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**CHEMICAL AND BIOLOGICAL CHARACTERIZATION  
OF PRODUCTS OF INCOMPLETE COMBUSTION FROM THE  
SIMULATED FIELD BURNING OF AGRICULTURAL PLASTIC**

**CONTROL TECHNOLOGY CENTER**

**SPONSORED BY:**

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## PREFACE

This project was funded as a cooperative effort by EPA's Control Technology Center (CTC) and EPA's Air Risk Information Support Center (AirRISC).

The CTC was established by EPA's Office of Research and Development (ORD) and Office of Air Quality Planning and Standards (OAQPS) to provide technical assistance to State and Local air pollution control agencies. Three levels of assistance can be accessed through the CTC. First, a CTC HOTLINE has been established to provide telephone assistance on matters relating to air pollution control technology. Second, more in-depth engineering assistance can be provided when appropriate. Third, the CTC can provide technical guidance through publication of technical guidance documents, development of personal computer software, and presentation of workshops on control technology matters. AirRISC is a similar organization focused on providing information related to determination of health effects and risk assessment.

The engineering assistance projects, such as this one, focus on specific problems or needs identified by a State or Local Agency. In this case, the Florida Department of Environmental Regulation requested information on emissions from this source. Since no data were available, the CTC agreed to conduct tests to determine the emissions. AirRISC later became involved in the project when the Florida DER expanded their request to include information on health effects.

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OF AGRICULTURAL PLASTIC

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## ABSTRACT

Chemical and biological analyses were performed to characterize products of incomplete combustion emitted during the simulated open field burning of agricultural plastic. A small utility shed equipped with an air delivery system was used to simulate pile burning and forced-air-curtain incineration of a nonhalogenated agricultural plastic that reportedly consisted of polyethylene and carbon black. Emissions were analyzed for combustion gases; volatile, semi-volatile, and particulate organics; and toxic and mutagenic properties. Emission samples, as well as samples of the used (possibly pesticide-contaminated) plastic, were analyzed for the presence of several pesticides to which the plastic may have been exposed. Although a variety of alkanes, alkenes, and aromatic and polycyclic aromatic hydrocarbon (PAH) compounds were identified in the volatile, semi-volatile, and particulate fractions of these emissions, a substantial fraction of higher molecular weight organic material was not identified. No pesticides were identified in either combustion emission samples or dichloromethane washes of the used plastic. When mutagenicity was evaluated by exposing *Salmonella* bacteria (Ames assay) to whole vapor and vapor/particulate emissions, no toxic or mutagenic effects were observed. However, organic extracts of the particulate samples were moderately mutagenic. This mutagenicity compares approximately to that measured from residential wood heating on a revertant per unit heat release basis. Compared to pile burning, forced air slightly decreased the time necessary to burn a charge of plastic. There was not a substantial difference, however, in the variety or concentrations of organic compounds identified in samples from these two burn conditions. This study highlights the benefits of a combined chemical/biological approach to the characterization of complex, multi-component combustion emissions. These results may not reflect those of other types of plastic that may be used for agricultural purposes, especially those containing halogens.

## INTRODUCTION

The agricultural industry in several States is increasingly using various types of plastic film for mulch purposes (ground moisture and weed control), and the disposal of these materials after the growing season is a concern to local, State, and Federal environmental agencies. As an alternative to removal and disposal in approved landfills or licensed incinerators, large quantities of plastic film are commonly burned either in situ in the crop row by means of a propane torch attached to a vehicle, or gathered into large piles and burned in the field. Questions regarding the nature and quantity of products of incomplete combustion (PICs) emitted during these field burns have been raised by the Department of Environmental Regulation (DER) of the State of Florida.

The use of agricultural plastic film to cover thousands of acres of Florida farmland offers farmers the economic advantages of reduced irrigation and pesticide needs. As an alternative to requiring that the material be transported to and disposed of at licensed landfills or incinerators, the State is considering a solution to allow farmers to burn the material in stationary "air-curtain incinerators." An air-curtain incinerator is defined as a portable or stationary combustion device that directs a plane of high-velocity forced-draft air through a manifold head into a pit with vertical walls in such a manner as to maintain a curtain of air over the surface of the pit and a recirculating motion of air under the curtain. An air-curtain incinerator is controlled burning as defined in Florida Administration Code Rule 17-7.020(15).<sup>1</sup> Specific questions the DER asked the U.S. Environmental Protection Agency (EPA) to address include:

- (a) What combustion emissions can be expected from burning the agricultural plastic?
- (b) What pesticides are present on the plastic and will these pesticides decompose or be emitted as air contaminants?

A set of experiments were conducted to characterize the combustion emissions from simulated pile burning and simulated air-curtain incineration of black agricultural plastic. These tests included continuous emission monitor (CEM) measurements of combustion gases CO, CO<sub>2</sub>, O<sub>2</sub>, and NO; characterization of the volatile and semi-volatile organic fractions by GC/MS and GC/FID; determination of the particulate concentrations, including analysis of non-volatile particulate organic extracts by GC/FID and for polycyclic aromatic hydrocarbons (PAHs) by HPLC; analysis of the used plastic and semi-volatile organic extracts for several commonly used pesticides; and examination of whole emissions and particulate extracts for toxic and mutagenic effects.

The volatile organic fraction is operationally defined as those compounds collected by volatile organic sampling train (VOST) method.<sup>2</sup> These compounds typically include those with boiling points less than 100°C. The semi-volatile organic fraction is defined as those compounds that pass through an unheated filter and are collected on XAD-2 resin. These compounds typically include those with boiling points between 100 and 300°C. The non-volatile organic fraction is defined as those organic compounds that remain on the particulate filter and typically include compounds with boiling points greater than 300°C. Filter or particulate samples contain both non-volatile extractable organics and non-extractable inorganic material.

## EXPERIMENTAL APPROACH

Sufficient quantities of used black agricultural plastic were gathered during a site visit, and a roll of unused plastic was provided by local farmers and delivered by the DER's West Palm Beach District Office to EPA's Environmental Research Center (ERC) facilities in Research Triangle Park, North Carolina. Trade literature reported that the black plastic used by the farmers and provided for testing consisted of polyethylene, carbon black (pigment), and possibly small quantities of phenols (anti-oxidant) and fatty amides (slip agent). No analysis was performed to determine whether there was a halogen component of the plastic tested.

### Test Facilities and Procedure

The tests were conducted in a small outbuilding (3.0 x 3.0 x 2.7 m, 10 x 10 x 9 ft). The temperature-controlled, combustion air delivery system was configured to permit the introduction of approximately 54 m<sup>3</sup>/min. (1900 scfm) of air (one air exchange every 30 sec) to the chamber. Deflectors were positioned so that incoming air did not blow directly on the burning plastic. In an attempt to simulate open field burning in a controlled environment, this air delivery system maintained ambient temperatures and ensured that chamber oxygen concentration always exceeded 20 percent (by volume). A diagram of the project facilities is presented in Figure 1.

The plastic charges were burned in a 30.5-cm (12-in.) square pit, 30.5 cm (12 in.) deep, made of 4.8-mm (3/16-in.) steel, and insulated from the wooden floor by a fire brick enclosure. A plastic charge of known weight [approximately 454 g (1 lb)] was balled (as in the field) and placed in the pit. A minimal amount of kerosene (K-1) was poured over the charge (as in the field) and ignited. Combustion times for each 454-g (1-lb) charge varied

from 20 to 40 min. To simulate air-curtain incineration, two 40.6-cm (16-in.) circular fans were positioned 45.7 cm (18 in.) above and to the sides of the pit so as to direct forced air across the flame. Forced-air experiments refer to those in which these fans were employed to simulate air-curtain incineration. Estimated volumetric flow rates and face velocities for each fan were approximately 21.7 m<sup>3</sup>/min. (765 scfm) and 235 m/min. (770 ft/min.), respectively. Pile experiments refer to those performed in the absence of forced air.

The test matrix is shown in Table 1. The study includes test burns of used and unused plastic under two conditions (pile and forced air), one hut (field) blank (hut sampling without burning plastic), a kerosene burn blank, and control blanks (unused VOST tubes, XAD-2, and filters). Nine charges [each charge nominally 454 g (1 lb)] were burned for each of the four plastic burn tests. The 454-g (1-lb) unused plastic charges were the equivalent of approximately 22.3 m<sup>3</sup> (240 ft<sup>2</sup>) of material. The 454-g (1-lb) used plastic charges contained significant moisture and extraneous organic material (vegetation). Due to its shredded condition, the area of the used plastic could not be determined. The used plastic was burned as received to simulate field practice.

The amount of kerosene poured over each charge was kept to a minimum so as not to add significantly to the emissions. In all cases, however, the charge was allowed to burn for 2 min. before organic sampling was started. This allowed time for combustion of the majority of the kerosene. The amount of kerosene added to each of the unused and used plastic pile burns differed due to the differences in their ignition characteristics and the desire to use a minimum amount of kerosene. In the case of the unused plastic pile burn, 50 ml of kerosene was used for each of the first three charges, and 10 ml was used for each of the remaining six charges (210 ml total). For the

used plastic pile burn, 10 ml was used for the first charge, and 50 ml was used for each of the remaining eight charges (410 ml total). The remaining two forced air tests (unused and used plastic) as well as the kerosene blank used 50 ml for each charge (450 ml total).

#### CEM and Volatile Organic Analyses

Continuous gas-phase samples were extracted from the combustion chamber through a heated 15.2-m (50-ft) long, 9.5-mm (3/8-in.) outside diameter Teflon sample line equipped with a particle filtration system. Part of this sample was further conditioned for the removal of moisture and analyzed by the individual CEMs (CO, CO<sub>2</sub>, O<sub>2</sub>, NO). A portion of the heated gas sample was collected and analyzed for volatile organics (boiling points < 100°C) using the VOST method.<sup>2</sup> Samples (20 L, each) were collected over a 20- to 30-min. period, which approximated the duration of one charge (454 g, 1 lb) of plastic.

Three VOST samples were collected for each burn and the hut blank condition. Two were used for GC/MS analysis and one for GC/FID analysis. The two GC/MS samples used for qualitative compound identification included one sample of the effluent from a single charge (single exposure) and a second sample collected from two sequential charges (double exposure). GC/FID samples used for compound quantification collected effluent from one charge (single exposure). A multipoint calibration using benzene, toluene, and ethyl benzene was used for quantification. Compounds were identified by computer library spectral matching and investigator judgement. VOST samples were refrigerated at 1°C prior to analysis to preserve sample integrity.

#### Semi-volatile Organic, Particulate, and Pesticide Analyses

The semi-volatile organic and particulate fractions were collected using an Andersen 0.1 m<sup>3</sup>/min. (4 scfm) medium-volume ambient sampler equipped with a

PM-10 head located in the combustion chamber. The semi-volatile organics were adsorbed on 170 g of XAD-2 resin held in stainless steel canisters designed for this system. The particulate was collected on a 130-mm glass microfiber filter (desiccated and tared) located immediately upstream of the XAD-2 filled canisters. Gas sample volumes were measured using a dry gas meter. A minimum sample time of 1 hr was required for the collection of adequate amounts of sample, and this required the sampling of multiple plastic charges. The sampling system, however, was shut off between charges. After determination of the particulate weight, the filters and XAD-2 resin were extracted separately with dichloromethane and the extracts concentrated.<sup>3</sup> Total chromatographable organic (TCO) by GC/FID (boiling point 100 to 300°C), and gravimetric (GRAV) (boiling point > 300°C) analyses were performed on each of the XAD-2 resin and filter organic extracts.<sup>3</sup> GC/MS analysis was also performed on the XAD-2 extracts, and HPLC analysis was performed on the filter extracts.<sup>4</sup> As with the VOST analyses, compounds were identified by computer library spectra matching and investigator judgement. Samples, extracts, and concentrates were kept refrigerated at 1°C prior to analysis to preserve sample integrity.

Samples of the used plastic were analyzed as received for the presence of several pesticides to which it may have been exposed. Samples of the unused plastic were also analyzed as a control for comparison. In both cases, plastic samples (nominally 454-908 g, 1-2 lb) were washed with dichloromethane, solvent exchanged to hexane, and this solvent rinse was then concentrated. Concentrates were then analyzed by GC/MS and GC/ECD for the presence of chloropicrin, permethrin, methomyl, and methamidophos.<sup>5</sup>

### Analysis of Volatile and Particulate Whole Emissions for Mutagenicity

In addition to the CEM, volatile, semi-volatile, particulate, and pesticide data, emissions from the burning plastic were sampled separately and analyzed for toxic and mutagenic activity. Exposure chambers were used to expose sets of petri dishes containing the bacterium Salmonella typhimurium strain TA98 in the presence and absence of Aroclor 1254-induced, Sprague-Dawley rat-liver activation system (S9) to whole emission effluent from the plastic combustion routed from the hut. This system was similar to that used previously for the measurement of mutagenic volatiles and particulates from wood smoke.<sup>6,7</sup> The dishes were exposed in eight separate chambers, each being supplied with effluent from the hut by individual Andersen pumps at the rate of 15 L/min. In four chambers, the emissions from the burning plastic were prefiltered using glass microfiber filters (105 mm diameter). This prefilter was used to reduce the probability of microbial contamination from the effluent. In the other four chambers, prefilters were omitted, permitting exposure of the bacteria to whole emissions. Postfilters were present in all eight chambers to collect particles that passed through the chamber. Three dishes with S9 (+S9) and three without S9 (-S9) were removed at each of three different periods of time per sample (three, six, and nine charges). Plates were then incubated for 3 days at 37°C, and the colonies were counted.<sup>8</sup> Each charge (454 g, 1 lb) lasted approximately 25-35 min. Consequently, the maximum exposure (nine charges) was approximately 5 hr. Each bioassay sample listed on Table 1 included three sets of exposures taken with increasing exposure times.

### Analysis of Particulate Organic Extracts for Mutagenicity

For each run, the three prefilters and the three postfilters, where prefilters were not used (two sets), representing three exposure periods,

were combined, extracted by sonication with dichloromethane,<sup>9</sup> and solvent exchanged to dimethyl sulfoxide (DMSO). Blank filters were extracted separately. Extracts were evaluated for mutagenic activity in strain TA98 of Salmonella typhimurium in the presence of S9 activation (S9). The plate-incorporation assay was performed as described by Maron and Ames.<sup>8</sup> Extracts were tested twice, once in singlet to determine the dose range, and once in duplicate. Results are the average +/- S.E.M. of the second experiment. Mutagenic potencies (revertants/ug or revertants/m<sup>3</sup>) were calculated from the linear portion of the dose-response curves using a nonweighted linear regression. Extracts were considered to be mutagenic if they produced a dose-related increase in the number of revertants/plate.

## RESULTS AND DISCUSSION

### Combustion Observations

The manner in which the unused and used plastic burned varied considerably. The unused plastic was highly combustible and, upon ignition, this plastic melted quickly to form a pool that burned from the surface. The used plastic, presumably due to its high moisture and organic (vegetation) content, was somewhat more difficult to ignite and did not melt to form a pool. Instead, a smoldering flame spread slowly from the middle of the pile to the edges. The time required to burn one charge each of the unused and used plastic also differed. The nominal time to (pile) burn each unused plastic charge was 25 to 35 min. Often, significant quantities of the (pile) used plastic were still smoldering after 35 min. The addition of the forced air fans slightly enhanced combustion of both types of charges. Both unused and used charges were completely consumed in 25 to 30 min. and 30 to 35 min., respectively, when forced air was used.

### CEM Measurements

The emission data indicated that oxygen concentrations exceeding 20 percent were always maintained in the burn hut. Approximately 0.2 to 0.4 percent oxygen differential was observed between hut baseline (ambient, 20.9 percent  $O_2$ ) and peak charge conditions.  $CO_2$  levels also changed minimally, ranging generally from 0.3 to 0.6 percent.  $NO$  was not detected during any burn. Concentrations of  $CO$ , however, varied greatly during the course of a burn. Table 2 shows the  $CO$  characteristics for each test. The burning of unused plastic, due to its more rapid combustion, produced higher  $CO$  concentrations than the used plastic. The use of forced air tended to extend the amount of time that  $CO$  levels exceeded 10 ppm. It should be emphasized that the lower

CO concentrations for the used plastic are not necessarily the consequence of better combustion, but rather due to the slower burn rate of this material.

#### Volatile Organics

Table 3 presents a list of compounds identified from the GC/MS chromatograms for six VOST samples. Evident from this list is the identification of alkylated mono aromatics ranging from benzene to ethenyl benzene, and straight chain alkanes and alkenes ranging from C<sub>6</sub> to C<sub>9</sub>.

The presence of mono aromatics, in particular benzene, as products of incomplete combustion (PICs) should not be considered to be exclusively a product of plastic burning. Benzene is a common PIC produced during combustion. The detection of straight-chain hydrocarbons is likely due to residual kerosene and plastic PICs. The most abundant of these hydrocarbons, 1-hexene, was measured in samples from all the plastic tests, and in smaller concentration in the kerosene blank. The two burn conditions (pile and forced air) did not seem to affect significantly the types of compounds generated.

The quantitative concentrations of several selected compounds measured over one charge are presented in Table 4. The data indicate that, of the four compounds quantified, the concentrations for all burn conditions and plastic types were typically less than 1 ppm, with benzene having the highest concentration. It is interesting to note that the forced air tests in general indicate slightly higher emissions in most cases compared to pile burning tests. This may be an artifact of the facilities or procedure or may indicate flame quenching due to the relatively cool forced air. It should also be noted that the relative concentrations from the hut blank and kerosene samples were over an order of magnitude lower than those from the plastic tests. Absolute concentrations should be interpreted with care, however, because it is unknown

whether the air flow rates used for these tests properly simulate full-scale dilution in field burns.

#### Semi-volatile Organics and Particulates

Qualitative analyses of the XAD-2 extracts revealed the same types of compounds found in the volatile organic samples. Table 5 lists compounds identified by GC/MS analysis of the XAD-2 extracts for each of the six samples. Substituted aromatics from methyl to butyl benzene and naphthalene were identified, as well as straight-chain hydrocarbons ranging from C<sub>8</sub> to C<sub>15</sub>. There does not seem to be any substantial variation in the types of compounds formed at the different burn conditions for the two plastic types.

Total chromatographable organic (TCO) and gravimetric (GRAV) analyses were performed on both the XAD-2 and particulate extracts. The results, presented in Table 6, show that (for all burn conditions and plastic types) over 85 percent of all extractable organics in the XAD-2 extracts were found in the TCO range. On the other hand, even though the extractable organic fractions of the collected filter particulate were high (typically 50 percent), less than 3 percent of this material was measurable in the TCO range. This is important, because it indicates that a significant fraction of the sample consisted of extractable organics not in the TCO range and, therefore, not chromatographable or identifiable by the GC/MS analysis techniques used. The GC/MS system used was not capable of analyzing compounds with boiling points exceeding 300°C. GC/MS analyses were not performed on the particulate extracts due to MS sensitivity and insufficient sample mass in the TCO fraction.

Table 6 indicates that approximately 50 percent of the particulate samples were nonorganic (nonextractable). The other 50 percent, over 97 percent of which are in the GRAV range, are organic (extractable) and likely composed of

heavy organic compounds with boiling points greater than 300°C. Concentrations of PAH compounds identified by HPLC analysis of the particulate extracts are presented in Table 7. It is interesting to note that although a number of these compounds were identified in all the combustion samples, including the kerosene test, the total weight of PAH material present in each sample is only a small fraction (0.1 to 2.0 percent) of the total organic extracts of the particulate filters. Thus, the identity of over 98 percent of this GRAV-range organic material remains unknown (approximately 25 percent of the total semi-volatile and particulate sample). Table 7 also shows that four PAH compounds (naphthalene, acenaphthalene, acenaphthene, and flourene) with boiling points less than 300°C are not present in the particulate extracts. Duplicate analyses confirmed these data, indicating that these compounds may be too volatile to reside in this fraction.

#### Pesticide Residue and Products of Combustion

As mentioned previously, one area of concern was the possible existence of pesticide residues on the plastic and the possibility of the emission of these residues as air contaminants during burning. Due to limited available resources and the uncertainty of the presence of each compound, pesticide stability information and sample history were used to determine the compounds for which the plastic should be analyzed from a list of possible pesticides, herbicides, and fungicides used during the growing season. A sample of used plastic (made available by the State of Florida) that had been left in the crop row and exposed to the elements for over 4 months after the end of the growing season was utilized for pesticide residue analyses. Because many of the possible pesticides used are water soluble, highly volatile, or subject to microbial or thermal decomposition, they were eliminated from the list of compounds for analysis. Ultimately, due to availability of resources and

analytical capabilities, four gas-chromatographable compounds were chosen for analysis.

The mass spectral data for chloropicrin, methamidophos, methomyl, and permethrin were used to screen both the XAD-2 extracts and dichloromethane washes of 454 g (1 lb) of used and unused plastic. None of these four compounds were detected in any of the semi-volatile (XAD-2) combustion samples or dichloromethane washes of the used plastic analyzed. Although no compound standards were used, estimated system detection limits of the mass spectrometer would have yielded compound concentrations of < 330 ug/4.1 kg burned and < 330 ug/0.5 kg unburned plastic.

In addition, a sample of used plastic was sent to an outside laboratory for analysis by GC/ECD. Standards of the four compounds were obtained from the U.S. EPA Pesticides and Industrial Chemicals Repository and supplied to the laboratory. Again, none of the four compounds were detected in the dichloromethane wash of the 1 kg sample. System detection limits would have yielded compound concentrations of < 5.0 ug/kg plastic for chloropicrin, permethrin, and methomyl, and a concentration of < 100 ug/kg plastic for methamidophos.

#### Bioassay Results

No microbial contamination was observed on the petri dishes exposed to the whole emissions. Although the cells were exposed for as long as 5 hr, no bacterial cytotoxicity (based in a thinning of the background bacterial lawn) or mutagenicity was observed from exposure to the whole emissions (data not shown). Although neither the whole particles nor emission gases were mutagenic, the mutagenic activities of dichloromethane extracts of the prefilter and

postfilter particulate materials were examined to determine the amount of mutagenic activity due to particle-bound organics.

Preliminary experiments indicated that the sample extracts were cytotoxic at 75 ug/plate (data not shown). Because of this, and because of limited amounts of samples, the sample extracts were tested at a maximum dose of 60 ug/plate. Blank filters were also extracted and tested at a maximum dose of > 80 ug/plate or > 0.3 m<sup>3</sup>/plate; however, no mutagenic activity was observed among the blank extracts at these doses (data not shown).

Table 8 shows the mutagenic activity of the extractable organics in Salmonella typhimirium strain TA98 +S9. The dose is expressed as m<sup>3</sup>/plate and as ug of extractable organics/plate. Based on the linear portion of the dose-response curves, the slopes (mutagenic potencies) were calculated using an unweighted linear regression and are shown in Table 9. Mutagenic potencies are expressed as revertants/ug and as revertants/m<sup>3</sup>. Comparisons of the mutagenic potencies to the concentrations of total PAH/m<sup>3</sup> are also shown in Table 9. Total PAHs are operationally defined as the total mass of those PAH compounds quantified by the HPLC method used.<sup>4</sup>

On a volumetric basis, (revertants/m<sup>3</sup>, Table 9), the data indicate that the samples were weakly mutagenic. However, when calculated on an equivalent fuel (revertants/kg fuel) or equivalent heat release (revertants/MJ) basis (Table 10), the mutagenic emission factors can be compared to those of other combustion sources.<sup>10</sup> Evident from Table 10 is that revertants/MJ in the range of 100,000 to 300,000 were determined for three of the plastic tests. This mutagenic emission factor is comparable to that measured from residential wood heating (250,000 revertants/MJ).<sup>10</sup> This is reasonable considering that

both are small-scale, relatively inefficient forms of combustion involving a nonhalogenated solid fuel.

In addition, the total PAH emission factors (Table 10) roughly parallel the mutagenic emission factors, indicating that PAH compounds may account for proportional amounts of the mutagenic activities observed among the different test conditions. However, other chemical classes (including PAH compounds not detected by the method used) may also account for portions of the observed mutagenic activity. These PAH results are not unexpected due to the sensitivity of the Salmonella assay to mutagenic PAH compounds.<sup>11</sup> Similar associations between mutagenic activity and PAH concentrations have been observed for other complex mixtures and combustion emissions.<sup>10</sup> It is interesting to note that, although the mutagenic potencies based on a volumetric basis (revertants/m<sup>3</sup>) were low, the mutagenic emission factors based on an equivalent fuel or heat release basis were moderately high. This can be explained by the high air flow rates (54 m<sup>3</sup>/min., 1900 scfm) used to maintain "ambient" oxygen concentrations in the burn hut. These dilution effects must be removed for proper comparison to other sources. In fact, this high dilution may explain the lack of detectable mutagenic activity for several of the samples. It is notable that the mutagenic emission factors for kerosene (Table 10) were comparable to those calculated for the plastic. This is reasonable considering that the combustion of kerosene in this manner (pool fire) is highly inefficient and, in this regard, similar to the combustion of polyethylene or wood.

Note that the chemical analyses presented above indicated that the measured concentrations of kerosene PICs were, in general, more than an order of magnitude lower than those measured from the plastic tests. Table 10 may indicate that the effluents from the unused plastic tests were slightly more

mutagenic than those from the used plastic tests under both pile and forced-air configurations. This would be consistent with the combustion characteristics discussed previously. The use of forced air may cause some slight reduction in the mutagenic activity of the effluent from the unused and used plastic tests compared to tests with no forced air. Forced air with the used plastic (Test 5) produced an effluent with no detectable mutagenic activity under the conditions of the test. It is difficult to draw conclusions in this regard, considering the limited data and small differences in the mutagenic emission factors.

The limitations and gaps in the chemical analyses highlight the need for coordinated chemical and biological analyses. Often, with respect to the complex multi-component nature of combustion samples, minor species may comprise the majority of the biological activity, whereas chemical analyses typically concentrate on identification and quantification of major species.<sup>10</sup>

## SUMMARY

The burning characteristics of unused and used plastic varied considerably. The unused plastic was highly combustible and melted quickly to form a pool that burned from the surface. The used plastic, presumably due to its high moisture and vegetation content, was much more difficult to ignite, did not melt, and burned at a much slower rate.

CEM measurements indicated that oxygen concentrations in the combustion chamber always exceeded 20 percent. CO<sub>2</sub> concentrations of 0.3 to 0.6 percent were measured. Average peak CO concentrations varied from 10 to 45 ppm. NO was not detected. CO emissions were higher for the unused plastic than for the used plastic for both pile and forced air conditions. This is likely due to the differences in the combustion characteristics.

Qualitative VOST analysis (GC/MS) indicated the presence of numerous peaks. Those identified included alkylated mono-aromatics ranging from benzene to styrene, and alkanes and alkenes ranging from C<sub>6</sub> to C<sub>9</sub>. The presence of alkanes and alkenes may be due to kerosene or plastic PICs. Quantitative VOST analysis (GC/FID) for four compounds (benzene, toluene, ethyl benzene, and 1-hexene) indicated concentrations of less than 1 ppm. Absolute concentrations should be interpreted with care because combustion air, at the rate of approximately 54 m<sup>3</sup>/min. (1900 scfm), was delivered to the combustion chamber. This may or may not adequately simulate open field burning. Forced-air tests, compared to pile-burn tests, indicate somewhat higher concentrations of these four VOST compounds. This may indicate flame quenching by the cool forced air.

Qualitative analysis of the semi-volatile XAD-2 extracts (GC/MS) showed many of the same types of compounds seen in the VOST samples, including substituted aromatics from methyl- to butylbenzene, naphthalene, and straight-chain hydrocarbons ranging from C<sub>8</sub> to C<sub>15</sub>. No substantial variation in the compounds identified due to the different plastic types and burn conditions was observed.

Over 85 percent of the organics in the XAD-2 extracts were found in the TCO range (bp 100-300°C). Although approximately 50 percent of the particulate material was extractable organics, less than 3 percent was found in the TCO range. The other GRAV range organic material (bp > 300°C) was unidentifiable using the GC/MS analysis methods available for this study.

Although a variety of PAH compounds were identified by HPLC in the organic extracts of the particulate samples, the mass of these species comprised less than 2 percent of the organic extract (GRAV) mass. The remaining organic material could not be identified.

The use of forced air slightly reduced the time necessary to burn each charge, but it did not affect the types or concentrations of PICs emitted. The addition of room fans used to simulate air curtain incineration did not seem to affect the plastic combustion. This is likely due to inadequacies in the simulation procedure. However, the effects that were observed, with respect to the use of forced air, were beneficial, with the exception of slightly increased volatile emissions.

No pesticides from the limited list examined were detected in the XAD-2 extracts of the combustion emissions or concentrated dichloromethane washes

of the used plastic. This may be due to the length of time between the end of the growing season and the sample analysis.

Results from the Salmonella assay in which bacteria were exposed to whole vapor and vapor/particulate emissions showed no toxic or mutagenic effects under the conditions of the tests. Such results may be due to adhesion of organics to the walls of the chambers<sup>6</sup> or to the lack of bioavailability of particle-bound organics.<sup>12</sup> The particulate extracts were toxic at high doses and only weakly mutagenic on a volumetric basis. However, when calculated on a weight of fuel or unit heat release basis, the mutagenic emission factors were moderately high and comparable to those of residential wood heating.

Chemical analyses cannot totally characterize all fractions and all species present in complex, multi-component combustion emissions. The limitations of chemical analyses highlight the need for biological analyses; the advantages of coordinated chemical and biological analyses are illustrated. Bioassay techniques may be used as a screening tool to direct the chemical analyses. Additionally, bioassay analyses determine a desired endpoint directly; i.e., the direct effects of complex combustion emissions on biological systems.

It should be noted that the plastic examined in this study was presumed to consist primarily of polyethylene and carbon black. These results may not be applicable (and should not be applied) to other types of plastics, especially halogen-containing plastics.

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## DISCLAIMER

The research described in this paper has been reviewed by the Air and Energy Engineering Research Laboratory and Health Effects Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Table 1. Black agricultural plastic test matrix.<sup>a</sup>

Test	Plastic	Burn Type	Volatile <sup>b</sup>	Semi-Volatile <sup>c</sup>	Particulated <sup>d</sup>	Whole Emission Bioassay <sup>e</sup>
1	NA <sup>f</sup>	Hut Blank <sup>g</sup>	3	1	1	-
2	Unused	Pile	3	1	1	1
3	Used	Pile	3	1	1	1
4	Unused	Forced Air	3	1	1	1
5	Used	Forced Air	3	1	1	1
6	NA	Kerosene	3	1	1	1
Control Blanks			4	1	1	1
Totals <sup>h</sup>			22	7	7	6

<sup>a</sup>Numbers in table indicate number and types of samples taken.

<sup>b</sup>Each volatile (VOST) set included two samples analyzed by GC/MS (compound identification) and one sample analyzed by GC/FID (compound quantification). Control blank samples were analyzed two each by GC/MS and GC/FID.

<sup>c</sup>Semi-volatile (XAD-2) organic extracts were analyzed to determine TCO (by GC/FID) and GRAV values, and GC/MS for compound identification. Additionally, these samples were analyzed by GC/MS and GC/ECD for the presence of four pesticide compounds.

<sup>d</sup>Particulate (filter) organic extracts were analyzed to determine TCO (by GC/FID) and GRAV values. GC/MS analyses were not performed due to low TCO values. HPLC analyses were done to determine PAH concentrations.

<sup>e</sup>Prefiltered and postfiltered whole emission bioassays were performed for each combustion test. Additional bioassay analyses were performed on the organic extracts of these prefilters and postfilters.

<sup>f</sup>Not applicable.

<sup>g</sup>Hut blanks sampled hut air, no combustion.

<sup>h</sup>In addition to these analyses, dichloromethane washes of the used and unused (for control) plastic (solvent exchange to hexane) were analyzed by GC/MS and GC/ECD for the presence of four pesticides.

Table 2. Carbon monoxide characteristics for each test charge.

Test	Condition	Duration Above 10 ppm <sup>a</sup> min.	Peak Conc. <sup>b</sup>		Average Conc. <sup>c</sup>	
			ppm	mg/m <sup>3</sup>	ppm	mg/m <sup>3</sup>
1	Hut Blank <sup>d</sup>	ND <sup>e</sup>	ND	ND	ND	ND
2	Unused/Pile	11	42	48	29	33
3	Used/Pile	7	13	15	12	14
4	Unused/ Forced Air	20	37	42	23	26
5	Used/ Forced Air	17	17	19	14	16
6	Kerosene <sup>f</sup>	0	7	8	5	6

<sup>a</sup>Average time during each charge that CO concentration exceeds 10 ppm.

<sup>b</sup>Average highest CO concentration (as measured) for each charge.

<sup>c</sup>Average CO concentration (as measured) over duration of each charge.

<sup>d</sup>Hut blank sampled hut air, no combustion, no CO detected.

<sup>e</sup>Not detected.

<sup>f</sup>Kerosene CO concentrations never exceeded 10 ppm.

Table 3. Volatile organic emissions identified by GC/MS from VOST samples.

Compound	Test					
	1 Hut Blank	2 Unused/ Pile	3 Used/ Pile	4 Unused/ Forced Air	5 Used/ Forced Air	6 Kerosene <sup>a</sup>
1-Hexene		X	X	X	X	X
Hexane			X			
Benzene		X	X	X	X	X
1-Heptene			X	X	X	
Heptane			X	X	X	
Toluene		X	X	X	X	X
1-Octene			X	X	X	
Octane			X	X	X	X
Hexamethyl Cyclotrisiloxane <sup>b</sup>	X	X	X	X	X	X
Ethyl Benzene		X	X	X	X	X
Dimethyl Benzene		X	X	X	X	X
1-Nonene		X	X	X	X	
Nonane		X	X	X	X	X
Ethenyl Benzene		X	X	X	X	

<sup>a</sup>Kerosene peak heights were approximately an order of magnitude smaller than those from the plastic tests.

<sup>b</sup>System contaminant.

Table 4. Volatile organic emissions quantified by GC/FID from VOST samples.<sup>a</sup>

Test Condition	Benzene		Toluene		Ethyl Benzene		1-Hexene <sup>b</sup>	
	ppm	mg/m <sup>3</sup>	ppm	mg/m <sup>3</sup>	ppm	mg/m <sup>3</sup>	ppm	mg/m <sup>3</sup>
1 Hut Blank	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2 Unused/ Pile	0.340	1.085	0.028	0.104	0.003	0.013	0.007	0.023
3 Used/ Pile	0.089	0.280	0.020	0.075	0.006	0.028	0.029	0.098
4 Unused/ Forced Air	0.205	0.653	0.049	0.183	0.015	0.066	0.098	0.336
5 Used/ Forced Air	0.174	0.554	0.075	0.282	0.029	0.126	0.145	0.499
6 Kerosene	0.008	0.026	0.003	0.010	0.001	0.006	0.003	0.011

<sup>a</sup>Data have not been corrected for hut blank values. Data have been corrected for control blank values.

<sup>b</sup>Estimated concentration, calculated using average benzene and toluene response factors.

Table 5. Semi-volatile organics identified by GC/MS from XAD-2 extracts.

Compound	Test					
	1 Hut Blank	2 Unused/ Pile	3 Used/ Pile	4 Unused/ Forced Air	5 Used/ Forced Air	6 Kerosene
Toluene		X	X	X	X	
1-Octene		X	X	X	X	
Octane		X	X	X	X	
Ethyl Benzene		X	X	X	X	
Dimethyl Benzene		X			X	
1-Nonene		X	X	X	X	
Nonane		X	X	X	X	X
Ethenyl Benzene		X	X	X	X	
Propyl Benzene		X	X		X	
Ethyl Methyl Benzene			X		X	
1-Decene		X	X	X	X	
Decane		X	X	X	X	X
Butyl Benzene		X	X		X	
1-Undecene		X	X	X	X	
Undecane		X	X	X	X	X
Naphthalene		X	X	X	X	X
1-Dodecene		X	X	X	X	
Dodecane		X	X	X	X	X
1-Tridecene		X	X	X	X	
Tridecane		X	X	X	X	X
1-Tetradecene		X	X	X	X	
Tetradecane		X	X	X	X	X
Pentadecane		X	X	X	X	X

Table 6. Semi-volatile organic and particulate data.<sup>a</sup>

Test Condition	Semi-volatile XAD-2 data					Particulate filter data					
	Volume Sampled m <sup>3</sup>	TCO mg	GRAV mg	Total Extract mg	XAD-2 % TCO	Extracted mg	TCO mg	GRAV mg	Total Extract mg	Part. % TCO	Extracts % GRAV
1 Hut Blank	13.01	0.07 (0.005) <sup>b</sup>	0	0.07 (0.005)	100	8.8 (0.676)	0.01 (0.001)	4 (0.31)	4.01 (0.31)	0	100
2 Unused/ Pile	24.06	71.43 (2.97)	9	80.43 (3.34)	89	387.4 (16.1)	1.59 (0.066)	84 (3.49)	85.59 (3.56)	2	98
3 Used/ Pile	34.67	65.48 (1.89)	12	77.48 (2.23)	85	153.6 (4.43)	0.65 (0.019)	81 (2.34)	81.65 (2.36)	1	99
4 Unused/ Forced Air	24.70	75.19 (3.04)	8	83.19 (3.37)	90	222.4 (9.00)	2.71 (0.110)	114 (4.62)	116.71 (4.73)	2	98
5 Used/ Forced Air	28.71	59.30 (2.07)	5	64.30 (2.24)	92	119.4 (4.16)	1.46 (0.051)	86 (3.00)	87.46 (3.05)	2	98
6 Kerosene	17.56	54.87 (3.12)	3	57.87 (3.30)	95	62.3 (3.55)	0.24 (0.014)	8 (0.46)	8.24 (0.47)	3	97

Test Condition	% of Particulate that are Extractable Organics		% of Total Extractable Organics Found on	
	XAD-2	Particulate	XAD-2	Particulate
1 Hut Blank	45.6	1.7	98.3	
2 Unused/Pile	22.1	48.4	51.6	
3 Used/Pile	53.2	48.7	51.3	
4 Unused/Forced Air	52.5	41.6	58.4	
5 Used/Forced Air	73.2	42.4	57.6	
6 Kerosene	13.2	87.5	12.5	

<sup>a</sup>Data have not been corrected for hut blank values. Data have been corrected for control blank values.

<sup>b</sup>Numbers in parentheses are in mg/m<sup>3</sup>.

Table 7. PAH compounds identified by HPLC from particulate extracts.<sup>a</sup>

Compound	Test					
	1 Hut Blank mg/sample (ug/m <sup>3</sup> )	2 Unused/ Pile	3 Used/ Pile	4 Unused/ Forced Air	5 Used/ Forced Air	6 Kerosene
Naphthalene	ND <sup>b</sup>	ND	ND	ND	ND	ND
Acenaphthalene	ND	ND	ND	ND	ND	ND
Acenaphthene	ND	ND	ND	ND	ND	ND
Fluorene	ND	ND	ND	ND	ND	ND
Phenanthrene	ND	0.110 <sup>c</sup> (4.57) <sup>d</sup>	0.033 (0.95)	0.045 (1.82)	0.019 (0.66)	0.004 (0.24)
Anthracene	ND	0.013 (0.54)	0.002 (0.05)	0.003 (0.10)	0.001 (0.03)	ND
Fluoranthene	ND	0.570 (23.69)	0.140 (4.04)	0.200 (8.10)	0.085 (2.96)	0.028 (1.59)
Pyrene	ND	0.370 (15.38)	0.048 (1.38)	0.110 (4.45)	0.013 (0.45)	0.014 (0.80)
Benzo(a) anthracene	ND	0.096 (3.99)	0.008 (0.22)	0.027 (1.09)	0.003 (0.09)	0.007 (0.40)
Chrysene	ND	0.100 (4.16)	0.010 (0.28)	0.032 (1.30)	0.003 (0.09)	0.008 (0.43)
Retene	ND	0.059 (2.45)	0.008 (0.22)	0.035 (1.42)	0.007 (0.23)	0.002 (0.13)
Benzo(e)pyrene	ND	0.059 (2.45)	0.004 (0.11)	0.018 (0.73)	ND	ND
Benzo(b) fluoranthrene	ND	0.063 (2.62)	0.004 (0.12)	0.019 (0.77)	0.002 (0.07)	0.003 (0.17)
Benzo(k) fluoranthrene	ND	0.025 (1.04)	0.002 (0.05)	0.005 (0.19)	ND	0.001 (0.08)
Benzo(a)pyrene	ND	0.076 (3.16)	0.004 (0.11)	0.014 (0.57)	ND	0.005 (0.30)
Dibenz(a,h) anthracene	ND	ND	ND	ND	ND	ND
Benzo(g,h,i) perylene	ND	0.090 (3.74)	0.005 (0.16)	0.028 (1.13)	ND	0.004 (0.22)
Indeno(1,2,3-cd) pyrene	ND	0.073 (3.03)	0.007 (0.21)	0.020 (0.81)	ND	0.006 (0.33)
Total PAH	ND	1.704 (70.82)	0.275 (7.92)	0.555 (22.48)	0.132 (4.60)	0.083 (4.70)

<sup>a</sup>Data have not been corrected for hut blank values.

<sup>b</sup>Not detected.

<sup>c</sup>Data presented in mg/sample extract.

<sup>d</sup>Numbers in parentheses are in ug/m<sup>3</sup>.

Table 8. Mutagenicity of particulate organic extracts in Salmonella strain TA98 +S9.

Test	Condition	Prefilter				Postfilter			
		Dose				Dose			
		m <sup>3</sup> / plate	ug/ plate	rev/ plate <sup>a</sup>	+/-	m <sup>3</sup> / plate	ug/ plate	rev/ plate <sup>a</sup>	+/-
1	Hut Blank	-	-	-	-	-	-	-	-
2	Unused/ Pile	0.0	0	40	1	0.0	0	40	1
		0.00224	5	50	1	0.00345	5	50	-
		0.00449	10	61	6	0.00691	10	68	-
		0.00898	20	77	2	0.01382	20	91	10
		0.01796	40	92	3	0.02763	40	123	13
		0.02694	60	156	11	0.04145	60	98	0
3	Used/ Pile	0.0	0	40	1	0.0	0	40	1
		0.00207	5	47	2	0.00327	5	34	2
		0.00414	10	45	6	0.00654	10	36	0
		0.00827	20	51	1	0.01309	20	42	0
		0.01654	40	61	3	0.02618	40	41	0
		0.02482	60	53	1	0.03927	60	39	1
4	Unused/ Forced Air	0.0	0	40	1	0.0	0	40	1
		0.00078	5	35	2	0.00137	5	59	5
		0.00155	10	42	0	0.00273	10	50	1
		0.00310	20	40	1	0.00546	20	45	2
		0.00620	40	54	0	0.01092	40	28	0
		0.00930	60	63	2	0.01638	60	36	2
5	Used/ Forced Air	0.0	0	40	1	0.0	0	40	1
		0.00099	5	46	7	0.00163	5	31	1
		0.00198	10	36	4	0.00326	10	50	4
		0.00396	20	41	0	0.00651	20	51	0
		0.00791	40	47	2	0.01302	40	40	2
		0.01187	60	32	0	0.01954	60	45	3
6	Kerosene	0.0	0	40	1	0.0	0	40	1
		0.02104	4.64	49	5	0.00594	5	31	1
		0.04208	9.28	50	0	0.01186	10	33	2
		0.08416	18.56	77	3	0.02372	20	41	3
		0.16832	37.12	126	5	0.04744	40	37	2
		0.25248	55.68	147	6	0.07116	60	51	1

<sup>a</sup>Results are the average +/- S.E.M. of two plates from a single experiment.

Table 9. Mutagenic potencies and total PAH concentrations of particulate organic extracts.<sup>a</sup>

Test	Condition	Mutagenic Potency <sup>b</sup>				Total PAH ug/m <sup>3</sup>
		rev/ug		rev/m <sup>3</sup>		
		Prefilter	Postfilter	Prefilter	Postfilter	
1	Hut Blank	-	-	-	-	ND
2	Unused/ Pile	1.8	2.1	3920	3026	70.82
3	Used/ Pile	0.2	NDC	1173	ND	7.92
4	Unused/ Forced Air	0.4	ND	2810	ND	22.48
5	Used/ Forced Air	ND	ND	ND	ND	4.60
6	Kerosene	2.1	0.2	455	189	4.70

<sup>a</sup>Total PAH concentrations defined as those PAH compounds quantified using Method 610.<sup>4</sup>

<sup>b</sup>Potencies are the slopes calculated from the linear portion of the dose-response curves generated by the data in Table 8.

<sup>c</sup>Potencies could not be calculated because the extracts were either nonmutagenic or did not produce linear dose-response curves.

Table 10. Comparison of total PAH and mutagenic emission factors.

Mutagenic Emission Factors						
Test	Condition	rev/kg fuel x10 <sup>5</sup>		rev/MJ <sup>a</sup>		Total PAH ug/MJ
		Prefilter	Postfilter	Prefilter	Postfilter	
1	Hut Blank	-	-	-	-	ND
2	Unused/ Pile	131	101	294,000	227,000	5,300
3	Used/ Pile	45	ND <sup>b</sup>	101,000	ND	700
4	Unused/ Forced Air	95	ND	213,000	ND	1,700
5	Used/ Forced Air	ND	ND	ND	ND	400
6	Kerosene	110	46	294,000	122,000	3,000
-----						
Residential Heating <sup>c</sup>						
	Wood		50		250,000	
	Oil		1		2,500	
Industrial and Utility Boilers and Power Plants <sup>c</sup>						
	Oil		0.03		70	
	Coal		0.06		230	
	Wood		0.20		1,000	

<sup>a</sup>Revertants per megajoule of heat.

<sup>b</sup>Potencies could not be calculated because the extracts were either nonmutagenic or did not produce linear dose-response curves.

<sup>c</sup>Taken from Lewtas, 1988.<sup>10</sup>

LIST OF FIGURES

Figure 1. Diagram of project facilities.

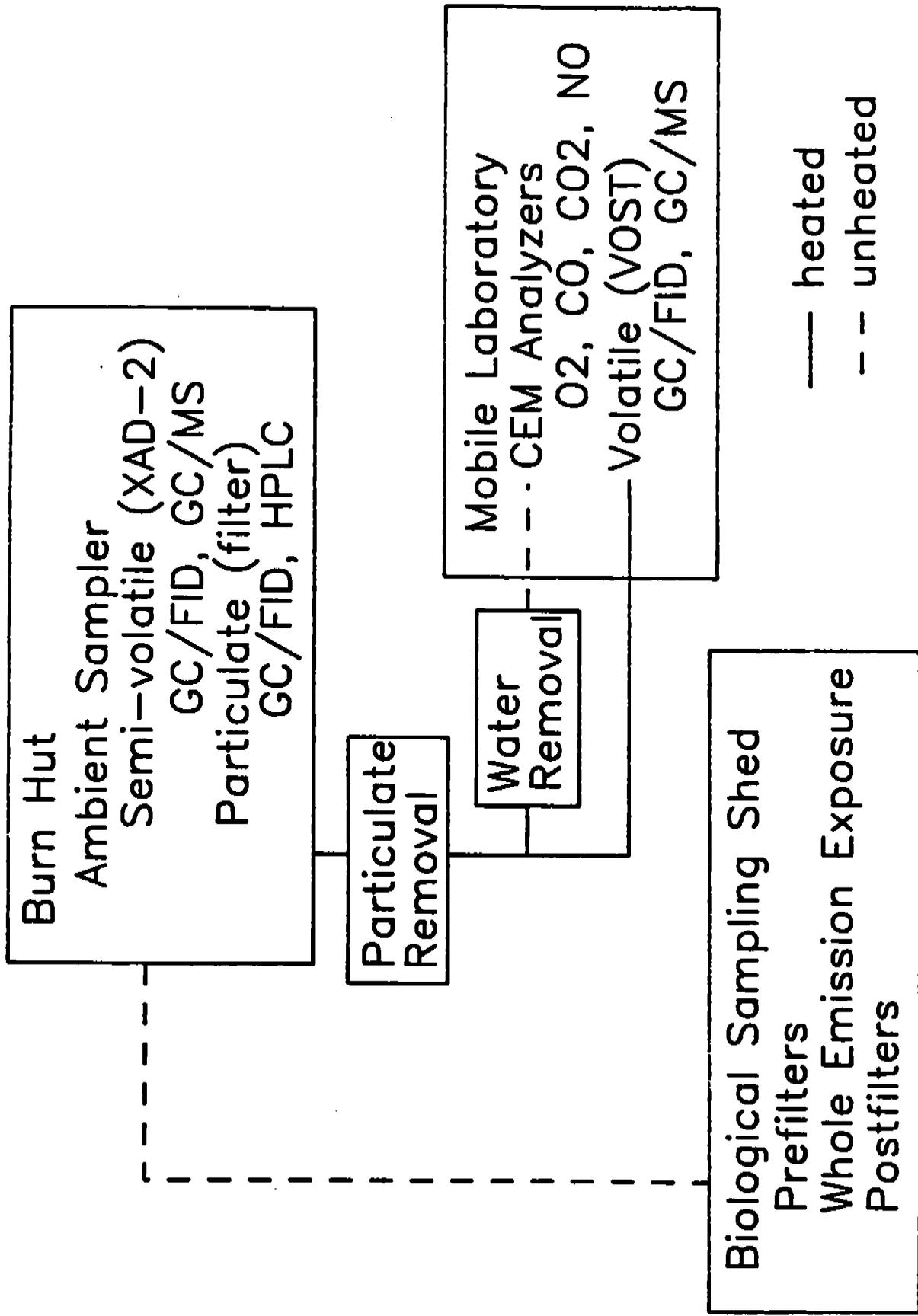


Figure 1.

