each thought was the most important research need. After that, the participants were asked to qualitatively take the criteria they had developed earlier and apply them in voting for their top priority research area among the areas that had been identified. This voting process gave the following results:

1. ***Fundamental mercury research***, including research on mercury chemistry under realistic conditions (8 votes).
2. ***Gasification of solids***, including coal gasification and biomass waste gasification, and particularly high pressure gasification (7 votes).
3. ***Combustion of alternative fuels***, including pollution impacts (7 votes).
4. ***Open burning***, including dioxin emissions (5 votes).
5. ***Analytical/Sampling devices development***, including devices for partitioning for mercury (4 votes).
6. ***Interaction of multi-pollutants/multi-control processes*** (4 votes).
7. ***Health effects engineering***, including understanding components of emissions that impact toxicity and how to control these emissions (4 votes).
8. ***CO₂ sequestration*** (2 votes).
9. ***Development of adaptive grid computational models of emissions/sources*** (2 votes).
10. ***Flaring of liquids and gases*** (1 vote).
11. ***Develop better understanding of measurement processes*** that might help develop better/cheaper measurement devices, including surrogate compounds and measurements (1 vote).

12. *Combustion and its place in homeland security*, e.g., disposal of agricultural residues (1 vote).

3.4.3 Conclusions

The principal issues identified in the prioritization of research needs are not typical EPA combustion issues, but these combustion researchers think that these issues are most important. This reflects a change in the universe since 1999, including United States and world conditions. The combustion community, which has traditionally been reactive, may need to be more proactive in setting research priorities. Industry is still interested in efficiency improvements, which would lead to reduced emissions. However, the gap between fundamental research and development and application of new technologies needs to be addressed.

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4. SUMMARY OF FINDINGS AND RESEARCH NEEDS

This section summarizes the findings of this synthesis report. This section shows how the results of the five research projects help meet the goals of the EPA RCRA Multi-Year Plan, indicates how the results of the projects can be used by others, and identifies future research needs related to combustion research.

4.1 SUMMARY OF FINDINGS

4.1.1 Contributions to the Waste Management Goal of the RCRA Multi-Year Plan

This section describes the contributions of these five projects to meeting the Waste Management goal of the ORD RCRA Multi-Year Research Plan (MYP) (EPA 2004a). The RCRA MYP provides part of the context of ORD's research goals and objectives to which these projects have contributed their research results.

The RCRA MYP reports plans for combustion research and identifies annual performance goals (APGs) in achieving long-term goals (LTGs) and associated annual performance measures (APMs). The Waste Management LTG, one of two LTGs in the MYP, is "Improve waste management for industrial and municipal waste to enhance sustainability by providing technical reports." Combustion research addresses this issue by seeking to develop improved approaches to monitor emissions that will lead to improved decision making on use of combustion and incineration

To help achieve this goal, ORD's combustion research has focused on addressing the following Waste Management Science Questions identified in the RCRA MYP:

- What easily monitored components of emissions can be used to predict more difficult-to-measure components (e.g., PCDD/PCDF)?
- How can complex mixtures of organic compounds in the stack gases be characterized with respect to risk assessment needs?
- What PCDD/PCDF formation issues exist during combustion of hazardous wastes?

These projects have addressed these questions through improved characterization of the mechanisms of formation of components of air emissions from combustion systems, and through development of improved methods of measuring and speciating such components. More specifically, they have investigated:

- The influence of transition-metal deposits on emissions of PCDD/PCDFs from combustion systems (Dellinger and Lomnicki).

- The effects of oxygenate additives on polycyclic aromatic hydrocarbons (PAHs) and soot formation (Senkan).
- The potential for variability in some relatively easy-to-measure compounds to be utilized for accounting for the variability of difficult-to-measure compounds such as PCDD/PCDFs (Taylor, Dellinger, and Lomnicki).
- The potential for the Aerosol Mass Spectrometer (AMS) analytical method to be utilized as a real-time monitor for air toxics that are present in the low parts per trillion range (Smith and Boudries).

The RCRA MYP includes APGs and APMs for Combustion and Incineration within the Waste Management LTG. These include APGs and APMs that are directly supported by the five projects.

- There is an APG for fiscal year 2005 that states, “Provide the results of fundamental and applied research on metals and analysis and modeling of organic compounds during combustion through reports from three grants.” This APG consists of the following three APMs. The project associated with meeting each APM is identified in the APM.
 - ▶ Demonstrate a detailed mechanism of formation of PCDD/PCDFs from ubiquitous combustion-generated hydrocarbons (Grant R828191; Dellinger and Lomnicki).
 - ▶ Develop improved analytical techniques to identify or speciate total organic emissions (TOE) (Grant R828190; Rubey, Striebich, and Taylor).
 - ▶ Provide fundamental research data to broaden a comprehensive gas-phase model of the transformation of PCDD under a wide range of conditions (Grant R828189; Taylor).
- There is an APG for fiscal year 2007 that states, “Provide technical information in the form of one paper and one draft guidance on the use of advanced monitoring techniques and surrogate organic performance indicators for incinerators.” This APG is supported by Grant R828192, for which Smith and Boudries are the PIs, and Grant R828190, for which Rubey, Striebich, and Taylor are the PIs.

4.1.2 Utilization of Results by EPA and Others

Research results provided by Taylor provide important inputs that may be built upon by other researchers towards the development of a comprehensive gas-phase model of the transformation of PCDDs under a wide range of combustion source conditions and wastes. Taylor indicates that the rate mechanisms and equations presented in the research results should

be evaluated by others using different techniques. The rate mechanisms may be applied by researchers investigating atmospheric transformation of dioxins and furans.

Research results presented by Dellinger and Lomnicki provide rate mechanisms for formation and transformation of dioxins and furans, and also identify precursor compounds. These results may be applied by other researchers towards development of models of formation and transformation of dioxins and furans as related to surface-modulated (or catalyzed) reaction in combustion systems and also applied to further investigations towards the development of surrogate compounds to indicate emissions of more difficult to monitor chlorinated dioxins and furans. The PIs have developed a comprehensive view of how PCDD and PCDF are formed in combustion systems and how the nature of surfaces control the cogener distribution, PCDD to PCDF ratio, and how yields are affected by temperature and excess air.

Research by Senkan includes data concerning trace species concentration profiles and soot and temperature profiles in combustion systems for intermediate species which were found in the limited tests for wastes. These results can be applied by other researchers in the following ways: (1) development of detailed chemical kinetic mechanisms describing combustion of brominated hydrocarbons in flames using results determined from intermediates; (2) development of abatement techniques for brominated dioxins and furans based on the identified mechanisms of formation; (3) identification of surrogate compounds to indicate emissions of more difficult to monitor brominated dioxins and furans; and (4) combination with fluid mechanical models to simulate, design, and develop abatement mechanisms for combustion systems.

Research results from Rubey, Striebich and from Taylor's project and Smith and Boudries' project can be directly applied toward further development, design, and implementation of real-time or near real-time monitoring systems for speciation of fine particulate emissions and organic compound emissions from combustion systems. Data generated by such systems can be applied directly to preparation of site-specific risk assessments for combustion systems.

4.2 SUMMARY OF RESEARCH NEEDS

Through their research projects, the PIs identified potential research needs specifically related to their project and to combustion in general. These research needs, listed by PI, are provided in Sections 3.1 and 3.2 of this report. As discussed in Section 3.3, during the EPA-AWMA Information Exchange and during the AFRC meeting, participants of a combustion research panel discussion that included the PIs, EPA, and other interested parties also identified potential research needs related to combustion emissions. In addition, following the Information Exchange, various combustion experts consisting of EPA staff, industry representatives, academia, and environmental consultants were contacted via phone and email to identify needs for future research in the field. The research needs identified through each of these means have been grouped into the following five categories:

- Mechanisms of formation of chemical compounds.

- Monitoring and analytical methods.
- Emissions characterization.
- Fate and transport.
- Toxicity, health effects, and risk assessment.

These research needs are summarized and presented in these categories below. For each category, the potential significance of additional research is also provided. The complete list of identified research needs is provided in Appendix B.

4.2.1 Mechanisms of Formation of Chemical Compounds

Significance of research: Improves understanding of the mechanisms of formation of chemical compounds in combustion systems, which can be used to develop new control technologies and operating parameters to limit emissions of pollutants and ultimately reductions in risk.

Summary of Identified Research Needs:

- Characterize the formation, destruction, and transformation of chlorinated and brominated dioxins/furans, PAHs, soot, and fine particulates during the combustion process.
- Currently, no one is working on comprehensive, multi-mechanism models for dioxin formation in incinerators; while this is an important research topic, it should not be conducted without the necessary resources for validation of the full-scale models.
- Explore possible modifications to combustion processes to minimize formation of metals and persistent organic compounds.
- Determine the effects of trace amounts of bromine on the kinetics of formation and destruction of PICs in combustion devices.
- Study composition of combustion by-products, particularly those formed in the post-flame zone.
- Improve speciation of products of incomplete combustion.
- Examine role of nanoparticles in pollutant formation.
- Assess whether emission limits on chlorinated dioxins and furans are also effective in controlling brominated dioxins and furans and other POM (e.g., PCBs).
- Characterize the formation, destruction, and transformation of chlorinated and brominated dioxins/furans, PAHs, soot, and fine particulates during processes aimed at gasification of solid wastes.

4.2.2 Monitoring and Analytical Methods

Significance of research: Leads to development of better monitoring, sampling, and analysis methods to more accurately characterize combustion emissions.

Summary of Identified Research Needs:

- Improve existing sampling and analytical methods by making them easier to use, less expensive, and more robust.
- Develop improved techniques for the study of high temperature surface reactions.
- Develop and improve systems capable of characterizing combustion effluents in real-time or near real-time.
- Develop performance specifications for Continuous Emission Monitoring Systems (CEMS) for PM, multimetals, and HCl and document that these CEMS can meet the specifications when installed on HWCs.
- Communicate the results of the advancements above to the design and user communities to include demonstration of performance (in all its dimensions) through field tests over significant time periods with commercial-scale combustion systems.

4.2.3 Emissions Characterization

Significance of research: Used to identify toxic fractions of combustion-related emissions to more accurately characterize risks.

Summary of Identified Research Needs:

- Further study of emerging pollutants associated with combustion (e.g., persistent bioaccumulative toxics, EDCs).
- Study difficult-to-incinerate materials or materials that will be increasingly found in the municipal solid waste stream (e.g., electronic wastes).
- Investigate how fuel and combustion conditions cause changes in the composition of combustion emissions.
- Better characterize emissions from different combustion technologies.
- Improve emission factors for combustion processes.

- Study the reduction in emissions by air pollution control systems (e.g. adsorption of pollutants by activated carbon, condensation and adsorption of pollutants on lime particles in spray dryer absorption systems used for acid gas reduction, destruction of PCDD/PCDF compounds in catalytic de-NO_x processes).

4.2.4 Fate and Transport

Significance of research: Improves knowledge related to the fate and transport of combustion-related emissions to better assess potential impacts of these materials on human health and the environment.

Summary of Identified Research Needs:

- Improve communication between combustion experts and fate and transport modelers.
- Improve understanding of dioxin/furan fate and transport.
- Develop better source terms for modeling.
- Research atmospheric processing of combustion particles and their eventual fate in the environment.

4.2.5 Toxicity, Health Effects, and Risk Assessment

Significance of research: Improves understanding of mechanisms of toxicity and potential health effects associated with combustion emissions, particularly for those compounds for which little or no information is available

Summary of Identified Research Needs:

- Assess relative environmental significance of combustion emissions.
- Quantify the impacts of the alternatives to combustion.
- Better understand the mechanisms of toxicity associated with EDCs.
- Continue to research health effects and risks associated with exposure to dioxins/furans, metals, and fine PM.

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5. CONCLUSIONS

These five projects have made important contributions to the characterization and monitoring of the combustion emissions from hazardous waste incinerators, boilers and industrial furnaces, and municipal solid waste incinerators. Some of the results of this research can be used for better understanding combustion emissions from other sources as well. Completion of these projects fulfilled two APGs and three associated APMs of the ORD RCRA MYP (EPA 2004a). The scientific papers and reports that came out of these projects will be added to the supporting technical basis for the MYP as it is revised in the future.

This document has served as a means to identify research needs related to combustion more generally than just this area of research. It offered the opportunity for academic, EPA in-house, and industrial researchers and consultants to jointly discuss what these research needs are. This in itself is a kind of collaborative planning that, according to the participants, has not previously occurred.

The utility of the research results that have been reported here and the research needs that have been identified lies in the application of the research results to help states, industries, and other organizations to mitigate the emissions and their resulting health effects. It also offers the opportunity for EPA program offices and the research office, as well as outside experts, to consider the need for additional research in combustion emissions in the future.

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APPENDIX A

LIST OF COMBUSTION EXPERTS INTERVIEWED

Combustion Experts Interviewed

Name	Affiliation	Phone Survey	E-mail Survey
Ballard, Gary	EPA, Office of Solid Waste	✓	
Cooper, John	Cooper Environmental Services		✓
Hall, Bob	EPA, ORD, National Risk Management Research Laboratory	✓	
Hoecke, David	Enercon Systems	✓	
Lemieux, Paul	EPA, ORD, National Risk Management Research Laboratory		✓
Lighty, JoAnn	University of Utah, Department of Chemical Engineering, Institute for Combustion and Energy Studies	✓	
Linak, Bill	EPA, ORD, National Risk Management Research Laboratory	✓	
Porter, Fred	EPA, Office of Air Quality Planning and Standards	✓	
Sarofim, Adel	University of Utah, College of Engineering, Institute for Combustion and Energy Studies/Reaction Engineering International	✓	
Themelis, Nickolas	Columbia University, Earth Engineering Center		✓
Trenholm, Drew	Research Triangle International, Air Pollution Control Technology Verification Center	✓	
Wendt, Jost	University of Arizona, Department of Chemical and Environmental Engineering		✓
Ziemann, Paul	University of California, Riverside, Department of Environmental Sciences		✓

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APPENDIX B
IDENTIFIED RESEARCH NEEDS

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Identified Research Needs

Summary of Research Need	Where/By Whom was the Research Need Identified?		
	Information Exchange ¹	Grantee Report ²	Other Combust. Expert ³
Mechanisms of Formation of Chemical Compounds in Combustion Systems			
Improve understanding of the formation of dioxins and furans as well as non-chlorinated analogs and mixed bromo-chloro dioxins/furans.			✓ (Lemieux)
Improve the understanding of the fate of dioxins and dioxin transformation in the atmosphere.		✓	
Determine how combustion processes can be modified to minimize the formation of mercury and persistent organic pollutants (e.g., dioxins and furans). Find methods to stabilize mercury emissions, so that more stable species are emitted.			✓ (Hall)
Study the role of chlorinated benzenes in the surface-mediated mechanisms of dioxin/furan formation.	✓	✓	
Examine the role of combustion-generated nanoparticles in pollutant formation. These fractions are sites of increased activity (compared to micron-size particles); much of the chemistry occurs at this level.	✓	✓	✓ (Ziemann)
Determine the origin and nature of gas-phase and particle-associated persistent free radicals.		✓	
Examine elementary reactions of chlorinated phenoxy and phenyl radicals.		✓	
Investigate photothermal reactions in flares and plumes.		✓	
Invoke new reaction mechanisms to describe the formation and destruction of PAHs during the combustion process.		✓	
Perform intensive field experiments to determine the composition of particulate and gas phase species in combustion emissions.		✓	
Determine whether chlorinated by-products (which are persistent in the environment) are products of combustion.	✓		
Study combustion by-products formed in the post-flame combustion zone.	✓		

Identified Research Needs

Summary of Research Need	Where/By Whom was the Research Need Identified?		
	Information Exchange ¹	Grantee Report ²	Other Combust. Expert ³
Develop better understanding of fine particulate formation and transformation as well as health effects of fine particles.		✓	✓ (Lighty; Linak)
Develop lower cost particle control technologies.			
Develop better understanding of soot formation and transformations.			✓ (Lighty)
Confirm activity from diesel fractions.			
Monitoring and Analytical Methods			
Develop better (simple, low cost, and reliable) sampling and analysis methods for toxic combustion emissions.			✓ (Cooper; Wendt)
Improve methods for analyzing the full composition of nanoparticle emissions. Specifically laser desorption methods need to be improved for efficient sampling and analysis of these very small particles.			✓ (Ziemann)
Improve methods for rapid quantitative analysis of black carbon emissions (associated with diesel vehicles and other combustion sources).			✓ (Ziemann)
Improve methods for identifying and quantifying emissions of oxidized organic compounds from combustion sources.			✓ (Ziemann)
Develop improved techniques for the study of high temperature surface reactions in time scales on the order of seconds.	✓	✓	
Design a more effective analysis system that combines TGPGC and TOFMS for characterizing PICs associated with combustion in a rapid, real-time or near real-time fashion. Thoroughly test this system to support its use in characterizing complex combustion effluents and in conducting site specific risk assessments.		✓	
Develop real-time in-field monitoring systems to detect toxic species.		✓	

Identified Research Needs

Summary of Research Need	Where/By Whom was the Research Need Identified?		
	Information Exchange ¹	Grantee Report ²	Other Combust. Expert ³
Improve instrumentation for conducting routine, in-field real time measurements. They need to be easier to run; those available currently are often difficult to use.	✓		✓ (Hoecke)
Develop more robust measurement techniques.	✓		✓ (Hoecke)
Develop new techniques to study larger intermediate molecules for gas-phase reactions.	✓		
Perform further study of multi-dimensional gas chromatography.	✓		
Study other tools of analysis other than EPA methods. EPA methods are too rigid. There are many tools available that are not consistent with EPA methods. More outreach needed for these other methods. More flexibility needed to use these other methods.	✓		
Build an integrated air pollution research facility in which there is a pollution generator, a plume chamber, and exposure chamber (with mice or other test species) to investigate how changes in fuel and combustion conditions cause changes in primary emissions, secondary atmospheric reactions, and health effects.			✓ (Wendt)
Perform intensive field experiments to determine the composition of particulate and gas phase species in combustion emissions.		✓	
Develop performance specifications for multimetal and HCl CEMS and document that PM, multimetal, and HCl CEMS can meet the specifications when installed on hazardous waste combustors.			✓ (Holloway)
Emissions Characterization			
Perform cool-zone studies. Radicals that may be formed in the "hot zone" are critical in the cool zone.	✓		✓ (Trenholm)
Look at degradation and reformation reactions in the combustion effluent when it reaches ambient temperatures.			

Identified Research Needs

Summary of Research Need	Where/By Whom was the Research Need Identified?		
	Information Exchange ¹	Grantee Report ²	Other Combust. Expert ³
Identify toxic fractions of combustion-related mixtures. We need to simplify fractions to figure out what is toxic in these mixtures. Need more study of "odd-ball" compounds, such as brominated, oxygenated compounds.	✓		✓ (Ballard)
Further study of the emerging pollutants associated with combustion, including endocrine disruptors, fluorinated compounds, brominated compounds, and non-traditional metals that might be found in combusted electronics wastes.			✓ (Lemieux)
Develop further understanding of heterogeneous reactions between organic molecules and fly ash-bound catalysts.			✓ (Lemieux)
Need to take a multi-pollutant approach when looking at alternative combustion technologies. We need to look at effects on multiple pollutants and not just a select few.			✓ (Sarofim)
Study how fuel and combustion conditions impact combustion emissions and potential risks. We need to push use of alternative fuels and study how use of these fuels affect combustion operations and emissions.			✓ (Sarofim)
Focus on better characterization of emissions from various combustion technologies and how various combustion phenomena affect those emissions.			✓ (Themelis)
Improve emissions data and emissions factors and the connection between research and modeling. Develop a forum for researchers and modelers to exchange information/ideas.	✓		✓ (Ballard)
Study the nature of particle surface structure and composition, since it is often interactions at the surface that are responsible for chemical reactions, water adsorption, and health effects.			✓ (Ziemann)
Fate and Transport			
Need further research to understand the atmospheric processing of combustion particles and their eventual fate and potential impacts on climate and human health.			✓ (Ziemann)
Develop better source terms for fate and transport modeling.			✓ (Lemieux)

Identified Research Needs

Summary of Research Need	Where/By Whom was the Research Need Identified?		
	Information Exchange ¹	Grantee Report ²	Other Combust. Expert ³
Toxicity, Health Effects, and Risk Assessment			
Focus more on health effects research. We need a better understanding of what's in combustion emissions, how different combustion conditions impact emissions, and how these emissions affect human health. Of particular concern are fine particulates.			✓ (Sarofim)
Evaluate poly-brominated compounds for androgenic and estrogenic activity.	✓ (Owens)		
Confirm activity from diesel fractions.	✓ (Owens)		
Improve toxicity information for many of the combustion by-products for risk assessment purposes.	✓		✓ (Ballard)
Develop more data on the health effects of combustion emissions other than diesel particulate.		✓	
Develop better understanding of health effects (down to the cellular level) of dioxin and mercury.			✓ (Hoecke; Lighty; Linak; Themelis; Wendt)
Further study is needed on the risk from and exposure to dioxins.			
Speciation of low levels of mercury compounds is also important.			
Assess relative environmental damage caused by combustion emissions.		✓	
Other Research Needs			
Make coal combustion one of the priority sources of study.	✓		
Perform further study to more fully understand the compounds released from inefficient and uncontrolled sources of combustion emissions (e.g., rural refuse incineration, fireplaces, forest fires, agricultural burning, other open burning situations).		✓	✓ (Hoecke; Sarofim)
Need to weight problems and spend money on the more important issues (i.e., sources other than "clean combustors", such as open burning).		✓	✓ (Hoecke; Sarofim)

Identified Research Needs

Summary of Research Need	Where/By Whom was the Research Need Identified?		
	Information Exchange ¹	Grantee Report ²	Other Combust. Expert ³
Study difficult to incinerate materials or materials that will be increasingly found in the municipal solid waste stream (e.g., electronic wastes, Teflon materials).		✓	
Evaluate the biomass of sugar cane that is burned and the quantity and composition of the emissions.	✓ (Owens)		
Increase funding for future combustion research studies.	✓		✓ (Hoecke)
Increase interaction among grantees, EPA, the academic community, and other researchers. Hold more discussion forums like the Information Exchange.	✓		
Focus future grant work on data/knowledge gaps instead of solely on regulatory needs.	✓		
Need more “real” data that identifies the real problems associated with combustion emissions and provides better education for the public.			✓ (Hoecke)
Encourage more interdisciplinary research. Promote further discussion and information exchange between researchers who characterize emissions and fate and transport experts.	✓		✓ (Wendt)
Research the impacts of changes in incineration practices under Superfund; specifically, moving from on-site incineration to on-site “thermal treatment” and off-site incineration.		✓	

Notes:

¹ Additional details regarding research needs identified during the AWMA Information Exchange may be found in Section 3.3.

² Additional details regarding research needs identified by grantees in their reports or other documentation may be found in Sections 3.1 and 3.2.

³ “Other combustion experts” were contacted via phone or email.

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