



# Research and Development

## Emissions of Organic Air Toxics from Open Burning

### Prepared for

Office of Research and Development

### Prepared by

National Risk Management  
Research Laboratory  
Research Triangle Park, NC 27711

## FOREWORD

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# **Emissions of Organic Air Toxics from Open Burning**

**Annual Performance Measure 90  
Goal 1 Clean Air**

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## ABSTRACT

Emissions from open burning, on a mass pollutant per mass fuel (emission factor) basis, are greater than those from well controlled combustion sources. Some types of open burning (e.g., biomass) are large sources on a global scale in comparison to other broad classes of sources (e.g., mobile and industrial sources). A detailed literature search was performed to collect and collate available data reporting emissions of organic air toxics from open burning sources. Availability of data varied according to the source and the class of air toxics of interest. Volatile organic compound (VOC) and polycyclic aromatic hydrocarbon (PAH) data were available for many of the sources. Non-PAH semivolatile organic compound (SVOC) data were available for several sources. Carbonyl and polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofuran (PCDD/F) data were available for only a few sources. There were several sources for which no emissions data were available at all. Several observations were made including:

Biomass open burning sources typically emitted less VOCs than open burning sources with anthropogenic fuels on a mass emitted per mass burned basis, particularly those where polymers were concerned.

Biomass open burning sources typically emitted less SVOCs and PAHs than anthropogenic sources on a mass emitted per mass burned basis. Burning pools of crude oil and diesel fuel produced significant amounts of PAHs relative to other types of open burning. PAH emissions were highest when combustion of polymers was taking place.

Based on very limited data, biomass open burning sources typically produced higher levels of carbonyls than anthropogenic sources on a mass emitted per mass burned basis, probably due to oxygenated structures resulting from thermal decomposition of cellulose.

It must be noted that local burn conditions could significantly change these relative levels.

Based on very limited data, PCDD/F emissions varied greatly from source to source and exhibited significant variations within source categories. This high degree of variation is likely due to a combination of factors, including fuel composition, fuel heating value, bulk density, oxygen transport, and combustion conditions. This highlights the importance of having acceptable test data for PCDD/F emissions from open burning so that contributions of sources to the overall PCDD/F emissions inventory can be better quantified.

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## 1.0 – INTRODUCTION

Emissions of air pollutants from the open burning of various materials is of concern to the public as well as local, state, federal, and foreign environmental regulatory agencies. Open burning is defined as the unenclosed combustion of materials in an ambient environment. This can include unintentional fires such as forest fires, planned combustion activities such as the burning of grain fields in preparation for the next growing season, arson-initiated fires at scrap tire piles, or even detonation of fireworks at public celebrations. Because of the diverse set of materials that are commonly burned in uncontrolled settings and the difficulties in acquiring representative environmental samples for estimation of emission factors, there is considerable uncertainty in the estimated emissions from open burning activities. The overall emissions from a source depend on both the emissions and the activity level. There is frequently significant uncertainty in the activity levels as well. This report only discusses emissions and not activity levels.

Ideally, when combustion takes place, sufficient mixing of the fuel and combustion air and sufficient gas-phase residence times at high temperatures couple to assure a high degree of completeness in the combustion process, which limits pollutant emissions due to incomplete combustion. Open burning, due to its less than ideal combustion conditions, typically produces soot and particulate matter (PM) that are visible as a smoke plume, carbon monoxide (CO), methane (CH<sub>4</sub>) and other light hydrocarbons, volatile organic compounds (VOCs) such as benzene, and semivolatile organic compounds (SVOCs) including polycyclic aromatic hydrocarbons (PAHs) such as benzo[a]pyrene. Depending on the source, varying amounts of metals such as lead (Pb) or mercury (Hg) may be emitted. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) or polychlorinated biphenyls (PCBs) can be emitted as well. Distinction is made between flaming combustion and smoldering combustion during open burning, which each exhibit different predominant chemical pathways.

Some of the compounds from these classes of pollutants are persistent, bioaccumulative, and toxic (PBT). This includes PCDDs/Fs, PCBs, hexachlorobenzene, and some of the PAHs such as benzo[a]pyrene.

Anthropogenic emissions from some open burning sources can be major contributors to overall emission inventories. For example, open burning of household waste in barrels is one of the largest airborne sources of PCDDs/Fs in the United States (U.S. EPA, 2000). As industrial sources reduce their emissions in response to environmental regulations, non-industrial sources such as open burning begin to dominate the emissions inventory.

Open burning emissions are troubling from a public health perspective because of several reasons:

- Open burning emissions are typically released at or near ground level instead of through tall stacks which aid dispersion;
- Open burning emissions are not spread evenly throughout the year; rather, they are typically episodic in time or season and localized/regionalized;
- Open burning sources are, by their very nature, non-point sources and are spread out over large areas; regulatory approaches that are effective on point sources, such as

mandated flue gas cleaning devices, cannot be applied to non-point sources such as those found in open burning situations;

- Compliance to any bans on open burning are difficult to enforce.

### ***1.1 – Sources of Open Burning Emissions Data***

In order to ascertain the current state of knowledge with regard to compound-specific emissions data from open burning sources, a computer-aided literature search was performed to locate articles related to emissions of air toxics from open burning. A Dialog® and Infoscout search was performed at the U.S. EPA's Information Center at Research Triangle Park, NC to search through several computer databases and produce a list of publications from technical journal articles, conference proceedings, and government reports since 1987. The sources that were considered are listed in Table 1-1.

The majority of the published emissions data from open burning sources has been of criteria pollutants, including CO, PM, and nitrogen and sulfur oxides (NO<sub>x</sub> and SO<sub>x</sub>). The U.S. EPA's AP-42 emission factor database (U.S. EPA, 1996a) contains a significant amount of information on emissions of criteria pollutants from a limited number of open burning sources, mainly from the agriculture industry. AP-42 has detailed information on the Quality Assurance/Quality Control (QA/QC) aspects of the data.

Data on emissions of PCDDs/Fs were taken from the open literature and from the EPA's source inventory component of the dioxin reassessment document (U.S. EPA, 2000). It must be noted that PCDD/F data from open burning sources is very limited or non-existent, and so many of these sources are not in the quantitative emission inventory, where emission factors are more well-developed.

Table 1-1 – Open Burning Sources Considered for this Report

Accidental Fires	Fiberglass
Agricultural Burning of Crop Residue	Fireworks
Agricultural Plastic Film	Grain Silo Fires
Animal Carcasses	Household Waste
Automobile Shredder Fluff Fires	Land Clearing Debris (biomass)
Camp Fires	Landfills/Dumps
Car-Boat-Train (the vehicle not cargo) Fires	Prescribed Burning & Savanna/Forest Fires
Construction Debris Fires	Structural Fires
Copper Wire Reclamation	Tire Fires
Crude Oil & Oil Spill Fires	Yard Waste Fires
Electronics Waste	

U.S. EPA, in conjunction with the State and Territorial Air Pollution Program Administrators/Association of Local Air Pollution Control Officials (STAPPA/ALAPCO), has also sponsored the Emissions Inventory Improvement Program (EIIP), which has provided additional information to supplement AP-42 in some areas.

Andreae and Merlet published a detailed review of emissions of air toxics, aerosols, and trace gases from open burning of biomass (Andreae and Merlet, 2001). In this

review article, data compiled from many disparate sources were analyzed statistically so that emissions data were reported with error bounds. Open burning data were presented from savanna/grassland fires, tropical and extratropical forest fires, and combustion of agricultural residues. This review, however, was limited to biomass emissions.

Based on the literature search, along with the aforementioned reviews and databases, information on emissions of air toxics from various sources was compiled so that the available literature could be analyzed for availability of different data types. Table 1-2 presents the results of the literature search compiled by data types and measurement methods.

Of the open burning sources listed in Table 1-1, there were several of which we were unable to find any published emissions data. These include combustion of animal carcasses, accidental fires, construction debris, and grain silo fires. Although no information about the emissions of air toxics from these sources exist, fires of these types do occur.

Table 1-2 – Summary of Open Burn Literature Search Results (Numbers of citations found by type)

Type of Open Burning	Total Citations	Types of Pollutant Reported							Type of Study							Coverd in Previous		
		Criteria Pollutant Data	Particulate Data	Speciated VOCs	Semi-volatiles	Metals Data	Acid Aerosols	PCDD/PCDF/PCB Data	Ambient Monitoring	Plume Sampling	Laboratory Simulation	Pilot-scale Simulation	Remote Sensing	Modeling	Review Article	AP-42	EIIP	Andrese
All	125.	79.	68.	35.	55.	26.	19.	18.	22.	36.	21.	25.	3.	1.	28.	—	—	—
Prescribed Burning	29.	15.	14.	4.	11.	5.	6.	0	6.	14.	1.	2.	2.	0	6.	X	—	X
Agricultural	15.	11.	8.	6.	6.	1.	2.	1.	0	4.	7.	1.	0	0	5.	X	—	X
Land Clearing	8.	7.	5.	5.	6.	0	1.	0	0	0	5.	2.	0	0	1.	—	X	—
Yard Waste	8.	7.	7.	0	2.	0	1.	0	2.	2.	1.	0	0	0	3.	X	X	—
Camp Fires	2.	0	0	0	1.	0	1.	1.	1.	1.	0	0	0	0	0	—	—	—
Animal Carcasses	0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Crude Oil	15.	11.	10.	5.	7.	5.	0	0	5.	9.	1.	5.	1.	0	0	—	—	—
Accidental Fires	0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Household Waste	12.	11.	10.	4.	6.	5.	4.	8.	0	0	1.	8.	0	0	3.	X	X	—
Landfills/Dumps	4.	1.	0	1.	2.	0	0	2.	2.	1.	0	1.	0	0	1.	—	—	—
Tire Fires	10.	6.	4.	5.	8.	6.	1.	1.	1.	0	3.	2.	0	0	4.	X	—	—
Fluff Fires	4.	3.	2.	1.	2.	1.	1.	1.	0	0	1.	2.	0	0	1.	—	—	—
Fiberglass	1.	1.	1.	1.	1.	1.	1.	0	0	0	0	1.	0	0	0	—	—	—
Agricultural Plastic Film	3.	1.	1.	2.	2.	0	0	0	0	0	0	1.	0	0	1.	X	—	—
Structural Fires	2.	1.	2.	1.	0	0	1.	0	0	1.	0	0	0	0	1.	—	X	—
Car/Boat/Train	2.	2.	2.	0	0	0	0	0	0	0	0	0	0	0	2.	X	X	—
Construction Debris	0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Grain Silo	0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Copper Wire	5.	0	0	0	1.	0	0	2.	3.	3.	0	0	0	0	0	—	—	—
Fireworks	5.	2.	2.	0	0	2.	0	2.	2.	1.	1.	0	0	1.	0	—	—	—

## ***1.2 – Purpose and Scope of the Report***

The purpose of this report is to summarize organic air toxic emissions data from open burning of various materials in order to assess commonalities between sources and discuss methodologies for estimating emissions. The detailed analysis of emissions is limited to those sources for which sufficient published data exist to perform the analysis. Sources which do not have sufficient published data will be discussed in the text, but not in the detailed analysis.

Sources that are of a very transient nature (e.g., open burning/open detonation of explosives and civilian detonation of explosives, such as in road building), underground fires (e.g., coal seam fires), and enclosed biomass combustion (e.g., charcoal production, biomass cooking) are not included in this report.

The air pollutants used in the detailed analysis will be limited to the air toxic VOCs and SVOCs that are found on the list of 189 hazardous air pollutants (HAPs) found in Title III of the 1990 Clean Air Act Amendments (U.S. EPA, <http://www.epa.gov/ttn/atw/188polls.html>). Metal HAPs will not be discussed, although their emissions are largely a function of their concentration in the material to be burned and the combustion temperature. Other air pollutants that are of concern but not on the HAP list will be discussed in the text as appropriate. Table 1-3 lists the target HAPs of primary interest that are to be addressed in this report.

For some sources, multiple data sets of emissions were published in multiple sources. Where possible, the quality of the data was evaluated based on experimental detail, representativeness, and QA/QC reporting. Based on these criteria, a composite data set was generated using data averaged across multiple experiments, but not across multiple references. The data tables presented in this report spell out which reference was used for the data in that table. In general, data of a given pollutant class all came from the same reference.

The data presented are generally limited to speciated HAP data. Total VOCs were not used, although total PAH data were used if no other data were available. In the tables, if an entry is blank it means that no data were available for that pollutant either because of non-detects or incomplete data sets.

The data presented will be limited to emissions-type data. No activity factors will be discussed, although activity factors are clearly important in order to convert emissions factor type data into a form suitable for examining emissions on a temporal, regional, national, or global basis.

Table 1-3 – Targeted HAPs from Open Burning

CAS Number	Pollutant	CAS Number	Pollutant	CAS Number	Pollutant
75-07-0	Acetaldehyde	121-69-7	N,N-Dimethylaniline	101-77-9	4,4'-Methylenedianiline
60-35-5	Acetamide	119-93-7	3,3'-Dimethylbenzidine	91-20-3	Naphthalene
75-05-8	Acetonitrile	79-44-7	Dimethylcarbamoyl chloride	98-95-3	Nitrobenzene
98-86-2	Acetophenone	68-12-2	N,N-Dimethylformamide	92-93-3	4-Nitrobiphenyl
53-96-3	2-Acetylaminofluorene	57-14-7	1,1-Dimethylhydrazine	100-02-7	4-Nitrophenol
107-02-8	Acrolein	131-11-3	Dimethyl phthalate	79-46-9	2-Nitropropane
79-06-1	Acrylamide	77-78-1	Dimethyl sulfate	684-93-5	N-Nitroso-N-methylurea
79-10-7	Acrylic acid	N/A	4,6-Dinitro-o-cresol (including salts)	62-75-9	N-Nitrosodimethylamine
107-13-1	Acrylonitrile	51-28-5	2,4-Dinitrophenol	59-89-2	N-Nitrosomorpholine
107-05-1	Allyl chloride	121-14-2	2,4-Dinitrotoluene	82-68-8	Pentachloronitrobenzene (Quintobenzene)
92-67-1	4-Aminobiphenyl	123-91-1	1,4-Dioxane (1,4-Diethyleneoxide)	87-86-5	Pentachlorophenol
62-53-3	Aniline	122-66-7	1,2-Diphenylhydrazine	108-95-2	Phenol
90-04-0	o-Anisidine	106-89-8	Epichlorohydrin (1-Chloro-2,3-epoxypropane)	106-50-3	p-Phenylenediamine
71-43-2	Benzene	106-88-7	1,2-Epoxybutane	75-44-5	Phosgene
92-87-5	Benzidine	140-88-5	Ethyl acrylate	7803-51-2	Phosphine
98-07-7	Benzotrichloride	100-41-4	Ethylbenzene	7723-14-0	Phosphorus
100-44-7	Benzyl chloride	51-79-6	Ethyl carbamate (Urethane)	85-44-9	Phthalic anhydride
92-52-4	Biphenyl	75-00-3	Ethyl chloride (Chloroethane)	1336-36-3	Polychlorinated biphenyls
117-81-7	Bis(2-ethylhexyl)phthalate (DEHP)	106-93-4	Ethylene dibromide (Dibromoethane)	1120-71-4	1,3-Propane sultone
542-88-1	Bis(chloromethyl) ether	107-06-2	Ethylene dichloride (1,2-Dichloroethane)	57-57-8	beta-Propiolactone
75-25-2	Bromoform	107-21-1	Ethylene glycol	123-38-6	Propionaldehyde
106-99-0	1,3-Butadiene	151-56-4	Ethyleneimine (Aziridine)	114-26-1	Propoxur
133-06-2	Captan	75-21-8	Ethylene oxide	78-87-5	Propylene dichloride (1,2-Dichloropropane)
63-25-2	Carbaryl	96-45-7	Ethylene thiourea	75-56-9	Propylene oxide
75-15-0	Carbon disulfide	75-34-3	Ethylidene dichloride	75-55-8	1,2-Propylenimine (2-Methylaziridine)
56-23-5	Carbon tetrachloride	50-00-0	Formaldehyde	91-22-5	Quinoline
463-58-1	Carbonyl sulfide	118-74-1	Hexachlorobenzene	106-51-4	Quinone (p-Benzoquinone)
120-80-9	Catechol	87-68-3	Hexachlorobutadiene	100-42-5	Styrene
133-90-4	Chloramben	N/A	1,2,3,4,5,6-Hexachlorocyclohexane	96-09-3	Styrene oxide
57-74-9	Chlordane	77-47-4	Hexachlorocyclopentadiene	1746-01-6	2,3,7,8-Tetrachlorodibenzo-p-dioxin
79-11-8	Chloroacetic acid	67-72-1	Hexachloroethane	79-34-5	1,1,2,2-Tetrachloroethane
532-27-4	2-Chloroacetophenone	822-06-0	Hexamethylene diisocyanate	127-18-4	Tetrachloroethylene (Perchloroethylene)
108-90-7	Chlorobenzene	680-31-9	Hexamethylphosphoramide	7550-45-0	Titanium tetrachloride
510-15-6	Chlorobenzilate	110-54-3	Hexane	108-88-3	Toluene
67-66-3	Chloroform	302-01-2	Hydrazine	95-80-7	Toluene-2,4-diamine
107-30-2	Chloromethyl methyl ether	7647-01-0	Hydrochloric acid (Hydrogen Chloride)	584-84-9	2,4-Toluene diisocyanate
126-99-8	Chloroprene	7664-39-3	Hydrogen fluoride (Hydrofluoric acid)	95-53-4	o-Toluidine
1319-77-3	Cresol/Cresylic acid	123-31-9	Hydroquinone	120-82-1	1,2,4-Trichlorobenzene
95-48-7	o-Cresol	78-59-1	Isophorone	79-00-5	1,1,2-Trichloroethane
108-39-4	m-Cresol	108-31-6	Maleic anhydride	79-01-6	Trichloroethylene
106-44-5	p-Cresol	67-56-1	Methanol	95-95-4	2,4,5-Trichlorophenol
98-82-8	Cumene	72-43-5	Methoxychlor	88-06-2	2,4,6-Trichlorophenol
334-88-3	Diazomethane	74-83-9	Methyl bromide (Bromomethane)	121-44-8	Triethylamine
132-64-9	Dibenzofuran	74-87-3	Methyl chloride (Chloromethane)	1582-09-8	Trifluralin
96-12-8	1,2-Dibromo-3-chloropropane	71-55-6	Methyl chloroform (1,1,1-Trichloroethane)	540-84-1	2,2,4-Trimethylpentane
84-74-2	Dibutyl phthalate	78-93-3	Methyl ethyl ketone (2-Butanone)	108-05-4	Vinyl acetate
106-46-7	1,4-Dichlorobenzene	60-34-4	Methylhydrazine	593-60-2	Vinyl bromide
91-94-1	3,3'-Dichlorobenzidine	74-88-4	Methyl iodide (Iodomethane)	75-01-4	Vinyl chloride
111-44-4	Dichloroethyl ether(Bis[2-chloroethyl]ether)	108-10-1	Methyl isobutyl ketone (Hexone)	75-35-4	Vinylidene chloride (1,1-Dichloroethylene)
542-75-6	1,3-Dichloropropene	624-83-9	Methyl isocyanate	1330-20-7	Xylenes
62-73-7	Dichlorvos	80-62-6	Methyl methacrylate	95-47-6	o-Xylene
111-42-2	Diethanolamine	1634-04-4	Methyl tert-butyl ether	108-38-3	m-Xylene
64-67-5	Diethyl sulfate	101-14-4	4,4'-Methylenebis(2-chloroaniline)	106-42-3	p-Xylene
119-90-4	3,3'-Dimethoxybenzidine	75-09-2	Methylene chloride (Dichloromethane)	N/A	Polycyclic Organic Matter
60-11-7	4-Dimethylaminoazobenzene	101-68-8	4,4'-Methylenediphenyl diisocyanate (MDI)		

## 2.0 – MEASUREMENT AND REPORTING OF EMISSIONS

### 2.1 – Methodology of Reporting Open Burning Emissions

When reporting emissions from open burning sources, there are several approaches that can be used. The published literature presents data in any or all of these forms. Delmas et al. published a paper detailing methodology for determining emission factors from open burning of biomass (Delmas et al., 1995). Open burning emissions data can be presented as:

- Raw concentrations either in the plume or in the ambient air some distance away from the plume. Raw concentrations are difficult to deal with because they give no information as to the amount of pollutants that were generated relative to the amount of material that was burned. Comparison of different sources cannot be quantified. Raw concentrations, however, are useful from a health effects perspective if the measurements are taken at the exposure point.
- Emission factors (EFs) in the form of mass of pollutant emitted per unit mass of material burned. EFs are very useful because comparing individual EFs to each other allows sources to be compared on a purely mass basis. Multiplying the EF by the activity factor, usually in terms of mass burned per unit time or area, can be used to compare sources on a daily basis or geographically in terms of local, national, or global basis.
- Emission Ratios (ERs) utilize a carbon balance to compare the concentrations of a species of interest to a reference species, such as CO or carbon dioxide (CO<sub>2</sub>). For example, the ER of chloromethane (CH<sub>3</sub>Cl) relative to CO is calculated using the formula shown in Equation 1-1 (Andreae and Merlet, 2001):

$$ER_{CH_3Cl/CO} = \frac{(CH_3Cl)_{Smoke} - (CH_3Cl)_{Ambient}}{(CO)_{Smoke} - (CO)_{Ambient}} \quad (1-1)$$

For calculation of ERs from smoldering fires, CO is generally used as the reference species. For flaming fires, CO<sub>2</sub> is generally used as the reference species (Andreae and Merlet, 2001). ERs have the advantage that they only require simultaneous measurement of the species of interest and the reference species in the smoke, and no information is required about the fuel composition, burning rates, or quantities combusted. Because of this, ERs are useful for analyzing field test results. ERs can be given on a mass basis or a molar basis.

When data are not available in EF units, it is possible to convert data given in ER units into EF units using Equation 1-2 (Andreae and Merlet, 2001):

$$EF_X = ER_{x/y} \frac{MW_x}{MW_y} EF_Y \quad (1-2)$$



where  $EF_X$  is the emission factor of species x,  $ER_{(x/y)}$  is the molar emission ratio of species x relative to species y,  $EF_Y$  is the emission factor of species y, and  $MW_x$  and  $MW_y$  are the molecular weights of species x and y, respectively. If the mass emission ratios are known, then the emission factors can be calculated using Equation 1-3:

$$EF_X = ER_{X|Y} EF_Y \quad (1-3)$$

where  $ER_{(X/Y)}$  is the mass emission ratio of species x relative to species y.

Each EF in the AP-42 database is given a rating from A through E, with A being the best. An EF's rating is a general indication of the reliability, or robustness, of that factor. Test data quality is rated A through D, and ratings are thus assigned:

- A - Excellent. Factor is developed from A- and B-rated source test data taken from many randomly chosen facilities in the industry population. The source category population is sufficiently specific to minimize variability.
- B - Above average. Factor is developed from A- or B-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with an A rating, the source category population is sufficiently specific to minimize variability.
- C - Average. Factor is developed from A-, B-, and/or C-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category population is sufficiently specific to minimize variability.
- D - Below average. Factor is developed from A-, B- and/or C-rated test data from a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source population.
- E - Poor. Factor is developed from C- and D-rated test data, and there may be reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population.

## 2.2 – *Ambient Sampling*

Ambient sampling involves the measurement of pollutant concentrations in the open atmosphere. Much of the available data on emissions of air toxics from open burning is based on ambient pollutant measurements. VOCs are commonly measuring using EPA Method TO-14 (Winberry et al., 1988a) using SUMMA canisters that are cleaned and evacuated prior to sampling. A fraction of each batch of canisters are typically analyzed before use to ensure adequate cleaning. Compound identification is based on retention time and the agreement of the mass spectra of the unknown to mass spectra of known standards. Figure 2-1 shows a SUMMA canister, flow meter, and sampling pump.



Figure 2-1 – SUMMA Canister and Gas Metering Equipment

SVOCs are sampled according to Method TO-13 (Winberry et al., 1988b), which consists of a filter followed by a polyurethane foam (PUF)-sandwiched XAD-2 bed vapor trap. These samplers typically operate at flow rates designed to achieve low detection limits for the quantification of generally dilute ambient concentrations. After sampling is complete, the filter and XAD trap are recovered, extracted with an organic solvent such as dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), concentrated, and analyzed by GC/MS. Figure 2-2 shows a Method TO-13 train.

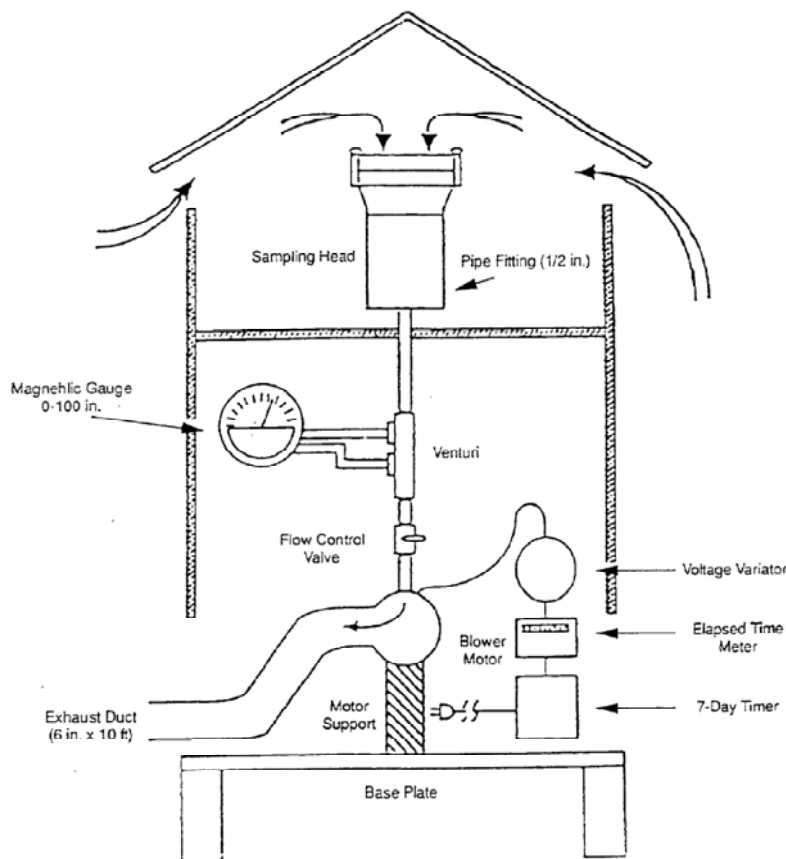


Figure 2-2 – Method TO-13 Train

### 2.3 – Plume Sampling (*Nomad sampler*)

Directly sampling in the smoky plume of a fire is a difficult proposition. Many uncontrolled fires are not easily approachable by sampling crews and exhibit temporal shifts in the position of the flame front; changes in wind directions make it difficult to position ambient sampling devices. The U.S. EPA is currently developing a hand-held boom sampler (*Nomad sampler*) to enable sampling crews to insert the suction end of a sampling probe directly into the smoke plume without needing to get extremely close to the smoke or fire (Gullett et al., 2002a). Figure 2-3 shows the concept of the *Nomad sampler*.



(Gullett et al., 2002b). In limited cases where field data are available to support measurements from the OBTF, results appeared to agree within an order of magnitude (Lemieux and DeMarini, 1992). In the OBTF, shown in Figure 2-4 as configured for experiments investigating open burning of household waste in barrels (Lemieux et al., 2002), there is a continuous influx of dilution air into the facility, simulating ambient dilution. Fans located around the interior maintain a high level of mixing. The burning mass of material is mounted on a weigh scale so that burning rates can be estimated. Ambient sampling equipment is positioned inside the interior of the facility, or extractive samples can be taken through the sample duct.

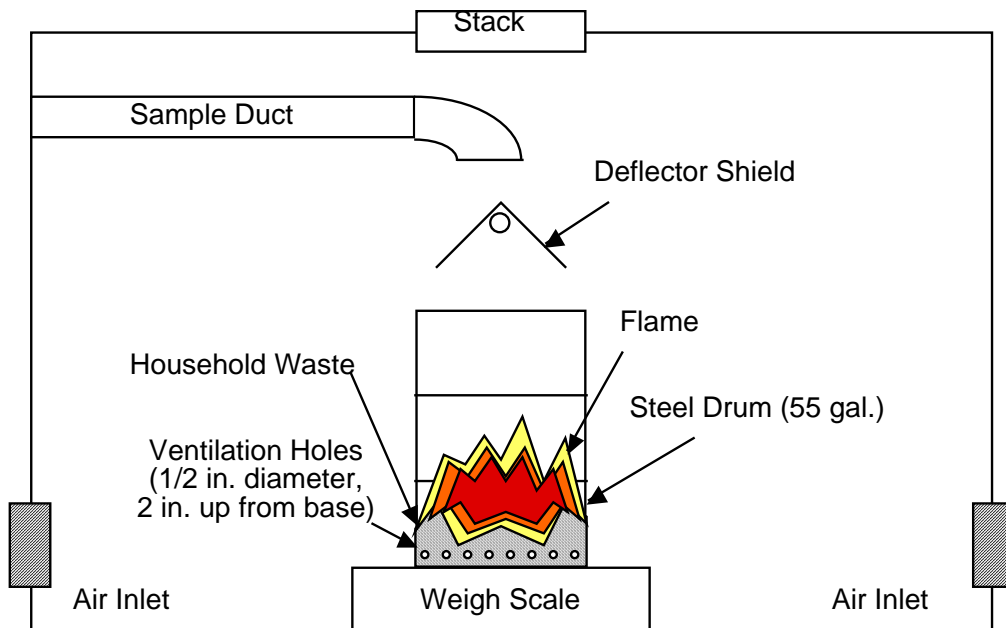


Figure 2-4 – U.S. EPA Open Burning Test Facility

Pollutant concentrations measured in the OBTF can be converted to the mass emissions of individual pollutants (emission factor units) using Equation 2-2:

$$EF = \frac{C_{\text{sample}} Q_{\text{OBTF}} \tau}{m_{\text{burned}}} \quad (2-2)$$

where EF = the emission factor in mg/kg waste consumed,  $C_{\text{sample}}$  = the concentration of the pollutant in the sample ( $\text{mg}/\text{m}^3$ ),  $Q_{\text{OBTF}}$  = the flow rate of dilution air into the OBTF in  $\text{m}^3/\text{min}$ ,  $\tau$  = the burn sampling time in minutes, and  $m_{\text{burned}}$  = the mass of waste burned (kg).

## 2.5 – Wind Tunnel Testing

The University of California at Davis developed a wind tunnel testing facility that has been used for testing emissions from open burning of agricultural residues (Jenkins et al., 1990). This type of facility can control important variables such as fuel moisture content, wind speed, fuel loading, and influence of soil bed conditions on combustion conditions. Figure 2-5 shows a diagram of the wind tunnel facility.

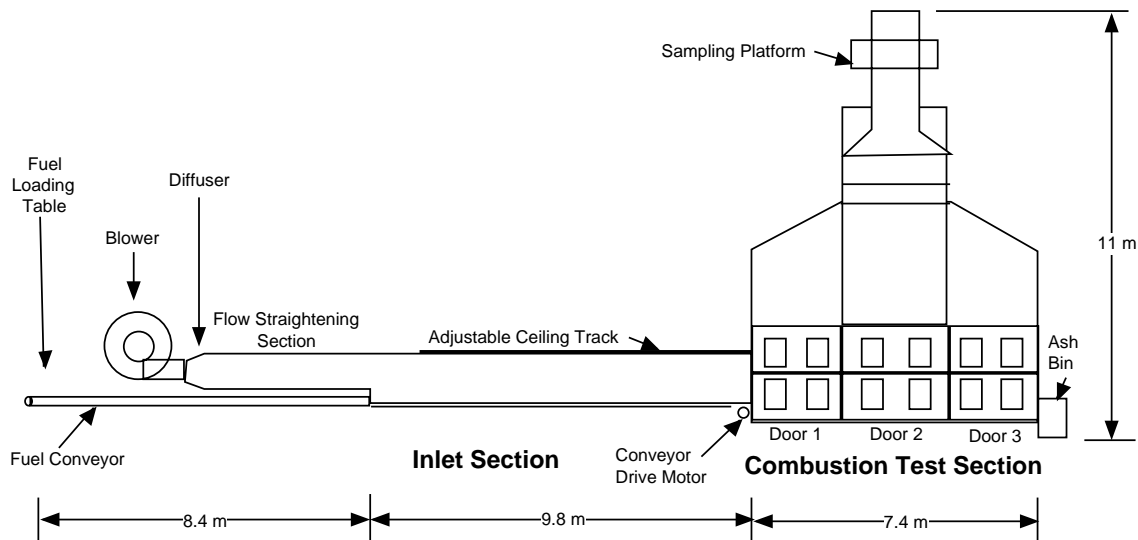


Figure 2-5 – U.C. Davis Wind Tunnel Facility

## 2.6 – Remote sensing

Aircraft and satellite remote sensing have been employed to collect emissions data from biomass burning for a multitude of programs including the South African Regional Science Initiative (SAFARI) in the year 1992 and 2000, the Experiment for Regional Sources of Sinks and Oxidants (EXPRESSO), the “Fire of Savannas” (FOS/DECAFE) experiments, Biomass Burning Airborne and Spaceborne Experiment in the Amazonas (BASE-A), and a Brazilian Institute for the Environment study. Such studies have utilized aircraft or satellite based instruments such as Extended Dynamic Range Imaging Spectrometer (a four-line infrared spectrometer developed by the National Aeronautics Space Administration), “Fire Mapper” spectrometer (infrared radiometer developed by the US Forest Service, the Brazilian Institute of the Environment, and Space Instruments Inc), and NOAA Advanced Very High Resolution Radiometer (AVHRR). However, these aircraft and satellite spectrometers were used primarily for ascertaining information related to fire spread, smoke spread and optical density, and criteria pollutants. The focus of the remote sensing studies to date has been to integrate aircraft and satellite information with ground-based (not remote) sensing data in order to predict and quantify the effects of biomass burning on the global climate.

Another method of developing emissions data from open burning sources in support of the above approach is through ground-based optical remote sensing. This approach

combines path-integrated optical sensing with meteorological measurements (Hashmonay et al., 2001). In a scale of several hundred meters, Fourier Transform Infrared instrumentation is typically used in an open path configuration (OP-FTIR) in which the IR source is coupled with a series of retroreflectors so that the overall path length is many times greater than the distance between the IR source and the retroreflector array. The long path length improves sensitivity so that detection limits can be achieved which are capable of measuring ambient concentrations of organic pollutants. When a several kilometer scale is needed, other instrumentation techniques including Differential optical absorption spectroscopy (DOAS), long path Tunable Diode Laser Absorption Spectroscopy (TDLAS), Light Detection and Ranging (LIDAR) for aerosol detection, and Differential absorption LIDAR (DIAL) for gaseous detection are also available (Hashmonay et al., 1999; Hashmonay and Yost, 1999; Grant et al., 1992). Most of the VOC compounds on the HAP list can be measured at low parts-per-billion levels using at least one of these techniques as well as long path particulate matter extinction measurements (Hashmonay et al., 1999).

## ***2.7 – Industrial Hygiene Samplers***

Frequently, initial responders to open burning situations do not have the capability to perform ambient or plume sampling. In cases such as this, there are colorimetric sampling methods available such as Draeger tubes. In a Draeger tube, a pump is used to pull an air sample through a tube containing a material that is sensitive to a given pollutant (e.g., hydrochloric acid), and based on a color change in the tube media, a concentration is determined. In most cases, Draeger tubes are not sufficiently sensitive to be used for quantitation of air toxics, although they are useful for crude estimates of criteria pollutant concentrations.

## ***2.8 – Wipe Samples and Ash Samples***

Another method of assessment of emissions from open burning is through the use of wipe samples or ash samples, either at the fire site or at sites of deposition downwind (e.g., horizontal outdoor surfaces). This method does not result in data that can be used to estimate emission factors or air emissions, but does provide qualitative data on what pollutants were released during the open burning situation, and this is frequently one of the only tools available for analysis once the burn has completed.

## ***2.9 – Extrapolation from Similar Sources***

Sometimes the only tools available to estimate emissions from open burning involve using expert judgment to estimate emissions from one source by examining emissions from another source. This approach is usually not sound from a quantitative basis; however, qualitative information can be generated that might be useful. An example of this approach would be for a reader that finds a source where no published emissions data

are available (e.g., automobile fires). The reader could look at emissions from burning similar materials (e.g., automobile shredder residue or pyrolysis of plastics) and make an educated guess as to the qualitative nature of the potential emissions and develop target analyte lists for any sampling activities.



### **3.0 – OPEN BURNING ACTIVITIES**

Emissions data on organic air toxics from various open burning sources have been published in available literature. The level of detail and units of the emissions data vary widely from source to source. The discussion in this section will be broken down in terms of the type of material being burned, since physical/chemical properties of the fuel have a significant effect on emissions. The four classes of materials open burned include biomass fuels, liquid fuels, solid anthropogenic fuels, and miscellaneous materials.

#### ***3.1 – Biomass Fuels***

Emissions from the burning of biomass are potentially major sources of air toxics. This category was broken up in terms of the types of biomass and the method of combustion. In general, data for emissions of criteria pollutants and greenhouse gases from biomass combustion were available and of generally good quality. However, data on emissions of air toxics were much more limited.

##### ***3.1.1 – Prescribed Burning, Savanna, and Forest Fires***

Grasslands are burned for various reasons, including manipulating vegetation, enhancing biological productivity and biodiversity, prairie restoration and maintenance, reduction of woody plants, or management for endangered species (Higgins et al., 1989). Savanna and forest fires may also occur naturally through lightning strikes. These types of fires are dynamic events where a moving flame front passes over the fuel source, such as a savanna or forest. Because of this behavior, both smoldering and flaming combustion zones exist with each type of combustion dominating at different times. VOCs and SVOCs are emitted in large quantities with a large variety of oxygenated organic compounds from the thermal decomposition of cellulose. Many of these oxygenated SVOCs are not on the HAP list.

The EPA's AP-42 emission factor database presents data on wildfires (U.S. EPA, 1996b) that has an emission factor rating of D, indicating that the emission factors are based on laboratory testing. Prescribed burning emission factors ratings vary from A to D, depending on the fuel species, with data derived from some field tests and experiments in laboratory hoods. AP-42 presents criteria pollutants and VOC data (methane and non-methane). No speciated VOC, SVOC, metals, or chloroorganic data (including PCDDs/Fs and PCBs) are presented.

A detailed study on the use of molecular tracers in organic aerosols from biomass burning was performed by Oros and Simoneit (Oros and Simoneit, 2001a; 2001b) which examined emissions of a large number of different compounds from both deciduous trees and temperate-climate conifers. Emissions from many different species of trees were reported. The objective of this study was to isolate potential compounds to use as tracers for source apportionment applications. Many of the compounds reported in this study are oxygenates and straight chain hydrocarbons and are not on the list of HAPs.

Masclet et al. reported PAH data from a field study of emissions from prescribed savanna burns (Masclet et al., 1995). Twelve PAHs were profiled and compared to other sources including urban air. Unfortunately this source only reported concentration data on the PAHs, and no other pollutants, such as CO, were reported so that emission factor units could be derived.

Kjällstrand et al. performed a laboratory study examining emissions of SVOCs from burning forest materials (Kjällstrand et al., 2000). They found that significant amounts of methoxyphenols were released.

Perhaps the most complete source of data for emissions of organic air toxics from open burning of biomass is the article by Andreae and Merlet, 2001. The authors compiled a list of pollutants from a wide variety of literature sources, and converted the emissions data into emission factor units along with estimates of the uncertainty in the reported values.

Because prior emission factors of PCDDs/Fs from forest fires were based on measurements made in woodstoves, those emission factors were rated as low quality by the U.S. EPA. Gullett et al. performed laboratory simulations to estimate the emission factor of PCDDs/Fs from forest fires (Gullett and Touati, 2002a) using samples of wood from Oregon and North Carolina. Their results showed a wide range of estimated emissions, with PCDD/F emissions varying over an order of magnitude. Prange et al., 2002, reported on elevated PCDD/F concentrations found during a prescribed forest fire in Australia; however, no emission factor units were estimated.

Yamasoe et al., 2000, performed a study examining trace element emissions from vegetation fires in the Amazon Basin. This study reported on inorganic pollutants and particulate. Emissions data on pollutant species such as sulfates, chlorides, and metals were presented.

Based on these sources of information, Table 3-1 was constructed, which lists the air toxics and other pollutants emitted from prescribed burning, grassland fires, and forest fires. The PCDD/F data from Gullett and Touati, 2002a, was reported as a range rather than an average value. PCDDs/Fs are reported in terms of total quantities and toxic equivalence quantities (TEQs). In addition, some data sets included data on the individual homologue groups including tetra-, penta-, hexa-, hepta-, and octa-substituted polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (TCDD, PeCDD, HxCDD, HpCDD, OCDD, TCDF, PeCDF, HxCDF, HpCDF, and OCDF, respectively).

### *3.1.2 – Agricultural/Crop Residue Burning*

Another class of open burning sources include the agricultural/crop burning sources. The agricultural industry uses open burning as a rapid method for disposing of crop residues, releasing nutrients for the next growing cycle, and clearing land. The AP-42 documents do not have any speciated air toxics data. Jenkins et al. published several papers and reports (Jenkins et al., 1996a, 1996b, 1996c, 1996d) for the California Air Resources Board that discussed a detailed series of laboratory tests on emissions from burning cereal crop residues in the U.C. Davis wind tunnel facility. The naphthalene and 2-methylnaphthalene data from those reports were flagged as questionable by the authors. Barley straw showed high emissions of styrene. Gullett et al. have performed laboratory

simulations to estimate emissions of PCDDs/Fs from rice straw and wheat straw (Gullett et al., 2002b).

Table 3-1 – Emissions of Air Toxics from Prescribed Burning and Forest Fires  
(mg/kg burned)

Class	Compound	Savanna and Grassland	Tropical Forest	Extratropical Forest
VOCs <sup>1</sup>	butadiene	70		60
	benzene	230	400	490
	toluene	130	250	400
	xlenes	45	60	200
	ethylbenzene	13	24	48
	styrene	24	30	130
	methyl chloride	75	100	50
	methyl bromide	2.1	7.8	3.2
	methyl iodide	0.5	6.8	0.6
	acetonitrile	110	180	190
SVOCs <sup>1</sup>	furan <sup>2</sup>	95	480	425
	2-methyl-furan <sup>2</sup>	46	170	470
	3-methyl-furan <sup>2</sup>	8.5	29	50
	2-ethylfuran <sup>2</sup>	1	3	6
	2,4-dimethyl-furan <sup>2</sup>	8	24	19
	2,5-dimethyl-furan <sup>2</sup>	2	30	50
	tetrahydrofuran <sup>2</sup>	16	16	20
	2,3-dihydrofuran <sup>2</sup>	12	13	17
	benzofuran <sup>2</sup>	14	15	26
	furfural <sup>2</sup>	230	370	460
	PAH	2.4	25	25
	phenol	3	6	5
Carbonyls <sup>1</sup>	methanol	1300	2000	2000
	formaldehyde	350	1400	2200
	acetaldehyde	500	650	500
	acrolein	80	180	240
	propionaldehyde	9	80	140
	butanals	53	71	210
	hexanals	13	31	20
	heptanals	3	3	4
	acetone <sup>2</sup>	435	620	555
	methyl ethyl ketone	260	430	455
	2,3-butanedione	570	920	925
	pentanones <sup>2</sup>	15	28	90
	heptanones <sup>2</sup>	6	2	5
	octanones <sup>2</sup>	15	19	20
	benzaldehyde <sup>2</sup>	29	27	36
PCDDs/Fs <sup>3</sup>	Total PCDDs/Fs			1.5(10 <sup>-4</sup> ) - 6.7(10 <sup>-3</sup> )
	TEQ PCDDs/Fs			2.0(10 <sup>-6</sup> ) - 5.6(10 <sup>-5</sup> )

<sup>1</sup> Source: Andreae and Merlet, 2001

<sup>2</sup> Compound of interest not on HAP list

<sup>3</sup> Source: Gullett and Touati, 2002

Sugarcane growers in Hawaii burn their crops prior to harvest to reduce the unused leaf mass that must be transported to sugar mills. Sugarcane crop burning is not practiced annually but rather on a two-year cycle for any given field (Hawaii, 1997). Emissions data for air toxics are not available, although EPA has a current research project to measure PCDD/F emissions from sugarcane burning.

Table 3-2 lists the emissions for air toxics from burning various agricultural/crop material.

### *3.1.3 – Land Clearing Debris*

Disposal of debris generated by land-clearing or landscaping activities has long been problematic. Land clearing is required for a wide variety of purposes such as construction, development, and clearing after natural disasters. The resultant debris is primarily vegetative in composition, but may include inorganic material. Landscaping activities, such as pruning, often generate similar vegetative debris. This debris is often collected and disposed of by municipalities. Open burning or burning in simple air-curtain incinerators is a common means of disposal for these materials, which has long been a source of concern. Air-curtain incinerators use a blower to generate a curtain of air in an attempt to enhance combustion taking place in a trench or a rectangular-shaped, open-topped refractory box.

As is the case of burning agricultural and crop material, the papers and reports by Jenkins et al. (Jenkins et al., 1996a, 1996b, 1996c, 1996d, 1996e) provide a wealth of information on emissions from spreading and pile fires of Douglas Fir, Almond, Walnut, and Ponderosa Pine slash based on wind tunnel studies. The U.S. EPA reported on a laboratory simulation study (Lutes and Kariher, 1996) to evaluate emissions of air toxics from land-clearing debris combustion. They also attempted to simulate an air-curtain incinerator in order to assess the effectiveness of those types of units. Testing was performed on land clearing debris samples from Tennessee and Florida. Although it was undetermined how effective air-curtain incinerators are, this study presented speciated data on VOC and SVOC air toxics. PCDDs/Fs were not measured in this study. For the purposes of presentation of these data in this report, all runs from a given type of land clearing debris were averaged together. Table 3-3 lists the air toxic emission factors from open burning of land clearing debris.

Table 3-2 – Emissions of Air Toxics from Agricultural/crop Burning (mg/kg burned)

Class	Compound	Barley Straw	Corn Stover <sup>1</sup>	Rice Straw	Wheat Straw
VOCs <sup>2</sup>	acetone <sup>3</sup>	3.77	4.34	4.01	4.39
	methylbutanone (isopropylmethyl ketone)			11	
	benzene				
	dimethylfuran <sup>3</sup>	177			
	2-methyl 2-cyclopenten-1-one <sup>3</sup>		36	127	48
	2-chloro phenol <sup>3</sup>	52	81	173	
	toluene		22		
	benzonitrile <sup>3</sup>		29		
	benzaldehyde	82	46	77	52
	methylphenol (hydroxy toluene) <sup>3</sup>			2	
	styrene	36	26	35	35
	xylene				
	benzofuran <sup>3</sup>	18		16	26
SVOCs	methoxymethylphenol (creosol)	72			
	furancarboxaldehyde (furfural) <sup>3</sup>			208	
	phenol			45	
PAHs <sup>2</sup>	naphthalene <sup>4</sup>	80.30	4.48	8.39	196.19
	2-methylnaphthalene <sup>3, 4</sup>	2.70	2.63	5.43	1.07
	acenaphthalene	11.75	0.40	1.06	1.50
	acenaphthene	9.31	0.66	0.31	0.17
	fluorene	2.70	0.12	0.36	0.32
	phenanthrene	17.35	1.61	1.54	4.09
	anthracene	3.00	0.19	0.27	1.07
	fluoranthene	2.30	0.80	0.45	3.93
	pyrene	3.58	0.77	0.35	2.47
	benzo[a]anthracene	1.13	0.19	0.15	1.30
	chrysene	1.43	0.27	0.17	1.37
	benzo[b]fluoranthene	2.40	4.66	0.15	1.14
	benzo[k]fluoranthene	0.60	2.85	0.10	0.48
	benzo[a]pyrene	0.78	9.56	0.08	0.41
	benzo[e]pyrene	1.01	11.26	0.11	0.59
	perylene	0.23	2.08	0.02	0.44
	benzo[g,h,i]perylene	0.52	0.57	0.04	1.05
	Indeno[1,2,3-cd]pyrene	0.59	9.67	0.06	0.67
	dibenz[a,h]anthracene	0.01	0.57		
PCDDs/Fs <sup>5</sup>	TEQ PCDDs/Fs			5.37(10 <sup>-7</sup> )	4.52(10 <sup>-7</sup> )

<sup>1</sup> Composite of two conditions

<sup>2</sup> Source: Jenkins et al., 1996c

<sup>3</sup> Compound of interest not on HAP list

<sup>4</sup> Data flagged as questionable by Jenkins et al.

<sup>5</sup> Source: Gullett et al., 2002b

Table 3-3 – Emissions of Air Toxics from Open Burning of Land Clearing Debris (mg/kg burned)

Class	Compound	Tennessee Debris <sup>1</sup>	Florida Debris <sup>1</sup>	Douglas Fir Slash <sup>2</sup>	Ponderosa Pine Slash <sup>2</sup>	Almond Prunings <sup>2</sup>	Walnut Prunings <sup>2</sup>
VOCs	1,2,4-trimethylbenzene <sup>3</sup>	18.0	7.5				
	1,3,5-trimethylbenzene <sup>3</sup>	4.5	1.5				
	1,3-butadiene	133.0	74.5				
	2-butanone	31.8	28.0				
	4-ethyltoluene <sup>3</sup>	32.5	8.5				
	acetone <sup>3</sup>	181.3	146.5				8.0
	benzaldehyde					8.0	8.0
	benzene	303.5	195.0	196.0	444.0	30.0	16.0
	benzofuran <sup>3</sup>					5.0	
	benzyl chloride	1.8					
	bromomethane		1.0				
	butyl methyl ether		1.0				
	chloromethane	5.3	94.0				
	cis-1,2-dichloroethene	14.3	32.0				
	ethyl benzene	32.0	15.0				
	limonene <sup>3</sup>	81.5					
	xylene	117.5	43.0		56.0	3.0	2.0
	methyl isobutanone						8.0
	methylene chloride	2.0	1.0				
	pinene <sup>3</sup>	98.8					
	styrene	72.8	28.5	137.0	271.0	10.0	7.0
	toluene	190.8	106.0	157.0	351.0	19.0	11.0
	trans-1,3-dichloropropene	1.7					
SVOCs	phenol			93	251	11	
	cumene <sup>3</sup>	10.10	0.97				
	creosol				403.0		
	furancarboxaldehyde (furfural) <sup>3</sup>				335.0	18.0	18.0
	1,1-biphenyl	2.39	1.49				
	phenol	56.98	54.35				
	cresol	53.60	55.85		202.00	9.00	
	2,4-dimethylphenol <sup>3</sup>	10.28	14.31				
	dibenzofuran	3.19	3.31				
	dibutyl phthalate		0.08				
PAHs	bis(2-ethylhexyl)phthalate	8.44	5.59				
	naphthalene	17.62	14.06	13.57	16.96	7.31	14.56
	2-methylnaphthalene <sup>3</sup>	7.64	6.25	2.58	2.27	0.15	1.98
	acenaphthylene	6.63	5.38	2.42	1.41	2.67	1.06
	acenaphthene	0.33		2.52	1.87	0.18	1.72
	fluoranthene	2.17	0.18	1.77	1.35	0.52	1.30
	pyrene	1.66	1.91	1.47	1.07	0.45	0.97
	chrysene	0.47	0.67	0.22	0.10	0.21	0.08
	benzo[a]anthracene	0.38	0.50	0.25	0.11	0.21	0.06
	benzo[b]fluoranthene	0.63	0.67	0.06	0.04	0.04	
	benzo[k]fluoranthene	0.71	0.67	0.14	0.04	0.05	
	benzo[a]pyrene	0.34	0.24	0.04	0.02	0.03	0.01
	Indeno[1,2,3-cd]pyrene	0.34	0.18				
	dibenz[a,h]anthracene	0.03					
	benzo[g,h,i]perylene	0.38	0.58	0.01		0.003	
	fluorene			0.86	0.68	0.05	0.93
	phenanthrene			3.94	2.59	2.04	1.99
	anthracene			0.72	0.43	0.32	0.37
	benzo[a]pyrene			0.05	0.02	0.02	0.02

<sup>1</sup> Source: Lutes and Kariher, 1996

<sup>2</sup> Source: Jenkins et al., 1996c

<sup>3</sup> Compound of interest not on HAP list

### 3.1.4 – Yard Waste

Burning leaves and other yard waste is yet another category of open burning which has data gaps in the available information. The AP-42 database and its expanded EIIP documents did not have any speciated VOCs, SVOCs, metals, or PCDD/F data. The early laboratory simulation study by Gerstle and Kemnitz, 1967, reported on PAH measurements from yard waste burning, but their data were not broken down in terms of the species of tree. The Illinois Institute of Natural Resources published a report (Illinois Institute of Natural Resources, 1978) on the health effects from leaf burning that included data on speciated SVOC from burning leaves from three different species of trees. Table 3-4 lists the air toxics measured from open burning of yard waste, showing the mean yields from 6 replicate measurements of three species and one composite sample.

Table 3-4 – Emissions of Air Toxics from Open Burning of Yard Waste (mg/kg burned)

Class	Compound	Red Oak	Sugar Maple	Sycamore	Composite
PAHs	anthracene/phenanthrene	10.567	5.24	5.967	4.97
	methyl anthracenes	3.368	3.172	2.92	3.967
	fluoranthene	4.31	2.143	1.767	2.108
	pyrene	2.802	1.538	1.823	1.562
	methylpyrene/fluoranthene	1.847	0.993	0.902	1.152
	benzo[c]phenanthrene	0.054	0.171	0.262	0.112
	chrysene/benzo[a]anthracene	1.277	0.943	0.67	0.523
	methyl chrysenes	0.98	0.393	0.438	0.253
	benzo fluoranthenes	0.369	0.137		0.377
	benzo[a]pyrene/ benzo[e]pyrene	0.26	0.467	0.457	0.193
	perylene		0.398	0.523	0.11
	Indeno[1,2,3,-cd]pyrene	0.963		0.695	0.245
	benzo[g,h,i]perylene	0.072		0.06	0.051
	dibenz[a,i and a,h] pyrenes			0.027	
	coronene			0.008	

Source: Illinois Institute of Natural Resources, 1978

### 3.1.5 – Camp Fires

Although camp fires and bonfires would be expected to have emissions within the range of those from the larger-scale events where similar fuels, such as conifer trees, are burned, there were citations in the literature specifically directed at this source. Simoneit et al., 2000, performed a study to examine conifer wood smoke from a campfire for potential organic biomarkers. Another study (Dyke et al., 1997) measured PCDD/F in ambient samples on “bonfire night” in England, a night where many bonfires of various fuel types and fireworks are set off. This study noted an increase in PCDD/F levels, although there was no way to distinguish whether the source of the increase was the bonfires or the fireworks.

### 3.1.6 – Animal Carcasses

Open burning of animal carcasses has been performed in cases where a biological agent has contaminated a herd of livestock (e.g., foot and mouth disease, mad cow disease). No leading references were found that could give any information on either criteria pollutants or air toxics from open burning of animal carcasses. It is unknown how significant this source might be.

## 3.2 – Liquid Fuels

The burning of pools of liquid fuel present a significantly different combustion scenario than exists in a fire involving solid biomass because of both differences in fuel composition and lack of air flow into the flame front from beneath. There are several sources of emissions data on air toxics from burning liquids.

### 3.2.1 – Crude Oil/Oil Spills

Just before the conclusion of the Gulf War, more than 800 oil wells were ignited by retreating Iraqi forces, more than 650 of which burned with flames for several months. Husain, 1994, and Stevens et al., 1993, reported on the characterization of the plume from those fires. Sampling was performed in the plume on the ground using remote sensing and in the plume aloft using aircraft outfitted with sampling devices. Data from those tests consisted primarily of criteria pollutants, although some analysis of metals and other elements was performed.

Ross et al., 1996, conducted experiments on *in-situ* burning of crude oil, where controlled spills consisting of 42,000 and 25,000 kg of crude oil were burned at sea while plume sampling was performed.

A series of experiments were conducted at the mesoscale (larger than laboratory-scale, but smaller than full-scale) to examine emissions from a large pool fire from burning oil. Those experiments were reported in a series of papers (Fingas et al., 1993, 1996, 1998, 1999) and included plume, upstream, and downstream sampling for various compounds, including particulate-bound PCDDs/Fs.

Another study (Booher and Janke, 1997) that included emission factors for criteria pollutants was given to convert the data to emission factor units using Equation 1-3, and using emission ratios relative to CO<sub>2</sub>. Based on those calculations, Table 3-5 was constructed to list the air toxics produced from burning pools of oil.



Table 3-5 – Emissions of Air Toxics from Burning Pools of Liquid Fuels<sup>1</sup> (mg/kg burned)

Class	Compound	Fuel Oil	Crude Oil
VOCs	benzene	1022	251
	toluene	42	
	ethylbenzene	10	
	xylene	25	
	ethyltoluenes <sup>2</sup>	22	
	1,2,4-trimethylbenzene <sup>2</sup>	32	
Carbonyls	formaldehyde	303	139
	acetaldehyde	63	32
	acrolein	39	11
	acetone <sup>2</sup>	35	20
	propionaldehyde		
	crotonaldehyde <sup>2</sup>	6	
	methyl ethyl ketone	13	7
	benzaldehyde <sup>2</sup>	104	44
	isovaleraldehyde <sup>2</sup>	17	5
	valeraldehyde <sup>2</sup>		
	<i>p</i> -tolualdehyde <sup>2</sup>		13
	methyl isobutyl ketone	11	
	hexanal <sup>2</sup>		
	2,5-dimethylbenzaldehyde <sup>2</sup>	13	
PAHs	naphthalene	162	44
	acenaphthalene	99	4
	acenaphthene	10	
	fluorene	1	0.5
	1-methylfluorene	26	0.2
	phenanthrene	13	6
	anthracene	15	1
	fluoranthene	20	4
	pyrene	2	5
	benzo[a,b]fluorene	4	0.3
	benzo[a]anthracene	5	1
	chrysene	9	1
	benzo[b&k]fluoranthene	7	2
	benzo[a]pyrene	5	1
	Indeno[1,2,3-cd]pyrene	5	1
	benzo[g,h,i]perylene		
PCDDs/Fs	TCDD		
	PeCDD		
	HxCDD		
	HpCDD		7.07(10 <sup>-5</sup> )
	OCDD		1.34(10 <sup>-4</sup> )
	TCDF		2.05(10 <sup>-4</sup> )
	PeCDF		
	HxCDF		1.86(10 <sup>-5</sup> )
	HpCDF		
	OCDF		
	Total PCDDs/Fs		4.28(10 <sup>-4</sup> )

<sup>1</sup> Source: pollutant concentrations from Fingas et al., 1996, and PM and CO emission factors from Boohar and Janke, 1997

<sup>2</sup> Compound of interest not on HAP list

### *3.2.2 – Accidental Fires (includes railroad tank cars)*

No data were found on emissions from accidental fires, such as what might occur if a railroad tanker catches fire. This source could be potentially important from a local standpoint, but these occurrences are probably not common enough for this source to likely be a major contributor to national emissions inventories.

## **3.3 – Solid Anthropogenic Fuels**

The combustion of solid anthropogenically produced fuels is a source of concern for air toxics both because of the potential for formation of pollutants of interest and because these sources typically are found in areas where more direct exposure of residents to the pollutants can occur. In addition, these sources typically contain polymeric materials such as plastics and resins.

### *3.3.1 – Open Burning of Household Waste*

Open burning of household waste, usually in barrels (dubbed “backyard barrel burning”) is commonly practiced in rural areas of the U.S. where local waste collection services are not available. It is also commonly practiced in developing countries as one of the primary waste management techniques. This source was one of those sampled in the original open burning experiments by Gerstle and Kemnitz, 1967. A study by the U.S. EPA (Lemieux, 1997; Lemieux et al., 2000) performed a laboratory simulation of barrel burning. A limited number of tests were conducted where a wide variety of criteria and air toxic pollutants were measured. Most of the pollutants, including VOCs, SVOCs, and PM, did not exhibit wide variations between duplicate tests. However, PCDDs/Fs varied over several orders of magnitude. Additional tests were performed to better characterize the PCDD/F emission factor from barrel burning (Gullett et al., 2001; Lemieux et al., 2002). The variation between duplicate runs of these later tests was significantly less than in the original ones. Based on these more recent studies, this source has been moved to the quantitative inventory of dioxin sources in the U.S. (U.S. EPA, 2000). Based on estimated activity factors, barrel burning appears to be one of the largest measured sources of PCDD/F in the U.S. now that maximum achievable control technology (MACT) standards have been implemented for all of the major industrial PCDD/F sources (it must be noted that other non-characterized sources could be as significant as barrel burning, but no data are available). Table 3-6 lists the emissions for air toxics from open burning of household waste in barrels. To derive the emissions estimates in Table 3-7, the data for the four experimental conditions described in Lemieux, 1997, were averaged, with non-detects set to zero. When compound-specific analyses were performed (e.g., PAHs, chlorobenzenes, and carbonyls), the data from the compound-specific analysis was used instead of the general screening analysis. PCDD/F and PCB data were taken from Lemieux et al., 2002, and represent the average of baseline conditions reported in their experiments.

Table 3-6 – Emissions of Air Toxics from Barrel Burning of Household Waste (mg/kg burned)

Class	Compound	Emissions
VOCs <sup>1</sup>	1,3-butadiene	141.25
	2-butanone	38.75
	benzene	979.75
	chloromethane	163.25
	ethyl benzene	181.75
	<i>m,p</i> -xylene	21.75
	methylene chloride	17.00
	<i>o</i> -xylene	16.25
	styrene	527.50
	toluene	372.00
SVOCs <sup>1</sup>	2,4,6-Trichlorophenol	0.19
	2,4-dichlorophenol <sup>2</sup>	0.24
	2,4-dimethylphenol <sup>2</sup>	17.58
	2,6-dichlorophenol <sup>2</sup>	0.04
	2-chlorophenol <sup>2</sup>	0.95
	2-methylnaphthalene <sup>2</sup>	8.53
	2-cresol	24.59
	3- or 4-cresol	44.18
	acetophenone	4.69
	benzyl alcohol <sup>2</sup>	4.46
	bis(2-ethylhexyl)phthalate	23.79
	di- <i>n</i> -butyl phthalate	3.45
	dibenzofuran	3.64
	isophorone	9.25
	pentachloronitrobenzene	0.01
	phenol	112.66
Chlorobenzenes <sup>1</sup>	1,3-dichlorobenzene	0.08
	1,4-dichlorobenzene	0.03
	1,2-dichlorobenzene <sup>2</sup>	0.16
	1,3,5-trichlorobenzene <sup>2</sup>	0.01
	1,2,4-trichlorobenzene	0.10
	1,2,3-trichlorobenzene <sup>2</sup>	0.11
	1,2,3,5-tetrachlorobenzene <sup>2</sup>	0.03
	1,2,4,5-tetrachlorobenzene <sup>2</sup>	0.02
	1,2,3,4-tetrachlorobenzene <sup>2</sup>	0.08
	1,2,3,4,5-pentachlorobenzene <sup>2</sup>	0.08
PAHs <sup>1</sup>	hexachlorobenzene	0.04
	acenaphthene	0.64
	acenaphthalene	7.34
	anthracene	1.30
	benzo[a]anthracene	1.51
	benzo[a]pyrene	1.40
	benzo[b]fluoranthene	1.86
	benzo[g,h,i]perylene	1.30
	benzo[k]fluoranthene	0.67
	chrysene	1.80
	dibenzo[a,h]anthracene	0.27
	fluoranthene	2.77
	fluorene	2.99
	Indeno[1,2,3- <i>cd</i> ]pyrene	1.27
	naphthalene	11.36
	phenanthrene	5.33
	pyrene	3.18

Continued

Table 3-6 – Continued

Class	Compound	Emissions
Carbonyls <sup>1</sup>	acetaldehyde	428.40
	acetone <sup>2</sup>	253.75
	acrolein	26.65
	benzaldehyde	152.03
	butyaldehyde <sup>2</sup>	1.80
	crotoaldehyde <sup>2</sup>	33.53
	formaldehyde	443.65
	isovaleraldehyde <sup>2</sup>	10.20
	<i>p</i> -tolualdehyde <sup>2</sup>	5.85
	propionaldehyde	112.60
PCDDs/Fs & PCBs <sup>3</sup>	Total PCDDs/Fs	5.80(10 <sup>-3</sup> )
	TEQ PCDDs/Fs	7.68(10 <sup>-5</sup> )
	Total PCBs	1.26(10 <sup>-1</sup> )
	TEQ PCBs	1.34(10 <sup>-6</sup> )

<sup>1</sup> Source: Lemieux, 1997<sup>2</sup> Compound of interest not on HAP list<sup>3</sup> Source: Lemieux, 2002

### 3.3.2 – Landfill Fires and Burning Dumps

For many of the same reasons that open burning of household waste in barrels is a major source of PCDDs/Fs, it is speculated that burning dumps and landfill fires might be similarly high emitters of PCDDs/Fs and other air toxics. There are currently very little data available on emissions of air toxics from these types of open burning. There were a few studies published that had data available on air toxics from research in Scandinavia. Ruokojarvi et al., 1995, presented data from both intentional and spontaneous fires at municipal landfills in Finland. Ettala et al., 1996, discussed occurrences and circumstances of landfill fires, also in Finland; little quantitative data were presented in this study, however. There was a study by Pettersson et al., 1996, that reported on emissions of criteria pollutants from both actual and simulated fires in Sweden. Table 3-7 lists the emissions of air toxics from burning dumps and landfill fires. Note that data were not sufficient to convert the information to emission factor units, so only plume concentrations are reported in Table 3-7. In light of the lack of emission factors, a qualitative comparison was performed between landfill fires and open burning of household waste in barrels. Comparing the relative emissions of individual PAHs and PCBs to Table 3-6 (backyard barrel burning), the total PCBs were somewhat higher than individual PAHs in the case of the landfill fires, but an order of magnitude or so less than individual PAHs in the case of the open burning of household waste in barrels, which suggests that different combustion conditions may dominate in a landfill fire than are predominant in a backyard burning situation and that it is not appropriate to extrapolate emissions from that source to this source.

Table 3-7 – Emissions of Air Toxics from Burning Dumps and Landfill Fires (ng/m<sup>3</sup>)

Class	Compound	Controlled Landfill Fire	Uncontrolled Landfill Fire
PAHs	acenaphthylene	90	60
	acenaphthene	50	30
	fluoranthene	100	50
	phenanthrene	520	30
	anthracene	160	85
	fluorene	120	180
	pyrene	120	170
	benzo[a]anthracene	60	60
	chrysene	80	70
	benzo[b&k]fluoranthene	50	20
	benzo[a]pyrene	20	15
	indeno[1,2,3-cd]pyrene	10	10
	dibenz[a,h]anthracene	10	10
	benzo[g,h,i]perylene	10	10
	Total PAHs	1480	810
	Total PCBs	15.5	590

Source: Ruokojarvi et al., 1995

### 3.3.3 – Tire Fires

Approximately 240 million scrap rubber tires are discarded annually in the U.S. (Sladek, 1987; U.S. EPA, 1991). Viable methods for reclamation exist. Some of the attractive options for use of scrap tires include controlled burning, either alone or with another fuel such as coal, in a variety of energy intensive processes, such as cement kilns and utility boilers (Kearney, 1990; Clark et al., 1991; Pirnie, 1991). Another potentially attractive option is the use of ground tire material as a supplement to asphalt paving materials. The Intermodal Surface Transportation Efficiency Act (U.S. Congress, 1991) mandates that up to 20 percent of all federally funded roads in the U.S. include as much as 20 lb (9 kg) of rubber derived from scrap tires per ton (907 kg) of asphalt by 1997. In spite of these efforts, less than 25 percent of the total amount of discarded tires are re-used or re-processed, and the remaining 175 million scrap tires are discarded in landfills, above-ground stockpiles, or illegal dumps. In addition, these reclamation efforts do little to affect the estimated 2 billion tires (18 million tonnes) already present in stockpiles.

A side effect of the problems associated with scrap rubber tires is the frequent occurrence of tire fires at tire stockpiles. These fires, which are often started by arsonists, generate large amounts of heat and smoke and are difficult to extinguish. This is partly due to the fact that tires, in general, have more heat energy by weight than coal does (37600 kJ/kg vs. 27200 kJ/kg) (Pirnie, 1991). Some tire fires have burned continuously for months, such as the 9-month Rhinehart tire fire in Winchester, VA. Such fires pollute not only the atmosphere but also the land and groundwater due to the liquefaction of the rubber during the combustion process.

Several EPA reports and subsequent journal articles have been published on a set of laboratory-scale simulations of a tire fire. These documents reported on VOC and SVOC

air toxics as well as PM and other criteria pollutants (Ryan, 1989; Lemieux and Ryan, 1993). PCDDs/Fs were not measured. A follow on study that was performed in collaboration with health effects researchers measured the mutagenic activity associated with tire fires (Lemieux and DeMarini, 1992). A paper study prepared by Reisman, 1997, collected data on ambient monitoring near tire fires and compared the results to laboratory simulations. Based on these studies, Table 3-8 was constructed using the average of the four test conditions described in Lemieux and Ryan, 1993.

Table 3-8 – Emissions of Air Toxics from Open Burning of Scrap Tires<sup>1</sup> (mg/kg burned)

Class	Compound	Emissions
VOCs	benzaldehyde <sup>2</sup>	314.4
	benzene	2180.55
	benzodiazine <sup>2</sup>	15.55
	benzofuran	12.55
	benzothiophene <sup>2</sup>	20.5
	butadiene	234.6
	dihydroindene <sup>2</sup>	41.7
	xylene	928.95
	dimethyl,methylpropyl benzene <sup>2</sup>	7.45
	dimethyldihydro indene <sup>2</sup>	19.85
	ethenyl benzene <sup>2</sup>	776.6
	ethenyl cyclohexene <sup>2</sup>	66.9
	ethenyl,dimethyl benzene <sup>2</sup>	15.45
	ethenyl,methyl benzene <sup>2</sup>	16.8
	ethenyldimethyl cyclohexene <sup>2</sup>	175.2
	ethenylmethyl benzene <sup>2</sup>	131.25
	ethyl benzene	377.95
	ethyl,methyl benzene <sup>2</sup>	405.15
	ethynyl benzene <sup>2</sup>	160.75
	ethynyl,methyl benzene <sup>2</sup>	394.65
	isocyano benzene <sup>2</sup>	318.55
	limonene <sup>2</sup>	460
	toluene	1367.75
	methyl indene <sup>2</sup>	228.25
	methyl thiophene <sup>2</sup>	9.05
	methyl,ethenyl benzene <sup>2</sup>	66.15
	methyl,methylethenyl benzene <sup>2</sup>	390.75
	methyl,methylethyl benzene <sup>2</sup>	197.45
	methyl,propyl benzene <sup>2</sup>	20.8
	methylene indene <sup>2</sup>	41.45
	methylethyl benzene <sup>2</sup>	152.15
	propyl benzene <sup>2</sup>	78.3
	styrene	652.7
	tetramethyl benzene <sup>2</sup>	127.85
	thiophene <sup>2</sup>	41.25
	trimethyl benzene <sup>2</sup>	60.9
SVOCs	1-methyl naphthalene <sup>2</sup>	279.15
	1,1'biphenyl,methyl <sup>2</sup>	5.55
	2-methyl naphthalene <sup>2</sup>	389.95
	benzisothiazole <sup>2</sup>	86.95

Continued

Table 3-8 – Continued

Class	Compound	Emissions
SVOCs (cont.)	benzo[b]thiophene <sup>2</sup>	22.1
	biphenyl	269.8
	cyanobenzene <sup>2</sup>	370.25
	dimethyl benzene <sup>2</sup>	620.05
	dimethyl naphthalene <sup>2</sup>	109.6
	methyl,dimethyl benzene <sup>2</sup>	136.2
	ethynyl benzene <sup>2</sup>	231.6
	hexahydro azepinone <sup>2</sup>	411.8
	indene <sup>2</sup>	421.3
	isocyano naphthalene <sup>2</sup>	4.7
	methyl benzaldehyde <sup>2</sup>	43.3
	phenol	533.05
	propenyl naphthalene <sup>2</sup>	11.75
	propenyl,methyl benzene <sup>2</sup>	261.8
	trimethyl naphthalene <sup>2</sup>	157.9
PAHs	naphthalene	650.95
	acenaphthylene	711.55
	acenaphthene	1368
	fluorene	223.65
	phenanthrene	245
	anthracene	52.95
	fluoranthene	398.35
	pyrene	92.75
	benzo[a]anthracene	92.3
	chrysene	81.2
	benzo[b]fluoranthene	78.9
	benzo[k]fluoranthene	86.85
	benzo[a]pyrene	99.35
	dibenz[a,h]anthracene	0.55
	benzo[g,h,i]perylene	112.7
	indeno[1,2,3-cd]pyrene	68.55

<sup>1</sup> Source: Lemieux and Ryan, 1993<sup>2</sup> Compound of Interest not on HAP list

### 3.3.4 – Automobile Shredder Fluff

When automobiles are recycled, the carcasses are typically shredded, and the metallic components are separated from the non-metallic components using a combination of magnetic or gravimetric methods (cyclones or floatation). The non-metallic residue is called automobile shredder “fluff”. The fluff is then usually baled and landfilled. Occasionally the bales of shredder fluff can catch fire. Combustion of automobile components (e.g., tires, seats, floor mats) was one of the sources presented in the original Gerstle and Kemnitz study in 1967. Ryan and Lutes, 1993, reported on a laboratory simulation study where small quantities of shredder fluff were combusted, and extremely high organic emissions resulted, exceeding 200 g per kg of fluff combusted. Emissions of PCDDs/Fs were exceedingly high, although only PCDD/F homologues were analyzed rather than specific isomers, which prevented calculation of TEQ units. Air toxics from automobile shredder residue combustion are listed in Table 3-9.

Table 3-9 – Emissions of Air Toxics from Open Burning of Automobile Shredder Residue<sup>1</sup> (mg/kg burned)

Class	Compound	Emissions
VOCs	acetaldehyde	761.7
	acrolein	1678.2
	acetonitrile	804.7
	acrylonitrile	772.3
	methyl furan <sup>2</sup>	54.3
	benzene	9583.7
	toluene	10692.8
	chlorobenzene	1718.0
	<i>m/p</i> -xylene	1678.0
	styrene	6528.0
	ethyl benzene	2400.0
	1,2-dichlorobenzene <sup>2</sup>	110.0
SVOCs	benzaldehyde <sup>2</sup>	1690.0
	benzenebutanenitrile <sup>2</sup>	3340.0
	biphenyl	330.0
	bis(2-ethylhexyl)phthalate	2058.0
	caprolactam	177.0
	ethyltoluene <sup>2</sup>	140.0
	ethynyl benzene <sup>2</sup>	460.0
	methylethylphenol <sup>2</sup>	260.0
	phenol	990.0
	phenylethanone <sup>2</sup>	1080.0
	phthalic anhydride	230.0
	quaterphenyl <sup>2</sup>	37.0
	terphenyl <sup>2</sup>	40.0
	trimethylbenzene <sup>2</sup>	140.0
PAHs	naphthalene	883.3
	acenaphthylene	150.0
	acenaphthene	13.3
	fluorene	38.0
	phenanthrene	231.3
	anthracene	35.7
	fluoroanthene	88.3
	pyrene	67.3
	benzo[a]anthracene	22.7
	chrysene	27.3
	benzo[b&k]fluoranthene	32.3
	benzo[a]pyrene	14.7
	indeno[1,2,3-cd]pyrene	23.3
	dibenzo[a,h]anthracene	5.0
	benzo[g,h,i]perylene	6.3
PCDDs/Fs	TCDD	0.16
	PeCDD	0.30
	HxCDD	0.13
	HpCDD	0.08
	OCDD	0.03
	TCDF	1.80
	PeCDF	1.40
	HxCDF	0.40
	HpCDF	0.10
	OCDF	0.05
	Total PCDDs/Fs	4.45

<sup>1</sup> Source: Ryan and Lutes, 1993

<sup>2</sup> Compound of interest not on HAP list



### 3.3.5 – Open Burning of Fiberglass

Fiberglass is used as a construction material for low-cost outbuildings such as sheds. It is also commonly used in boat construction. In response to requests from state and local environmental agencies, the EPA performed a laboratory simulation of open burning of various types of fiberglass materials (Lutes and Ryan, 1993). Numerous air toxics were measured in that study, a summary of which is shown in Table 3-10.

Table 3-10 – Emissions of Air Toxics from Open Burning of Fiberglass<sup>1</sup> (mg/kg burned)

Class	Compound	Emissions	
		Boating Industry	Building Industry
VOCs	chloromethane	435.9	420.8
	vinyl chloride	0.8	
	bromomethane	1.7	772.6
	chloroethane	0.8	
	1,1-dichloroethene <sup>2</sup>	0.8	
	acetone <sup>2</sup>	155.6	158.0
	trans-1,2-dichloroethene <sup>2</sup>	0.3	
	1,1-dichloroethane <sup>2</sup>	0.8	
	chloroform	36.9	23.9
	1,1,1-trichloroethane <sup>2</sup>	0.5	
	carbon tetrachloride	0.6	
	benzene	5921.3	10,472.7
	1,2-dichloroethane <sup>2</sup>	0.7	
	trichloroethene	0.8	
	1,2-dichloropropane <sup>2</sup>	1.0	
	bromodichloromethane <sup>2</sup>	0.7	
	cis-1,3-dichloropropene	0.7	
	toluene	3633.2	4723.7
	trans-1,3-dichloropropene	7.6	
	1,1,2-trichloroethane	0.8	
	tetrachloroethene	0.9	
	dibromochloroethane <sup>2</sup>	0.9	
	chlorobenzene	2.0	
	ethyl benzene	700.7	2686.0
	<i>m,p</i> -xylene	468.0	1523.2
	<i>o</i> -xylene	4.5	8.1
	styrene		9931.6
	bromoform	0.9	
	1,1,2,2-tetrachloroethane	2.6	
	1,2-dichlorobenzene <sup>2</sup>	1.5	
	1,4-dichlorobenzene	1.8	
	1,3-dichlorobenzene	1.1	
SVOCs	acetophenone	77.0	286.0
	benzoic acid <sup>2</sup>	1288.0	781.0
	biphenyl	689.0	1936.0
	cumene <sup>2</sup>		251.0
	dibenzofuran	105.0	945.0
	<i>n,n</i> -diethylaniline		353.0
	<i>di-n</i> -butylphthalate		24.0
	bis(2-ethylhexyl)phthalate		60.0
	2-methylnaphthalene <sup>2</sup>	89.0	516.0
	2-cresol	125.0	400.0
	3/4-cresol		1731.0
	phenol	328.0	6830.0

Continued

Table 3-10 – Continued

Class	Compound	Emissions	
		Boating Industry	Building Industry
PAHs	acenaphthene		
	acenaphthylene	533.0	733.0
	anthracene	353.0	202.0
	benzo[a]anthracene	171.0	214.0
	benzo[a]pyrene	86.0	72.0
	benzo[b]fluoranthene	284.0	
	benzo[g,h,i]perylene	33.0	
	benzo[k]fluoranthene	48.0	
	chrysene	323.0	458.0
	dibenzo[a,h]anthracene	16.0	
	fluoranthene	314.0	694.0
	fluorene	453.0	409.0
	indeno[1,2,3-cd]pyrene	28.0	
	naphthalene	1913.0	5915.0
	phenanthrene	902.0	2156.0
	pyrene		

<sup>1</sup> Source: Lutes and Ryan, 1993

<sup>2</sup> Compound of interest not on HAP list

### 3.3.6 – Agricultural Plastic

Agricultural activities frequently result in the open burning of plastic materials. Pesticides, including Thimet and Atrazine, are delivered in plastic bags, which are commonly burned in the open in the farm fields. Oberacker et al., 1992, performed a series of tests in which air toxics from this practice were measured. Measurements were made from burning empty bags from both types of pesticides and from burning bags that had trace amounts of residual pesticides remaining in the bags. PCDD/F measurements were made on the Atrazine bag tests, and those results suggest that the Atrazine traces remaining in the bags contributed to the PCDDs/Fs rather than the bags themselves. These results are summarized in Table 3-11, using the assumption that each bag weighed 0.1 kg.

Sheets of black plastic film are used in agricultural settings for mulching purposes, such as ground moisture and weed control. At the end of the growing season, this film is gathered in a pile and burned in the open. Linak et al., 1989, performed a laboratory simulation to evaluate emissions of air toxics from this practice. The results from this laboratory simulation were not presented in units that could be converted to emission factors; however, there was some additional work done during this study during which mutagenicity of the analytical extracts was measured using bioassay techniques.

### 3.3.7 – Structural Fires

Although criteria pollutant data and non-specified VOC data from structural fires are presented in EIIP and a paper by Brown et al., 1989, no data on air toxic emissions from structural fires could be found.

Table 3-11 – Emissions of Air Toxics from Open Burning of Pesticide Bags<sup>1</sup> (mg/kg burned)

Class	Compound	Emissions			
		Empty Thimet Bags	Thimet Bags	Empty Atrazine Bags	Atrazine Bags
VOCs	acetone <sup>2</sup>	140.0	630.0	140.0	220.0
	benzene	50.0	850.0	120.0	220.0
	2-butanone	120.0	100.0	20.0	30.0
	chloromethane	10.0	70.0	10.0	10.0
	ethylbenzene	50.0	50.0	10.0	20.0
	methylene chloride	40.0	840.0	30.0	220.0
	styrene	140.0	120.0	20.0	90.0
	toluene	70.0	360.0	20.0	120.0
	xylene	110.0	110.0		10.0
SVOCs	phenol	84.0	130.0	8.0	20.0
	2-cresol		60.0		
	4-cresol	37.0	100.0		3.0
	2,4-dimethylphenol <sup>2</sup>	12.0	30.0		
	2-methylnaphthalene <sup>2</sup>	8.0	20.0		10.0
	benzoic acid <sup>2</sup>				90.0
	dibenzofuran	4.0	8.0		
	diethylphthalate				3.0
	bis(2-ethylhexyl)phthalate		8.0		
	thimet <sup>2</sup>		180.0		
PAHs	atrazine <sup>2</sup>				420.0
	naphthalene	370.0	230.0	49.0	130.0
	acenaphthalene	12.0	30.0		
	fluorene	4.0	9.0		
	phenanthrene	13.0	20.0		
	fluoranthene	3.0	6.0		
PCDDs/Fs	pyrene	3.0	6.0		
	TCDD				8.0(10 <sup>-6</sup> )
	PeCDD				
	HxCDD				2.7(10 <sup>-5</sup> )
	HpCDD				1.0(10 <sup>-4</sup> )
	OCDD				4.0(10 <sup>-5</sup> )
	TCDF				6.7(10 <sup>-6</sup> )
	PeCDF				
	HxCDF				3.3(10 <sup>-5</sup> )
	HpCDF				3.3(10 <sup>-5</sup> )
	OCDF				
	TEQ				9.0(10 <sup>-6</sup> )

<sup>1</sup> Source: Oberacker et al., 1992 (assuming each bag weighed 0.1 kg)

<sup>2</sup> Compound of interest not on HAP list

### 3.3.8 – Vehicle Fires

This category of burning refers to fires of the vehicle itself, such as an automobile or train. Emissions from any cargo the vehicle would be carrying are covered separately, such as under liquid fuels. Although criteria pollutant data from vehicular fires are presented in AP-42 and EIIP, they were derived primarily from Gerstle and Kemnitz, 1967, and no data on air toxic emissions could be found from this source.

#### *3.3.9 – Construction Debris*

No sources of data on emissions of criteria pollutants or air toxics from open burning of construction debris could be found. Given the prevalence of this practice and its similarities to other sources that have been found to be significant, such as open burning of household waste in barrels, this source presents a potentially important data gap that should be addressed.

#### *3.3.10 – Grain Silo Fires*

No sources of data on emissions of criteria pollutants or air toxics from grain silo fires could be found.

#### *3.3.11 – Open Burning of Electronics Waste*

As the quantity of discarded computer equipment and other consumer electronics increases, the possibility of open burning as a disposal technique becomes more likely. There are reports of sham recycling activities in developing countries where open burning is used on electronics waste (Hileman, 2002), but no emissions data were found.

### **3.4 – Miscellaneous Fuels**

#### *3.4.1 – Copper Wire Reclamation*

Copper wire is frequently coated with a plastic insulation material. It is a common practice in many parts of the world to use open burning to remove the insulation so that the underlying copper wire can be reclaimed for value. Current understanding of the formation mechanisms of PCDDs/Fs proposes copper-based catalysts as an important contributor to PCDD/F emissions. The presence of significant quantities of copper and, possibly, chlorine coupled with the oxygen-limited combustion conditions found in open burning suggest that copper wire reclamation activities might be a significant source of PCDDs/Fs. Ambient sampling for PAHs was performed in the vicinity of areas where scrap metal was recovered by open burning and found elevated levels of PAHs near the operation (Tsai et al., 1995a; Tsai et al., 1995b). Another study was performed to examine the mutagenicity of airborne particulates near an operation where copper wire was reclaimed by open burning (Lee et al., 1994). Another article presented PCDD/F results from surface and ash sampling at a metal recovery facility where open burning was used (Harnly et al., 1995) that showed parts per million levels of PCDDs/Fs in ash samples. However, none of these studies presented data that could be converted into emission factors for comparison to other sources. Although this practice is uncommon in the U.S., it is still widely practiced in developing countries. This source could be a potentially important data gap in the preparation of dioxin inventory documents.

#### *3.4.2 – Fireworks*

The detonation of fireworks, although an infrequent occurrence, typically occurs over a wide area during a fairly short time interval. Local concentrations of pollutants have been shown to increase during those times (Noordjik, 1993). There have been several studies that attempted to estimate emissions due to fireworks. Dyke et al., 1997,

measured emissions during “bonfire night” in England, which involves bonfires and fireworks in an annual event. They found a fourfold increase in the ambient concentrations of PCDDs/Fs during bonfire night but were not able to attribute emissions to any given source, and emission factors were not calculated. Fleischer et al., 1999, performed a laboratory study where fireworks were set off and the residues analyzed for PCDDs/Fs. They found very low or non-detectable concentrations of most of the congeners and only found significant concentrations of OCDD and OCDF. The authors postulated that the increased levels of PCDDs/Fs that were found by Dyke et al. were probably due to the bonfires and not the fireworks. Another study on emissions from fireworks examined only metals (Perry, 1999).

## 4.0 – EMISSIONS ANALYSIS

Based on all of the data that were collected and presented in Section 3.0, Table 4-1 was constructed to visualize the completeness of the data set. As can be seen from this table, some sources are better-characterized than others, some are poorly characterized, and some are not characterized at all. PAH data are available for all of the sources, and VOC data are available for most of the sources. Non-PAH semivolatile data are limited for most sources. Carbonyl and PCDD/F data are non-existent for most sources. Because of the lack of robustness of the data set between sources, it is not possible to directly compare speciated organics as a whole. Rather, the approach that will be taken is to compare sources by selecting certain key pollutants within general classes of pollutants. For the purposes of this analysis, measurements within sources were averaged so that a single value could be used for that source. When available, error bars have been added to illustrate the range of emission values for that source; if the lower error bar is missing, it means that the lower bound was zero, and could not be displayed on a semi-logarithmic plot.

Of the VOCs, benzene, toluene, ethyl benzene, xylenes, and styrene were selected for comparison. They are commonly produced during combustion processes, and data are available for most of the sources. Figure 4-1 shows the relative quantities of the VOCs produced across all the sources for which data were available. The biomass sources generally had less emissions of VOCs than the other sources. In particular, the sources where significant amounts of polymer plastics were involved (automobile shredder residue, fiberglass) produced fairly prodigious amounts of VOCs, approaching percent levels of the initial mass of material. The pesticide bags, although made from plastics, did not show as high of emissions as other sources containing large quantities of plastics. It is possible that in those experiments, ambient air influx was sufficient to allow more efficient combustion of the material.

For the SVOCs, naphthalene, benzo[a]pyrene, and total non-naphthalene PAHs were chosen for comparison. It must be noted that, for agricultural burning, naphthalene was not included because of the reference's authors' doubts on the veracity of the data. Figure 4-2 compares the SVOC emissions from the various sources (note the logarithmic scale). As was the case with the VOCs, the combustion of biomass produced less SVOCs than combustion of various man-made products. Pool fires of liquid fuels produced significant amounts of PAHs. However, the tire fires and combustion of fiberglass produced the most PAHs. Tire fires produced nearly 100 mg of benzo[a]pyrene per kg of tire combusted.

Table 4-1 – Summary of Available Data

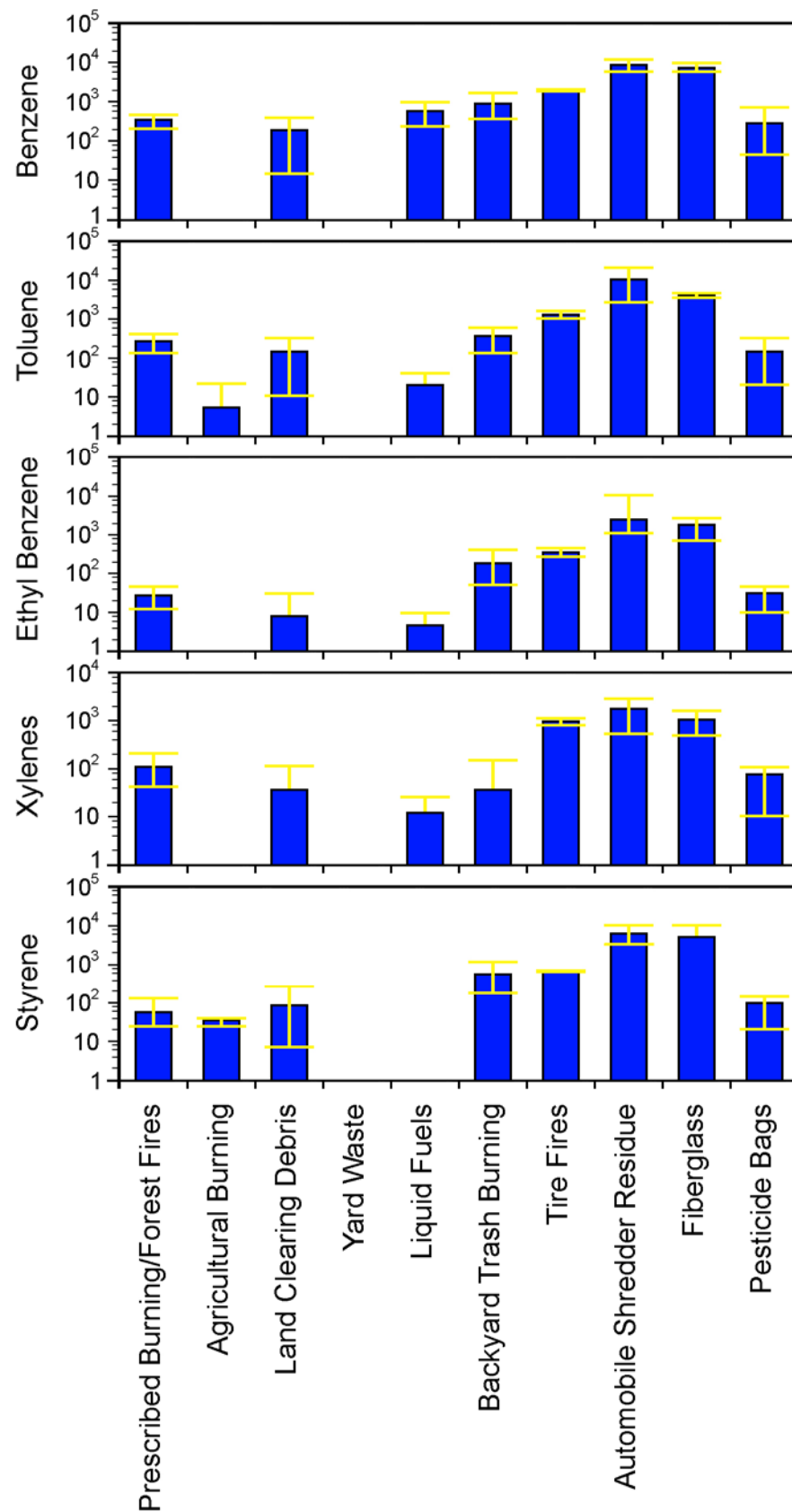


Figure 4-1 – VOCs from Open Burning Sources (mg/kg burned)



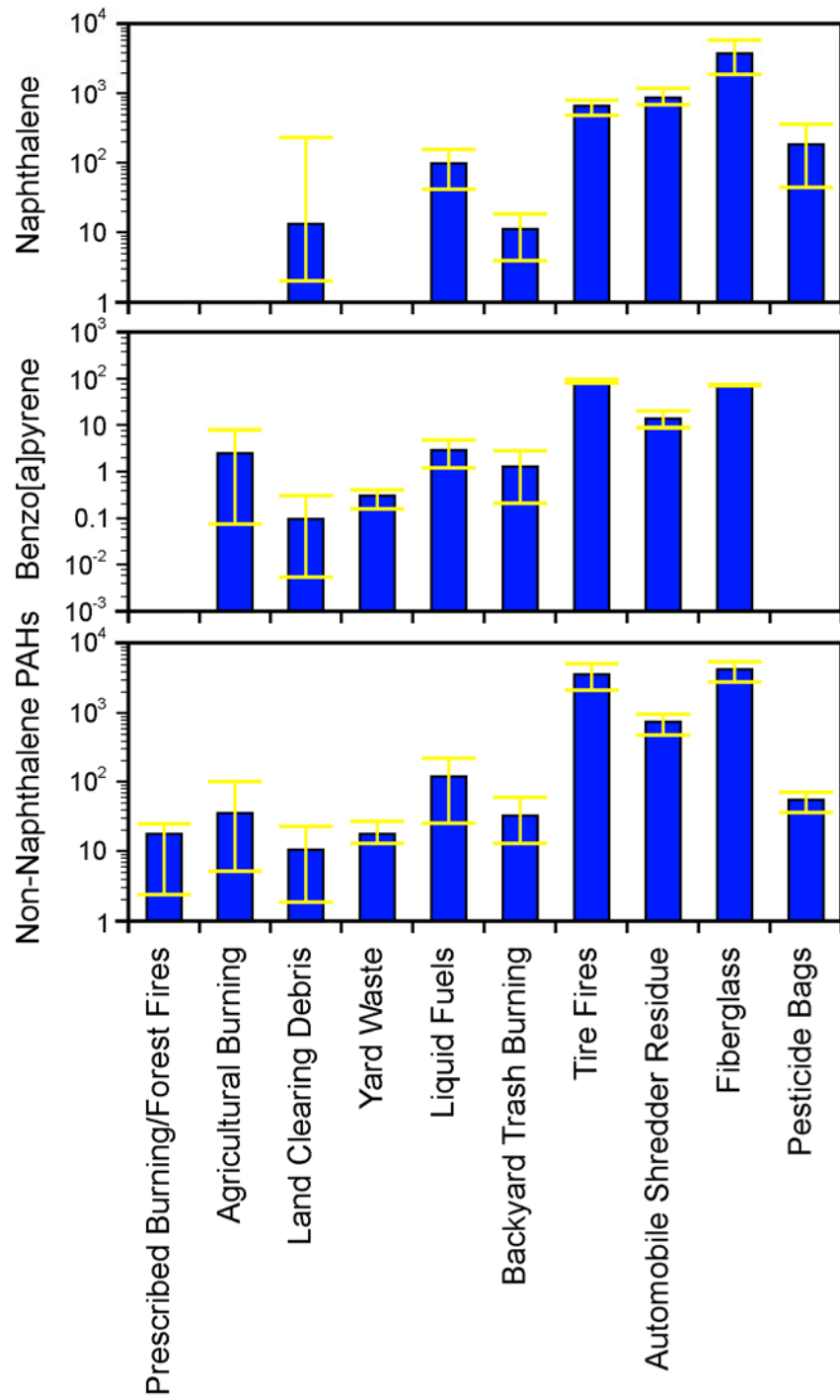


Figure 4-2 – SVOCs from Open Burning Sources (mg/kg burned)

The available data for carbonyls is much more limited. For this analysis, formaldehyde was chosen as the compound for comparison between sources. Figure 4-3 illustrates the relative emissions of formaldehyde from open burning. Although the data set is much more limited, the combustion of biomass produced significantly more formaldehyde than the other open burning sources. This is likely due to the high levels of elemental oxygen bound within the cellulose structures found in biomass.

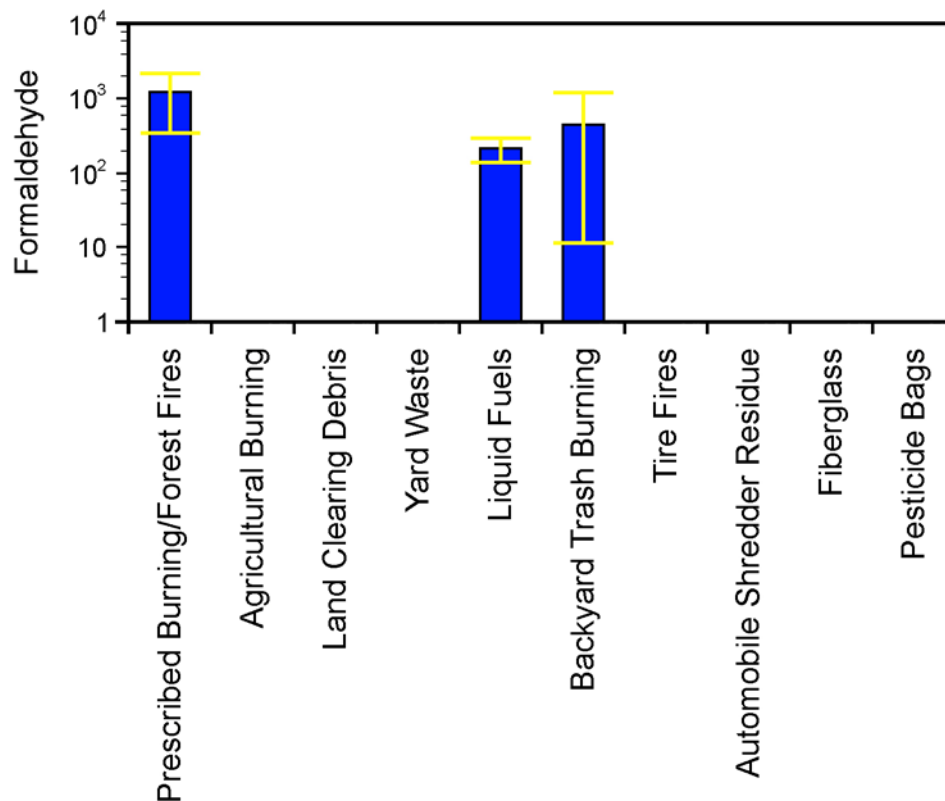


Figure 4-3 – Formaldehyde from Open Burning Sources (mg/kg burned)

Emissions of PCDDs/Fs showed significant differences between somewhat similar sources. As can be seen in Figure 4-4, open burning of agricultural residues such as wheat and rice straw produced almost 2 orders of magnitude less PCDDs/Fs per kg of material burned than forest fires, both on a total and a TEQ basis. Open burning of household waste in barrels shows similar emissions to that of forest fires. Automobile shredder residue emitted several orders of magnitude higher PCDDs/Fs than any of the other sources. This is likely due to the smoldering combustion that occurred during the fluff combustion experiments (Ryan and Lutes, 1993). During the backyard burning experiments (Lemieux et al., 2002) it was found that the smoldering combustion stage produced higher levels of PCDDs/Fs from that source than the flaming combustion stage. Automobile shredder fluff contains significant amounts of copper (from shredded electrical components), and chlorine (from vinyl seat cushions), which are consistent with formation of PCDDs/Fs. Given the high degree of variability between sources and within sources, it is not likely that PCDD/F emissions could be estimated with even a poor degree of certainty without the presence of test data. Given the magnitude of the PCDD/F annual emissions for the U.S. ( $\approx 1$  kg TEQ/yr), the possibility exists that additional test data for different sources could significantly improve the accuracy of the inventory. Particular sources of concern for which additional data would be useful include:

- Forest fires
- Land-clearing debris
- Construction debris

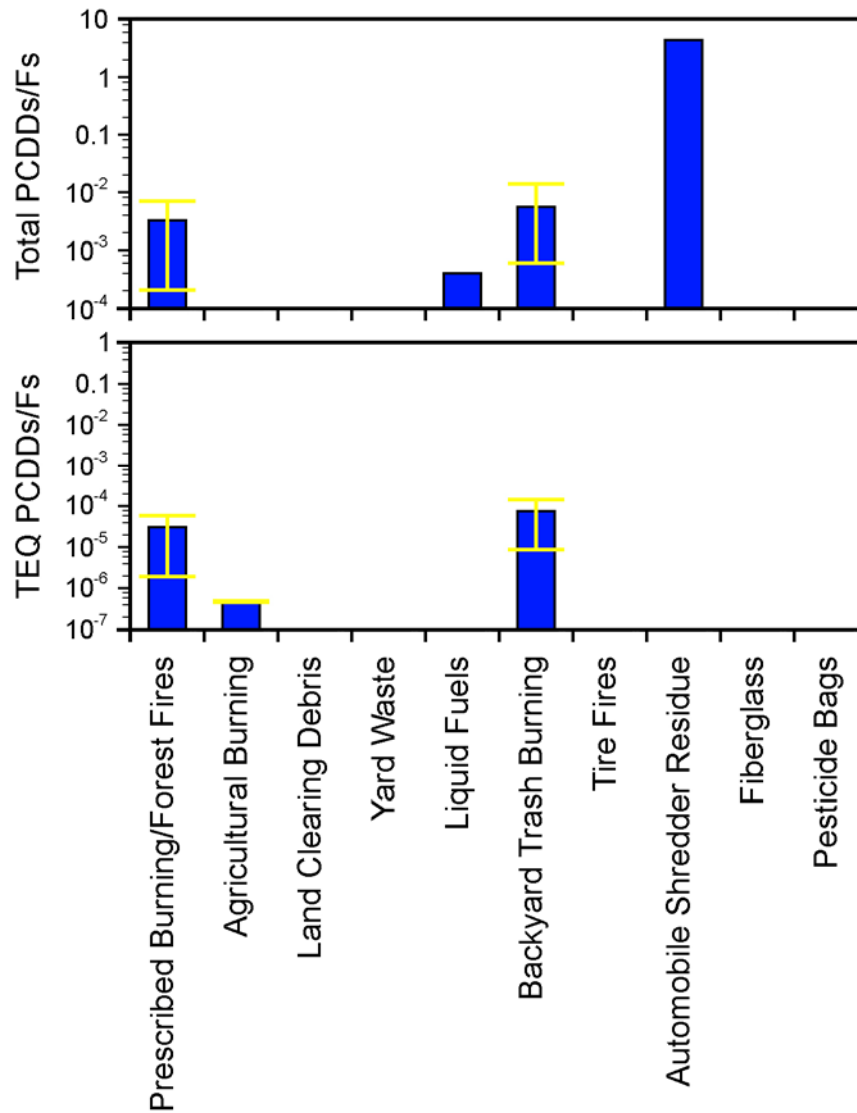


Figure 4-4 – PCDDs/Fs from Open Burning Sources (mg/kg burned)

## **5.0 – CONCLUSIONS**

### ***5.1 – Purpose of Document***

The purpose of this document is:

- To report on types of open burning activities and the availability of organic air toxics emissions data;
- To report on methodologies for developing open burning air toxics emissions data, including methods for measuring emissions and for converting the data into forms useful for emissions inventory development and source emissions comparisons;
- To compare emissions of different organic air toxic pollutants within open burning source classifications on a per mass of material burned basis;
- To compare emissions of different organic air toxic pollutants from open burning in general on a per mass of material burned basis;

### ***5.2 – Summary of Findings***

A detailed literature search was performed to collect and collate available data reporting emissions of organic air toxics from open burning sources. Availability of data varied according to the source and the class of air toxics of interest. VOC and PAH data were available for many of the sources. Non-PAH SVOC data were available for several sources. Carbonyl and PCDD/F data were available for only a few sources. There were several sources for which no emissions data were available at all. Several observations were made of the data including:

Biomass open burning sources typically emitted less VOCs than anthropogenic sources per kg of material burned, particularly those where polymers were concerned.

Biomass open burning sources typically emitted less SVOCs and PAHs than anthropogenic sources per kg of material burned. Burning pools of crude oil and diesel fuel produced significant amounts of PAHs relative to other types of open burning. PAH emissions were highest when combustion of polymers was taking place.

Based on very limited data, biomass open burning sources typically produced higher levels of carbonyls than anthropogenic sources per kg of material burned, probably due to oxygenated structures resulting from thermal decomposition of cellulose.

Based on very limited data, PCDD/F emissions per kg of material burned varied greatly from source to source, and exhibited significant variations within source categories. This high degree of variation is likely due to a combination of factors, including fuel composition, fuel heating value, bulk density, oxygen transport, and combustion conditions. This highlights the importance of having acceptable test data for PCDD/F emissions from open burning so that contributions of sources to the overall PCDD/F emissions inventory can be better quantified.

### ***5.3 – Data Gaps and Recommendations***

Several sources appear to have the potential for being significant sources of pollutants, and for some of the compounds that are considered persistent bioaccumulative

toxics (PBTs), including PCDDs/Fs, PAHs, and hexachlorobenzene, there exists potentially important data gaps that should be filled by additional research. Particular sources of concern for which additional data would be useful include:

- Forest fires;
- Land-clearing debris;
- Landfill fires and burning dumps;
- Construction debris;
- Copper wire reclamation.

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16. ABSTRACT A detailed literature search was performed to collect and collate available data reporting emissions of organic air toxics from open burning sources. Availability of data varied according to the source and the class of air toxics of interest, and there were several sources for which no emissions data were available at all. Several observations were made including 1) biomass open burning sources typically emitted less VOCs than open burning sources with anthropogenic fuels on a mass emitted per mass burned basis, particularly those where polymers were concerned; 2) biomass open burning sources typically emitted less SVOCs and PAHs than anthropogenic sources on a mass emitted per mass burned basis; burning pools of crude oil and diesel fuel produced significant amounts of PAHs relative to other types of open burning; PAH emissions were highest when combustion of polymers was taking place; 3) based on very limited data, biomass open burning sources typically produced higher levels of carbonyls than anthropogenic sources on a mass emitted per mass burned basis, probably due to oxygenated structures resulting from thermal decomposition of cellulose. Local burn conditions could significantly change these relative levels. Based on very limited data, PCDD/F emissions varied greatly from source to source and exhibited significant variations within source categories.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Polycyclic Aromatic Hydrocarbons Organic Compounds Chemical Properties Toxicity Dioxins  Furans		Air Pollution Control Stationary Sources	13B  07C  07D 06T
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