

Dates: March 1, 2002 – August 1, 2002

**HYDROCARBONS, IRRITATING AND TOXIC PHENOLS, AND
OTHER BIOLOGICAL TOXINS IN SMOKE FROM BURNING
WHEAT STUBBLE**

**Annual Report
Submitted by:**

**Candis S. Claiborn, Ph.D.
Laboratory for Atmospheric Research
Department of Civil and Environmental Engineering and
Center for Multiphase Environmental Research
Washington State University
Pullman, WA 99164-2910**

And

**Jeff Corkill, Ph.D.
Department of Chemistry
Eastern Washington University
Cheney, WA**

**Submitted to:
U.S. Environmental Protection Agency Region 10
May 28, 2002**

Introduction

The primary objective of this research is to quantitate benzo (a)pyrene (B(a)P) and other selected toxic and carcinogenic polycyclic aromatic hydrocarbons (PAHs), irritating and toxic phenols, and other persistent biological toxins [PBTs] in smoke from burning wheat stubble. A secondary objective is to quantitate the particulate dioxin fraction, in order to allow for dioxin emission factors to be estimated. This also entails quantifying the fine particulate emission factor. The project further measures air quality impacts near burning agricultural fields and in selected nearby communities. These objectives are being accomplished by measuring respirable particulate matter and chemical constituents of interest at the sources as well as in nearby communities and surrounding areas during the burn season.

Four tasks were originally envisioned to carry out this work including:

- (1) conducting small-scale controlled burns (approximately 1 kg biomass) to collect air samples for particulate matter (PM), phenols and PAH analysis;
- (2) conducting additional controlled burns in EPA's "burn hut" (approximately 20 kg biomass per sample) to collect air samples for dioxins and PAH analysis as well as to estimate emission factors;
- (3) mobile mapping of particulate and phenols and PAH concentration fields and particulate sample collection in regions near field burns; and
- (4) operating one continuous particulate measurement site in Pullman, WA.

This project is being conducted as a cooperative agreement with EPA in RTP (Dr. Brian Gullett, PI). Dr. Gullett's interests lie in the quantification of dioxins and furans in biomass smoke. Dr. Gullett's group provided access to the test burn facility in RTP, NC, and also supported the project with a number of support measurements including temperature, carbon monoxide, hydrocarbons, oxygen, and mass of fuel.

Results To Date

This project began in spring 2001 with a small-scale research burn experiment, fixed site operation, and biomass sample collection. During the year, two sets of biomass samples were transported to Research Triangle Park (RTP) for burns at the test facility. A set of experiments was conducted in the spring (May), and another was conducted in the late summer (August). Sample analysis is still in progress.

Ideally, complete combustion of organic material (hydrocarbons) results in products of carbon dioxide and water vapor. Incomplete combustion results in a plethora of byproducts including carbon monoxide, soot, and many hydrocarbon-based species, including PAHs. The factors determining the

combustion efficiency are the available oxygen, combustion temperature, residence time, and amount of mixing or turbulence. Small, controlled burns in which the biomass was randomly piled were expected to have much different combustion characteristics than field burns, because the degree of contact between the fuel and available oxygen would be much different, due to the difference in fuel orientation. It was thus determined very early in the project that it would be important to simulate field conditions as much as possible, even while conducting a controlled experimental burn, so that the emission factors determined would be relevant (i.e., the combustion efficiency would be similar to that in actual field conditions). The burn experiments conducted at the EPA facility in Research Triangle Park (RTP) provided an opportunity to configure the biomass in a way that resembled its orientation in the field. Our EPA collaborators (Dr. Brian Gullett et al.) constructed a platform with a screen that allowed us to stand some of the fuel as it would be found in the field. A 1-inch mesh screen (77.4% open area) provided the base of the burn area. The platform was 3 feet by 3 feet and consisted of two woven wire mesh screens. The top screen was covered with coarse gravel and dirt to simulate the field surface. Combustion occurred only at the top of the top screen.

The biomass tested was wheat straw (*Triticum aestivum* L., variety Madsen) from Washington State University's Lind Dryland Research Station in Lind, WA, in the arid (<25 cm rainfall/year), central part of Washington State. Wheat straw was collected and sorted according to whether it was standing, partially standing, laying flat, or partially decomposed litter. The relative proportion of each as found on the field were recorded and later reconstructed in the chamber experiments. Prior to combustion, samples of each of the sorted materials were characterized according to moisture and ash content.

During the combustion experiments, 1.8 pounds of stubble was burned at a time. Typically the flaming stage lasted no more than 3 minutes but sampling was carried out for a total of 15 minutes to capture the smoldering stage emissions. We used both low-volume (5 L min^{-1}) samplers (Airmetrics) and a DataRam 2000 (MIE, Inc.) nephelometer for continuous measurements. The low-volume samplers were fitted with Teflon and Quartz filters for capturing particles and semi-volatile organic compounds, respectively. Polyurethane foam samplers and resin adsorbent samplers were also deployed to collect PAHs and oxygenated hydrocarbons, respectively. The EPA personnel in RTP operated CO, CO₂, O₂, and total hydrocarbon (THC) analyzers, dioxin samplers, and a dilution sampler. They also provided continuous fuel mass measurements as well as ambient and burn hut conditions during the burns.

In May 2001, 30 burn tests were conducted over 4 days (6 experiments of 5 burns each).

| Sample | Filter Media | Number of Samples |
|-------------------|-------------------------------|-------------------|
| PM _{2.5} | Teflon (with quartz backings) | 30 |
| PM _{2.5} | Quartz | 30 |
| PM ₁₀ | Teflon | 4 |

All Teflon filters have been weighed and the data analysis is nearly complete. Preliminary results were presented at the Annual Meeting of the Pacific Northwest International Section of the Air and Waste Management Association held last November in Big Sky, Montana. These results were compared to preliminary results from field burns on wheat stubble fields in Columbia County, Washington State (AirSciences and Missoula Fire Lab), with reasonable correlations, when examined as a function of combustion efficiency.

The filters collected during the May 2001 experiments have not yet been extracted for subsequent GC-MS analysis. The filters will be composited for GC-MS analysis.

In August 2001, a total of 31 burn experiments were conducted over 4 days (4 experiments of 6 burns and 1 experiment of 7 burns).

| Sample | Filter Media | Number of Samples |
|-------------------|-----------------------------|-------------------|
| PM _{2.5} | Teflon (no quartz backings) | 31 |
| PM _{2.5} | Quartz | 31 |
| PM ₁₀ | Teflon | 31 |

To date, all of the Teflon filters have been weighed. Of the August filters, 21 Teflon filters and 23 quartz filters have been extracted and analyzed via GC-MS, however because of low detectability, the extracts will be composited, and the composited extracts will be re-analyzed.

To determine the PM emission factors as a function of combustion efficiency, the combustion efficiency was determined from the amount of CO₂ evolved as a fraction of the total carbon evolved (in CO₂, CO, particulate matter, and total hydrocarbons). For comparison, experiments in which no attention was given to fuel orientation were also conducted. We found that the fuel orientation of the simulated field conditions does increase the combustion efficiency when compared to randomly piled biomass. *This is an important result because it has implications for sampling for emissions from combustion processes.*

Dr. Gullett has presented a paper on some of the preliminary dioxin results from the test burn facility experiments. The abstract of that paper is attached. Particulate and PAH samples were also collected downwind of actual field burns during field burning experiments conducted by AirSciences and the Missoula

Fire Lab, during August of 2001, on Kentucky Bluegrass seed stubble. Those samples are also currently undergoing analysis.

Continuous PM10 and PM2.5 were monitored throughout the spring and fall burn seasons of 2001, from the rooftop of Dana Hall on the campus of Washington State University. During these two seasons, several incidents in which smoke from burning agricultural fields impacted the site. These incidents are being analyzed by another WSU graduate student, whose thesis is in draft form.

Work Remaining

During the remaining time on this project, the filters, PUFs and resin samples will be analyzed via GC-MS in the Department of Chemistry at Eastern Washington University (EWU), under the direction of Dr. Jeff Corkill. The graduate student, Ranil Dhammapala, that has been involved in this experiment will be working with an undergraduate chemistry student for the summer to complete these analyses. The results will be analyzed and a manuscript will be prepared for submission to a peer-reviewed journal.