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Progress in Energy and Combustion Science 30 (2004) 1–32

PROGRESS IN ENERGY AND COMBUSTION SCIENCE

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Emissions of organic air toxics from open burning: a comprehensive review

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Received 15 December 2002; accepted 14 August 2003

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. The sources that were included in this paper are: Accidental Fires, Agricultural Burning of Crop Residue, Agricultural Plastic Film, Animal Carcasses, Automobile Shredder Fluff Fires, Camp Fires, Car–Boat–Train (the vehicle not cargo) Fires, Construction Debris Fires, Copper Wire Reclamation, Crude Oil and Oil Spill Fires, Electronics Waste, Fiberglass, Fireworks, Grain Silo Fires, Household Waste, Land Clearing Debris (biomass), Landfills/Dumps, Prescribed Burning and Savanna/Forest Fires, Structural Fires, Tire Fires, and Yard Waste Fires. 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 semi-volatile 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 known sources for which no emissions data were available at all. It is desirable that emissions from those sources be tested so that the relative degree of hazard they pose can be assessed. 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 and other persistent bioaccumulative toxic (PBT) 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 and PBT emissions from open burning so that contributions of sources to the overall PCDD/F and PBT emissions inventory can be better quantified.

Keywords: Uncontrolled combustion; Open burning; HAPS; Air toxics; Emissions

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doi:10.1016/j.pecs.2003.08.001

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1. 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 (EFs), 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 review 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 (conversion to water [H_2O] and carbon dioxide [CO_2]) 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_4) and other light hydrocarbons, volatile organic compounds (VOCs) such as benzene, and semi-volatile 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 [1]. As industrial sources reduce their emissions in response to environmental regulations, non-industrial sources such as open burning begin to dominate the emissions inventory.

Air emissions from open burning can also have impacts to other environmental media such as surface water and the sensitive species that occur in these media [2].

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.
- Open burning is a transient combustion phenomenon, frequently with heterogeneous fuels; it is difficult to attribute emissions to a single component of the fuel.

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 US 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 following databases were included in the search: CAB Abstracts, Energy Science and Technology, Environmental Bibliography, General Science Abstracts, NTIS, EI Engineering and Environment and PubSci. It is probable that other references exist, but these literature searches of these databases did not yield them.

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_x and SO_x). The US EPA's AP-42 EF database [3] 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 [1]. 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 EFs are more well-developed.

US 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 [4], which has provided additional information to supplement AP-42 in some areas.

Andreae and Merlet [5] published a detailed review of emissions of air toxics, aerosols, and trace gases from open burning of biomass. 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 presents the results of the literature search compiled by data types and measurement methods.

Of the open burning sources listed in Table 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.

For general information on the prevalence, science, ecological role, and history of open burning processes the reader may wish to consult the five volume ‘Cycle of Fire’ series [6]. Country by country summaries of fire activity are regularly published in the International Forest Fire News [7], a UN related publication edited by the Johann Goldammer of the Fire Ecology Research Group at the Max Planck Institute for Chemistry (http://www.uni-freiburg.de/fireglobe/).

1.2. Purpose and scope of the review

The purpose of this review 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 review.

The air pollutants used in the detailed analysis will emphasize 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 [8]. 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 (such as HAP precursors) will be discussed in the text as appropriate. Table 2 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 (AFs) will be discussed in detail, although AFs 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.

2. 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 EFs from open burning of biomass [9]. 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.
- 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 AF, 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. It must be noted that for open burning situations, particularly for organic air toxics, combustion condition factors are likely to significantly impact the EFs, perhaps

Table 1
Summary of open burn literature search results

	Total citations	Type of pollutant reported							Type of study							Covered in previous reviews		
		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	Andreae
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	×		×
Agricultural burning	15	11	8	6	6	1	2	1	0	4	7	1	0	0	5	×		×
Land clearing	8	7	5	5	6	0	1	0	0	0	5	2	0	0	1		×	
Yard waste	8	7	7	0	2	0	1	0	2	2	1	0	0	0	3	×	×	
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	×	×	
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	×		
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	×		
Structural fires	2	1	2	1	0	0	1	0	0	1	0	0	0	0	1		×	
Car–boat–train	2	2	2	0	0	0	0	0	0	0	0	0	0	0	2	×	×	
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			

Number of citations found by type.

Table 2
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	Dimethylcarbamoylchloride	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	Dimethylphthalate	79-46-9	2-Nitropropane
79-06-1	Acrylamide	77-78-1	Dimethylsulfate	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	Allylchloride	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	Ethylacrylate	7803-51-2	Phosphine
98-07-7	Benzotrichloride	100-41-4	Ethylbenzene	7723-14-0	Phosphorus
100-44-7	Benzylchloride	51-79-6	Ethylcarbamate (urethane)	85-44-9	Phthalicanhydride
92-52-4	Biphenyl	75-00-3	Ethylchloride (chloroethane)	1336-36-3	Polychlorinated biphenyls
117-81-7	Bis(2-ethylhexyl)phthalate (DEHP)	106-93-4	Ethylenedibromide (dibromoethane)	1120-71-4	1,3-Propanesultone
542-88-1	Bis(chloromethyl)ether	107-06-2	Ethylenedichloride (1,2-dichloroethane)	57-57-8	β-Propiolactone
75-25-2	Bromoform	107-21-1	Ethyleneglycol	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	Ethyleneoxide	78-87-5	Propylenedichloride (1,2-dichloropropane)
63-25-2	Carbaryl	96-45-7	Ethylenethiourea	75-56-9	Propyleneoxide
75-15-0	Carbon disulfide	75-34-3	Ethylidenedichloride	75-55-8	1,2-Propylenimine (2-methylaziridine)
56-23-5	Carbon tetrachloride	50-00-0	Formaldehyde	91-22-5	Quinoline
463-58-1	Carbonylsulfide	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	Styreneoxide
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	Hexamethylenediisocyanate	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	Chloromethylmethylether	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	Maleicanhydride	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	Methylbromide (bromomethane)	121-44-8	Triethylamine
132-64-9	Dibenzofuran	74-87-3	Methylchloride (chloromethane)	1582-09-8	Trifluralin
96-12-8	1,2-Dibromo-3-chloropropane	71-55-6	Methylchloroform (1,1,1-trichloroethane)	540-84-1	2,2,4-Trimethylpentane
84-74-2	Dibutylphthalate	78-93-3	Methylethylketone (2-butanone)	108-05-4	Vinylacetate
106-46-7	1,4-Dichlorobenzene	60-34-4	Methylhydrazine	593-60-2	Vinylbromide
91-94-1	3,3′-Dichlorobenzidine	74-88-4	Methyliodide (iodomethane)	75-01-4	Vinylchloride
111-44-4	Dichloroethylether(bis[2-chloroethyl]ether)	108-10-1	Methylisobutylketone (hexone)	75-35-4	Vinylidenechloride (1,1-dichloroethylene)
542-75-6	1,3-Dichloropropene	624-83-9	Methylisocyanate	1330-20-7	Xylenes
62-73-7	Dichlorvos	80-62-6	Methylmethacrylate	95-47-6	*o*-Xylene
111-42-2	Diethanolamine	1634-04-4	Methyl-*tert*-butylether	108-38-3	*m*-Xylene
64-67-5	Diethylsulfate	101-14-4	4,4′-Methylenebis(2-chloroaniline)	106-42-3	*p*-Xylene
119-90-4	3,3′-Dimethoxybenzidine	75-09-2	Methylenechloride (dichloromethane)	N/A	Polycyclic organic matter
60-11-7	4-Dimethylaminoazobenzene	101-68-8	4,4′-Methylenediphenyldiisocyanate (MDI)		

even more significantly than the impacts of the fuel itself. Because of this, there are usually greater uncertainties in the EFs of organic air toxics from open burning than with criteria pollutants from combustion of the same fuels.

- 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_2). For example, the ER of chloromethane (CH_3Cl) relative to CO is calculated using the formula shown in Eq. (2.1) [5]:

$$\mathrm{ER}_{\mathrm{CH_3Cl/CO}} = \frac{(\mathrm{CH_3Cl})_{\mathrm{smoke}} - (\mathrm{CH_3Cl})_{\mathrm{ambient}}}{(\mathrm{CO})_{\mathrm{smoke}} - (\mathrm{CO})_{\mathrm{ambient}}} \tag{2.1}$$

For calculation of ERs from smoldering fires, CO is generally used as the reference species. For flaming fires, CO_2 is generally used as the reference species [5]. 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 Eq. (2.2) [5]

$$\mathrm{EF_x} = \mathrm{ER_{(x/y)}} \frac{\mathrm{MW_x}}{\mathrm{MW_y}} \mathrm{EF_y} \tag{2.2}$$

where $\mathrm{EF_x}$ is the emission factor of species x; $\mathrm{ER_{(x/y)}}$, the molar emission ratio (ER) of species x relative to species y; $\mathrm{EF_y}$, the emission factor of species y; $\mathrm{MW_x}$ and $\mathrm{MW_y}$ are the molecular weights of species x and y, respectively. If the mass ERs are known, then the emission factors can be calculated using Eq. (2.3)

$$\mathrm{EF_x} = \mathrm{ER_{(x/y)}} \mathrm{EF_y} \tag{2.3}$$

where $\mathrm{ER_{(x/y)}}$ is the mass ER of species x relative to species y.

Each EF in the AP-42 database [3] is given a rating from *A–E*, with *A* being the best. An EFs rating is a general indication of the reliability, or robustness, of that factor. Test data quality is rated *A–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. Activity factors

In order to determine the contribution of a given source to the emissions inventory on a local, national, or global basis, the AF is defined in terms of the mass combusted per unit time or per unit area within the region or facility of interest. The desired units of AFs vary depending on the needs of the individual estimating the emissions. Examples of alternative AF needs include:

- a reader who is interested in how open burning contributes to global or regional inventories or ambient concentrations of a given air toxic probably would be interested in activity data on a global or regional scale (depending on how persistent/globally transported the air toxic of interest was)
- a reader who is interested in assessing a given local problem (i.e. 'is my town getting built up enough that we need prohibit burning yard waste' or 'is that tire fire on the other side of the fence a reason to evacuate my school') needs activity data on a local scale.

Estimation of AFs can be done many ways; although estimating AFs is outside the scope of this paper, the EIIP documents, especially the EIIP open burning emission factor guidance document [10] describes several ways to estimate AFs.

Eq. (2.4) illustrates how emissions are calculated using EFs and AFs:

$$\text{emissions} = \text{EF} \times \text{AF} \tag{2.4}$$

Table 3 lists sources for AFs and values of emission factors of criteria pollutants for the sources listed in this paper, where available.

2.3. 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 are based on ambient pollutant measurements. VOCs are commonly measuring using EPA Method TO-14 [28] using SUMMA canisters that are cleaned and evacuated prior to sampling. A fraction of each batch of canisters is 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. Fig. 1 shows a SUMMA canister, flow meter, and sampling pump.

SVOCs are sampled according to Method TO-13 [29], 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 (CH_2Cl_2), concentrated, and analyzed by GC/MS. Fig. 2 shows a Method TO-13 train.

2.4. 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 US 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 [30]. Fig. 3 shows the concept of the Nomad sampler.

2.5. Laboratory simulations

An effective way to develop emission factors for open burning sources is through laboratory simulations using a flux chamber approach. In a laboratory simulation, small amounts of the material in question are combusted in as representative a manner as possible while making detailed measurements of the mass of burning material, combustion air and dilution air flow rates, relevant temperatures, and the concentrations of the pollutants of interest.

The earliest laboratory simulation of open burning that attempted measurement of air toxics and other similar pollutants was reported in 1967 [31]. This study used a conical shaped tower suspended above the burning bed to capture the plume in such a way that conventional stack sampling approaches could then be used.

The US EPA's National Risk Management Research Laboratory has an Open Burning Test Facility (OBTF) located in Research Triangle Park, NC. The OBTF has been used for several test programs to evaluate emissions from a wide variety of open burning sources. Sources that have been tested in the OBTF include tire fires [17,32,33], fiberglass burning [26], open burning of land clearing debris [24], automobile shredder fluff fires [18], open burning of household waste in barrels [34–37], agricultural plastics [38], forest fires [30], and agricultural burning [39]. In limited cases where field data are available to support measurements from the OBTF, results appeared to agree within an order of magnitude [32]. In the OBTF, shown in Fig. 4 as configured for experiments investigating open burning of household waste in barrels [37], 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.

Pollutant concentrations measured in the OBTF can be converted to the mass emissions of individual pollutants (emission factor units) using Eq. (2.5)

$$\mathrm{EF} = \frac{C_{\mathrm{sample}} Q_{\mathrm{OBTF}} \tau}{m_{\mathrm{burned}}} \tag{2.5}$$

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

2.6. 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 [40]. 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. Fig. 5 shows a diagram of the wind tunnel facility.

2.7. Bang box sampling

The US Army, as part of a test program to determine emissions from Open Burning/Open Detonation (OB/OD) of old munitions, built a facility specially designed for emissions testing of munitions. This facility, called a ‘Bang Box’ is located at the Dugway Proving Grounds [41] and consists of a 1000 m^3 vinyl plastic air-inflated dome that contains a blast shield and analytical equipment and allows researchers to investigate a half-pound of explosives per blast or five pounds of propellant per burn.

2.8. Remote sensing

Aircraft and satellite remote sensing has been employed to collect emissions data from biomass burning for a multitude of programs including the South African Regional Science Initiative in the year 1992 and 2000, the Experiment for Regional Sources of Sinks and Oxidants, 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. 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. Other groups are using remote sensing data coupled with GIS databases to document the complex interaction between fuel loads, land use and open burning and the effect of these open burning processes have on endangered species preservation and surface water quality [42].

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 [43]. In a scale of several hundred meters, Open Path Fourier Transform Infrared (OP-FTIR) instrumentation is typically used, where 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 several kilometer scale is needed, other instrumental techniques including Differential optical absorption spectroscopy, long path Tunable Diode Laser Absorption Spectroscopy, and Light Detection and Ranging (LIDAR) for aerosol detection and Differential absorption LIDAR for gaseous detection are also available [44–46]. 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 PM extinction measurements [44].

Table 3
Activity factors and criteria pollutant emission factors for open burning sources

Source	Activity factor information	CO emission factor (g/kg material burned)	SO_2 emission factor (g/kg material burned)	PM emission factor (g/kg material burned)	NO emission factor (g/kg material burned)	TOC methane (g/kg material burned)	TOC non-methane (g/kg material burned)	EF source	EF notes
Prescribed burning, savanna and forest fires	In 2002, the US had 99,702 fires consuming 2,291,401 ha [7]. Conversion factors between area (ha) and mass (kg) are discussed for various fuel types in EIIP, [10]. See also Ref. [11]. Updated information worldwide is reported at the web address in Ref. [12]. Updated US information is at National Interagency Fire Center [13]. See also Refs. [14,15]	114.7		16.6				[23]	Averaged over all regions
Agricultural burning	Included in the Global Vegetation Fire Inventory [12]. See also Refs. [14,15]	58.0		11.0		2.7	9.0	[23]	Entry for 'unspecified' used
Land clearing	Discussed in EIIP, mostly for application on a state and regional scale [10]. Included in the Global Vegetation Fire Inventory [12]	16.0		10.3	0.1	8.0		[24]	Averaged over all conditions; OC as methane; PM as PM10
Yard waste	Discussed in EIIP, mostly for application on a state and regional scale [10]	56.0		19.0		6.0	14.0	[23]	Entry for 'unspecified' used
Camp fires									
Animal carcasses									
Crude oil		30.0		170.0				[25]	
Accidental fires									
Household waste	[1]	42.0	0.5	8.0	3.0	6.5	15.0	[23]	
Landfills/dumps	FEMA [16] cites a figure of 8400 fires per year in the US for this category								
Tire fires	Ryan [17] cites a figure of 170 million scrap tires discared per year in the US in landfills, above ground stockpiles and illegal dump: the fraction eventually subject to open burning is not known			119.0				[17]	

Fluff fires	Approximately 9.1 × 10^8 kg per year of fluff is produced in the US; the fraction eventually subject to open burning is unknown [18]. Information on the size of individual fires also included in Ref. [18]	62.0		50.0	2.0	5.0	16.0	[23]	
Fiberglass		122.8		248.5		157.4		[26]	Average of all conditions; TOC as methane
Agricultural plastic film				5.7				[27]	Average of baseline and test; assumes 0.1 kg bag
Structural fires	Activity factors for structure fires are extensively discussed in EIIP [10]. See also Ref. [11]. Updated information on residential structure fire numbers (but not mass) are at FEMA [19]								
Car–boat–train	EIIP [10] cites 402,000 vehicle fires per year in the US and an available fuel load of 500 lb per vehicle. See also Ref. [11].	62.4		50.0	2.0	5.0	16.0	[23]	
Construction debris	One source estimates 126 million tons of construction and demolition (C&D) debris was produced in 2001 [20]. Another source [21] estimated 300–325 million tons of C&D debris is produced annually in the US, about half of which is recycled								
Grain silo									
Copper wire	US EPA [1] reports that the activity factor for this source is unknown. Semi-quantitative information on the destruction of various electronic wastes during recycling is reported in Ref. [22]								

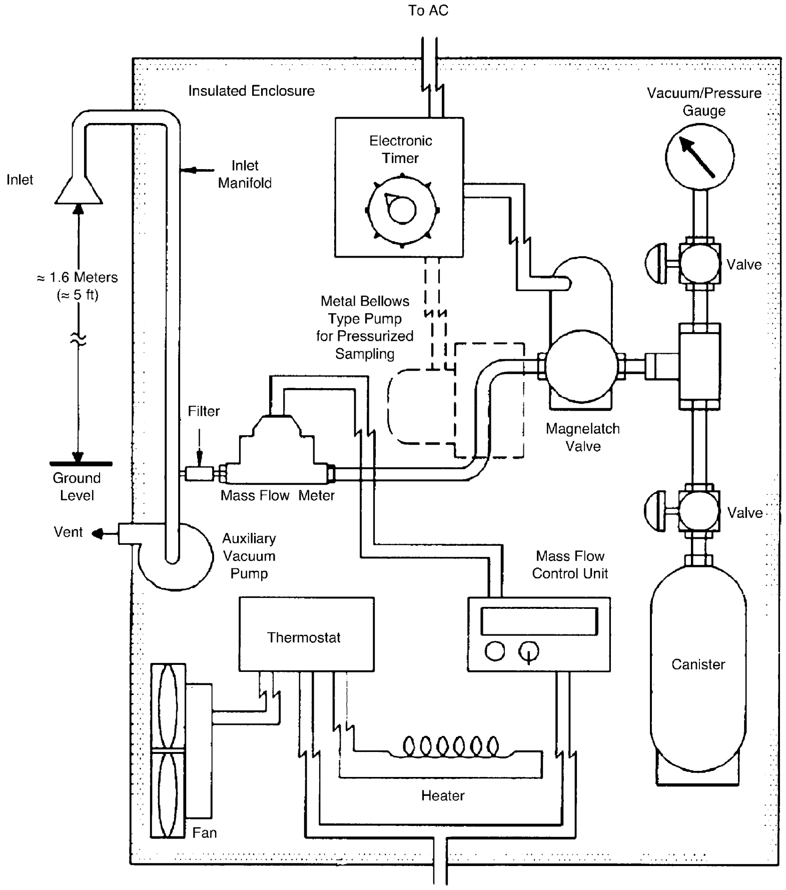

Fig. 1. SUMMA canister and gas metering equipment.

2.9. 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.

2.10. 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

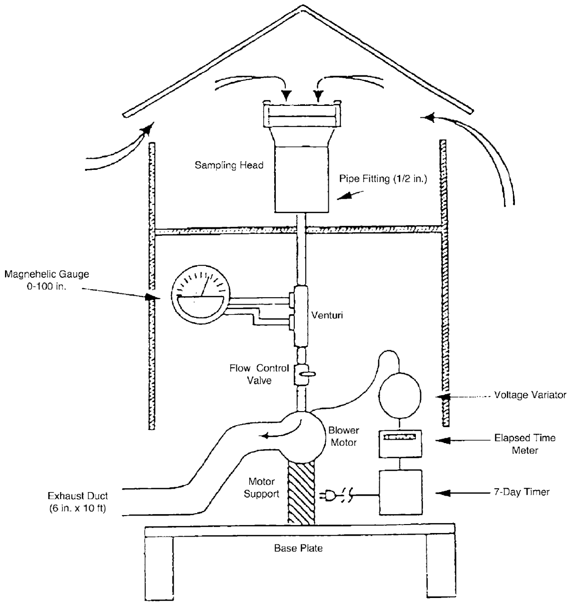

Fig. 2. Method TO-13 train.

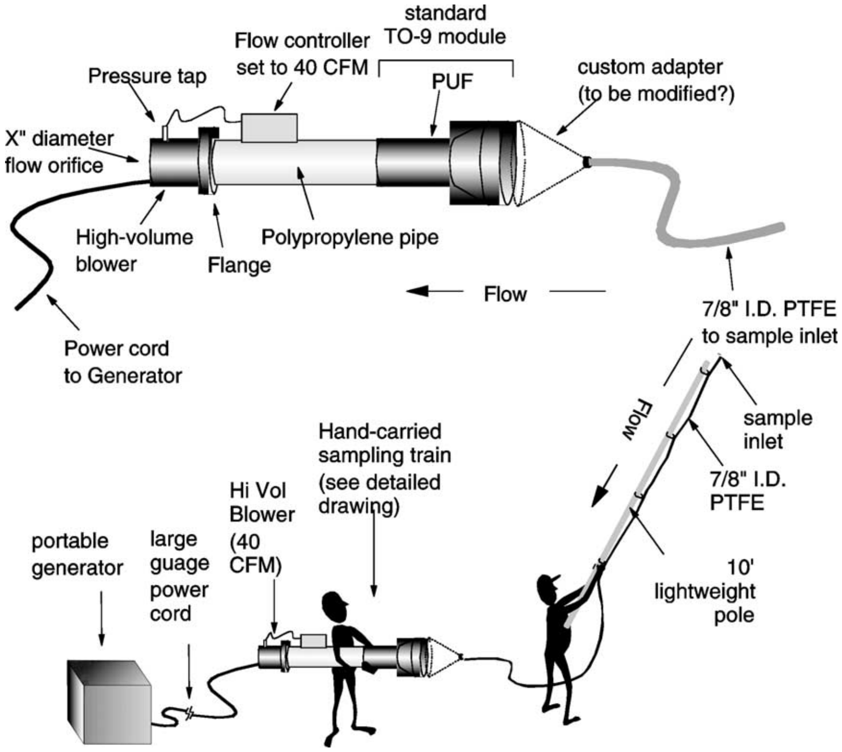

Fig. 3. Nomad sampler.

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.

2.11. 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 analysis lists for any sampling activities.

3. 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 being open burned include: biomass fuels, liquid fuels, solid anthropogenic fuels, and miscellaneous materials. It must be noted that unlike emissions of criteria pollutants, where fuel type as opposed to combustion conditions dominates the emissions, organic air toxics emission levels are frequently determined by local combustion conditions within the burn.

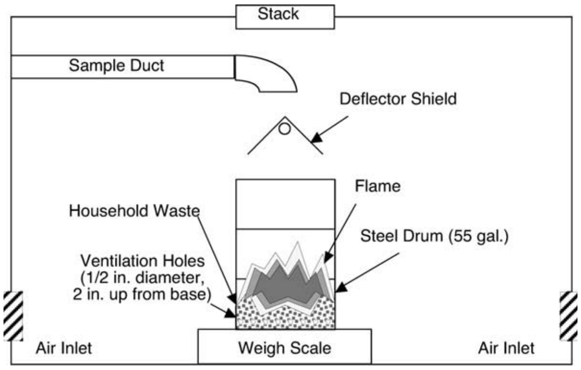

Fig. 4. US EPA open burning test facility.

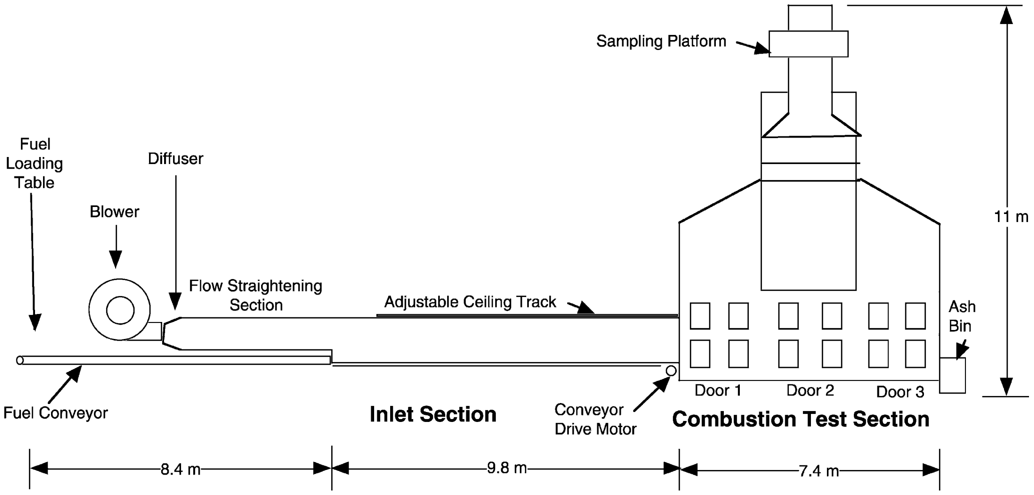

Fig. 5. U.C. Davis wind tunnel facility.

Some pollutants, such as PCDDs/Fs, exhibit order of magnitude variations between identical test conditions [37].

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 [47]. 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 [23] 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 [48,49] 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. [50] reported PAH data from a field study of emissions from prescribed savanna burns. 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. [51] performed a laboratory study examining emissions of SVOCs from burning forest materials. 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 [5]. 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 US EPA. Gullett et al. [30] performed laboratory simulations to estimate the emission factor of PCDDs/Fs from forest fires 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. [52], reported on elevated PCDD/F concentrations found during a prescribed forest fire in Australia; however, no emission factor units were estimated.

Yamasoe et al. [53], 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.

Barber et al. [2] reported that biomass burning, specifically temperate region forest fires, could produce fly and bottom ash containing various cyanide species. These cyanide compounds could then be leached into adjacent waterways placing sensitive fish species at risk.

Based on these sources of information, Table 4 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 [30], was reported as a range rather than an average value. PCDDs/Fs are reported in terms of the total quantities and in terms of the toxic equivalence quantities (TEQs). In addition, some data sets included data on the individual homologue groups including tetra-, penta-, hexa-, hepta-, and

Table 4
Emissions from prescribed burning and forest fires (mg/kg burned)

Class	Compound	Savanna and grassland	Tropical forest	Extratropical forest
VOCs (1)	Butadiene	70		60
	Benzene	230	400	490
	Toluene	130	250	400
	Xylenes	45	60	200
	Ethylbenzene	13	24	48
	Styrene	24	30	130
	Methylchloride	75	100	50
	Methylbromide	2.1	7.8	3.2
	Methyliodide	0.5	6.8	0.6
	Acetonitrile	110	180	190
SVOCs (1)	Furan[a]	95	480	425
	2-Methylfuran[a]	46	170	470
	3-Methylfuran[a]	8.5	29	50
	2-Ethylfuran[a]	1	3	6
	2,4-Dimethylfuran[a]	8	24	19
	2,5-Dimethylfuran[a]	2	30	50
	Tetrahydrofuran[a]	16	16	20
	2,3-Dihydrofuran[a]	12	13	17
	Benzofuran[a]	14	15	26
	Furfural[a]	230	370	460
	PAH	2.4	25	25
	Phenol	3	6	5
Carbonyls (1)	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[a]	435	620	555
	Methylethylketone	260	430	455
	2,3-Butanedione[a]	570	920	925
	Pentanones[a]	15	28	90
	Heptanones[a]	6	2	5
	Octanones[a]	15	19	20
	Benzaldehyde[a]	29	27	36
PCDDs/Fs (2)	Total PCDDs/Fs			1.5×10^{-4}–6.7×10^{-3}
	TEQ PCDDs/Fs			2.0×10^{-6}–5.6×10^{-5}

Source. (1) Ref. [5]. (2) Ref. [30].

[a] Compound of interest not on HAP list.

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. Agricultural activities use 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. [54–57] published several papers and reports 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. [39] have performed laboratory simulations to estimate emissions of PCDDs/Fs from rice straw and wheat straw. Guyton et al. [58] performed sampling from sugar cane field burning, but no emission factor units were presented. PCDDs/Fs were sampled but not detected. Several VOC and SVOC compounds were qualitatively identified but not quantified. The differences in emissions between seemingly similar fuels that are illustrated in Table 5 is an example of how combustion conditions under which the sampling occurred could account for some of the variations.

Table 5
Emissions from agricultural/crop burning (mg/kg burned)

Class	Compound	Barley straw	Corn stover (3)	Rice straw	Wheat straw
VOCs (1)	Acetone[a]	3.77	4.34	4.01	4.39
	Methylbutanone (isopropylmethylketone)			11	
	Furancarboxaldehyde (furfural)[a]			208	
	Benzene				
	Dimethylfuran[a]	177			
	2-Methyl-2-cyclopenten-1-one[a]		36	127	48
	2-Chlorophenol[a]	52	81	173	
	Toluene		22		
	Benzonitrile[a]		29		
	Benzaldehyde	82	46	77	52
	Methylphenol (hydroxytoluene)[a]			2	
	Styrene	36	26	35	35
	Xylene				
	Benzofuran[a]	18		16	26
SVOCs	Methoxymethylphenol (creosol)	72			
	Phenol			45	
PAHs (1)	Naphthalene (4)	80.30	4.48	8.39	196.19
	2-Methylnaphthalene[a] (4)	2.70	2.63	5.43	1.07
	Acenaphthylene	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
	Benz[*aj*]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[*ghi*]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 (2)	TEQ PCDDs/Fs			5.37×10^{-7}	4.52×10^{-7}

Source. (1) Ref. [56]. (2) Ref. [39]. (3) Composite of 2 conditions. (4) Data flagged as questionable by Jenkins et al.

[a] Compound of interest not on HAP list.

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 [59]. Emissions data for air toxics are not available, although EPA has a current research project to measure PCDD/F emissions from sugarcane burning.

Table 5 lists the emissions for air toxics from various agricultural/crop burning sources.

3.1.3. Land clearing debris

Disposal of debris generated by landclearing 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 was the case for agricultural and crop burning, the papers and reports by Jenkins et al. [54–57,60] provided a wealth of information on emissions from spreading and pile fires for Douglas Fir, Almond, Walnut, and Ponderosa Pine slash based on wind tunnel studies. The US EPA reported on a laboratory simulation study [24] 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 6 lists the air toxic emission factors from open burning of land clearing debris.

3.1.4. Yard waste

The burning of leaves and other yard waste is yet another category of open burning which has data gaps in the available information. The AP-42 database [3] and its expanded EIIP documents [4,10] did not have any speciated VOCs, SVOCs, metals, or PCDD/F data. The early laboratory simulation study by Gerstle and Kemnitz [31], 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 [61] on the health effects from leaf burning that included data on speciated SVOC from burning leaves from three different species of trees. Table 7 lists the air toxics measured from open burning of yard waste, showing the mean yields from six replicate measurements of three species and one composite sample.

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. [62] performed a study to examine conifer wood smoke from a campfire for potential organic biomarkers. Another study [63] 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, although the authors did postulate that the increase was probably due to the bonfires and not 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). The Department of Health from the UK published a report on their web site giving guidance on how to reduce environmental impacts from open burning of animal carcasses on pyres [64]. The data presented in that report were based primarily on emissions from the fuels used to sustain the pyres. The contributions of the animal carcasses to the emissions were based on assuming that the animal carcasses had the same emission factors as straw or crematoria emissions. Because these emission results were based on extrapolation of emissions from similar (and not similar) sources, the quality of the data are highly questionable, so they are not included in this analysis. 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 [65] and Stevens et al. [66] reported on the characterization of the plume from those fires. Sampling

Table 6
Emissions from open burning of land clearing debris (mg/kg burned)

Class	Compound	Tennessee debris (1)	Florida debris (1)	Douglas fir slash (2)	Ponderosa pine slash (2)	Almond prunings (2)	Walnut prunings (2)
VOCs	1,2,4-Trimethylbenzene[a]	18.0	7.5				
	1,3,5-Trimethylbenzene[a]	4.5	1.5				
	1,3-Butadiene	133.0	74.5				
	2-Butanone	31.8	28.0				
	4-Ethyltoluene[a]	32.5	8.5				
	Acetone[a]	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[a]					5.0	
	Benzylchloride	1.8					
	Bromomethane		1.0				
	Butylmethylether		1.0				
	Chloromethane	5.3	94.0				
	cis-1,2-Dichloroethene	14.3	32.0				
	Ethylbenzene	32.0	15.0				
	Limonene[a]	81.5					
	Xylene	117.5	43.0		56.0	3.0	2.0
	Methylisobutanone						8.0
	Ethylenechloride	2.0	1.0				
	Pinene[a]	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[a]	10.10	0.97				
	Creosol				403		
	Furancarboxaldehyde (furfural)[a]				335	18	18
	1,1-Biphenyl	2.39	1.49				
	Phenol	56.98	54.35				
	2-Cresol	20.83	17.57				
	2,4-Dimethylphenol[a]	10.28	14.31				
	Dibenzofuran	3.19	3.31				
	Dibutylphthalate		0.08				
	Bis(2-ethylhexyl)phthalate	8.44	5.59				
PAHs	Naphthalene	17.62	14.06	13.57	16.96	7.31	14.56
	2-Methylnaphthalene[a]	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[*ghi*]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[*e*]pyrene			0.05	0.02	0.02	0.02

Source. (1) Ref. [24]. (2) Ref. [56].

[a] Compound of interest not on HAP list.

Table 7
Emissions 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
	Methylanthracenes	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/benz[*a*]anthracene	1.277	0.943	0.67	0.523
	Methylchrysenes	0.98	0.393	0.438	0.253
	Benzofluoranthenes	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. Ref. [61].

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. [67] 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 [68–71] and included plume, upstream, and downstream sampling for various compounds, including particulate-bound PCDDs/Fs.

Another study [25] that included emission factors for criteria pollutants was given to convert the data to emission factor units using Eq. 2.2, and using ERs relative to CO_2. Based on those calculations, Table 8 was constructed to list the air toxics produced from burning pools of oil.

There has been a significant amount of work performed to model the behavior of pool fires from a heat and mass transfer standpoint, although these models do not predict air toxics formation. Fisher et al. [72] modeled small-scale pool fires and successfully compared the results to field measurements. McGrattan et al. [73] modeled PM emissions from large-scale pool fires. Planas-Cuchi and Casal [74] made measurements of temperatures within pool fires and developed empirical correlations to predict temperature distributions within pool fires. It may be that complex chemical kinetics could be coupled with models such as these to predict emissions of organic air toxics from pool fires if emissions data are not available.

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 US 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 [31]. A study by the US EPA [34,35] 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

Table 8
Emissions from burning pools of liquid fuels (mg/kg burned)

Class	Compound	Fuel oil	Crude oil
VOCs	Benzene	1022	251
	Toluene	42	
	Ethylbenzene	10	
	Xylenes	25	
	Nonane	13	
	Ethyltoluenes[a]	22	
	1,2,4-Trimethylbenzene[a]	32	
Carbonyls	Formaldehyde	303	139
	Acetaldehyde	63	32
	Acrolein	39	11
	Acetone[a]	35	20
	Propionaldehyde		
	Crotonaldehyde[a]	6	
	Methylethylketone	13	7
	Benzaldehyde[a]	104	44
	Isovaleraldehyde[a]	17	5
	Valeraldehyde[a]		
	p-Tolualdehyde[a]		13
	Methylisobutylketone	11	
	Hexanal[a]		
	2,5-Dimethylbenzaldehyde[a]	13	
PAHs	Naphthalene	162	44
	Acenaphthylene	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*]fluorine	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^{-5}
	OCDD		1.34×10^{-4}
	TCDF		2.05×10^{-4}
	PeCDF		
	HxCDF		1.86×10^{-5}
	HpCDF		
	OCDF		
	Total PCDD/F		4.28×10^{-4}

Source. Based on pollutant concentrations from Ref. [69] and PM and CO emission factors from Ref. [25].

[a] Compound of interest not on HAP list.

characterize the PCDD/F emission factor from barrel burning [36,37]. The variation between duplicate runs of the 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 US [1]. Based on estimated AFs, barrel burning appears to be one of the largest measured sources of PCDD/F in the US now that maximum achievable control technology 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 9 lists the emissions for air toxics from open burning of household waste in barrels. To derive the emissions estimates in Table 10, the data for the four experimental conditions [34], 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 Ref. [37], and represent the average of baseline conditions reported in their experiments.

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. [75] presented data from both intentional and spontaneous fires at municipal landfills in Finland. Ettala et al. [76] 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. [77] that reported on emissions of criteria pollutants from both actual and simulated fires in Sweden. Table 10 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 10. 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 9 (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.

3.3.3. Tire fires

Approximately 240 million scrap rubber tires are discarded annually in the US [78,79]. 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

Table 9
Emissions from barrel burning of household waste (mg/kg material burned)

Class	Compound	Emissions
VOCs (1)	1,3-Butadiene	141.25
	2-Butanone	38.75
	Benzene	979.75
	Chloromethane	163.25
	Ethylbenzene	181.75
	m,*p*-Xylene	21.75
	Methylenechloride	17.00
	o-Xylene	16.25
	Styrene	527.50
	Toluene	372.00
SVOCs (1)	2,4,6-Trichlorophenol	0.19
	2,4-Dichlorophenol[a]	0.24
	2,4-Dimethylphenol[a]	17.58
	2,6-Dichlorophenol[a]	0.04
	2-Chlorophenol[a]	0.95
	2-Methylnaphthalene[a]	8.53
	2-Cresol	24.59
	3- or 4-Cresol	44.18
	Acetophenone	4.69
	Benzylalcohol[a]	4.46
	Bis(2-ethylhexyl) phthalate	23.79
	Di-*n*-butylphthalate	3.45
	Dibenzofuran	3.64
	Isophorone	9.25
	Pentachloro nitrobenzene	0.01
	Phenol	112.66
Chlorobenzenes (1)	1,3-Dichlorobenzene	0.08
	1,4-Dichlorobenzene	0.03
	1,2-Dichlorobenzene[a]	0.16
	1,3,5-Trichlorobenzene[a]	0.01
	1,2,4-Trichlorobenzene	0.10
	1,2,3-Trichlorobenzene[a]	0.11
	1,2,3,5-Tetrachloro benzene[a]	0.03
	1,2,4,5-Tetrachloro benzene[a]	0.02
	1,2,3,4-Tetrachloro benzene[a]	0.08
	1,2,3,4,5-Pentachloro benzene[a]	0.08
	Hexachlorobenzene	0.04
PAHs (1)	Acenaphthene	0.64
	Acenaphthylene	7.34
	Anthracene	1.30
	Benzo[*a*]anthracene	1.51
	Benzo[*a*]pyrene	1.40
	Benzo[*b*]fluoranthene	1.86
	Benzo[*ghi*]perylene	1.30
	Benzo[*k*]fluoranthene	0.67
	Chrysene	1.80
	Dibenzo[*ah*]anthracene	0.27
	Fluoranthene	2.77
	Fluorine	2.99
	Indeno[1,2,3-*cd*]pyrene	1.27
	Naphthalene	11.36
	Phenanthrene	5.33
	Pyrene	3.18
Carbonyls (1)	Acetaldehyde	428.40
	Acetone[a]	253.75
	Acrolein	26.65
	Benzaldehyde	152.03
	Butyraldehyde[a]	1.80
	Crotonaldehyde[a]	33.53
	Formaldehyde	443.65
	Isovaleraldehyde[a]	10.20
	p-Tolualdehyde[a]	5.85
	Propionaldehyde	112.60
PCDDs/Fs and PCBs (2)	Total PCDDs/Fs	5.80×10^{-3}
	TEQ PCDDs/Fs	7.68×10^{-5}
	Total PCBs	1.26×10^{-1}
	TEQ PCBs	1.34×10^{-6}

Source. (1) Ref. [34]. (2) Ref. [37].
[a] Compound of interest not on HAP list.

processes, such as cement kilns and utility boilers [80–82]. Another potentially attractive option is the use of ground tire material as a supplement to asphalt paving materials. The Intermodal Surface Transportation Efficiency Act [83] mandates that up to 20% of all federally funded roads in the US include as much as 20 lb (9 kg) of rubber derived from scrap tires per ton (907 kg) of asphalt by 1997. Lutes et al. [84] measured the air emissions from adding tire rubber to asphalt. In spite of these efforts, less than 25% of the total amount of discarded tires are reused or reprocessed, and the remaining 175 million scrap tires are discarded in landfills, above-ground stockpiles, or illegal dumps. In addition,

Table 10
Emissions from burning dumps and landfill fires (ng/m^3)

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. Ref. [75].

these reclamation efforts do little to affect the estimated 2 billion tires (18 million tons) 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 (37,600 vs. 27,200 kJ/kg) [82]. 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 [17,33]. 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 [32]. A paper study prepared by Reisman [85] collected data on ambient monitoring near tire fires and compared the results to laboratory simulations. Based on these studies, Table 11 was constructed using the average of the four test conditions described in Ref. [33].

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. These occurrences are not frequent, but do happen on occasion. Combustion of automobile components (e.g. tires, seats, floor mats) was one of the sources presented in the original Gerstle and Kemnitz study [31]. Ryan and Lutes [18], reported on a laboratory simulation study where small quantities of shredder fluff were combusted, and extremely high organic emissions resulted, exceeding 200 g/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 12.

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 [26]. The types of fiberglass tested included samples from boat fabrication and building construction, where the glass fibers were bound within a resinous substrate. Data did not include fiberglass insulation. Numerous air toxics were measured in that study, a summary of which is shown in Table 13.

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. [27] 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 14, 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 control 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. [38] 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 where mutagenicity of the analytical extracts was measured using bioassay techniques.

3.3.7. Structural fires

Although criteria pollutant data and non-speciated VOC data from structural fires are presented in EIIP [4] and a paper by Brown et al. [86] no data on air toxic emissions from structural fires could be found. Carroll [87] examined emissions from burning of various components of structures, particularly PVC. Although generic emission factors were not reported, references were made to emissions data from some of the components that might be found in structures (e.g. insulation, wood, plastic).

3.3.8. Vehicle fires

This category of burning refers to fires of the vehicle itself, such 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 [3] and EIIP [4], they were derived primarily from Gerstle and Kemnitz [31] 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, although the work of Carroll [87] regarding emissions from structural fires may be applicable. The composition of the debris would have a profound

Table 11
Emissions from open burning of scrap tires (mg/kg burned)

Class	Compound	Emissions
VOCs	Benzaldehyde[a]	314.4
	Benzene	2180.55
	Benzodiazine[a]	15.55
	Benzofuran	12.55
	Benzothiophene[a]	20.5
	Butadiene	234.6
	Dihydroindene[a]	41.7
	Xylenes	928.95
	Dimethylhexadiene[a]	59.6
	Dimethyl,methylpropyl benzene[a]	7.45
	Dimethyldihydroindene[a]	19.85
	Ethenylbenzene[a]	776.6
	Ethenylcyclohexene[a]	66.9
	Ethenyl,dimethylbenzene[a]	15.45
	Ethenyl,methylbenzene[a]	16.8
	Ethenyldimethylcyclohexene[a]	175.2
	Ethenylmethylbenzene[a]	131.25
	Ethylbenzene	377.95
	Ethyl,methylbenzene[a]	405.15
	Ethynylbenzene[a]	160.75
	Ethynyl,methylbenzene[a]	394.65
	Isocyanobenzene[a]	318.55
	Limonene[a]	460
	Toluene	1367.75
	Methylindene[a]	228.25
	Methylthiophene[a]	9.05
	Methyl,ethenylbenzene[a]	66.15
	Methyl,methylethenylbenzene[a]	390.75
	Methyl,methylethylbenzene[a]	197.45
	Methyl,propylbenzene[a]	20.8
	Ethyleneindene[a]	41.45
	Methylethylbenzene[a]	152.15
	Propylbenzene[a]	78.3
	Styrene	652.7
	Tetramethylbenzene[a]	127.85
	Thiophene[a]	41.25
	Trimethylbenzene[a]	60.9
SVOCs	1-Methylnaphthalene[a]	279.15
	1,1′-Biphenyl,methyl[a]	5.55
	2-Methylnaphthalene[a]	389.95
	Benzisothiazole[a]	86.95
	Benzo[*b*]thiophene[a]	22.1
	Biphenyl	269.8
	Cyanobenzene[a]	370.25
	Dimethylbenzene[a]	620.05
	Dimethylnaphthalene[a]	109.6
	Ethyl,dimethylbenzene[a]	136.2
	Hexahydroazepinone[a]	411.8
	Indene[a]	421.3
	Isocyanonaphthalene[a]	4.7
	Methylbenzaldehyde[a]	43.3
	Phenol	533.05
	Propenylnaphthalene[a]	11.75
	Propenyl,methylbenzene[a]	261.8
	Trimethylnaphthalene[a]	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
	Benz[*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

Source. Ref. [33].

[a] Compound of interest not on HAP list.

impact on the emissions from open burning of those materials. Construction debris would include various plastics (vinyl siding, housewrap) and wood (both treated and untreated), so the open burning of construction debris would likely have different emissions from conventional scrap wood burning or land clearing debris burning activities. 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 [22], 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

Table 12
Emissions from open burning of automobile shredder residue (mg/kg burned)

Class	Compound	Emissions
VOCs	Acetaldehyde	761.7
	Acrolein	1678.2
	Acetonitrile	804.7
	Acrylonitrile	772.3
	Methylfuran	54.3
	Benzene	9583.7
	Toluene	10,692.8
	Chlorobenzene	1718.0
	Ethylbenzene	4963.5
	m/*p*-Xylene	1678.0
	Styrene	6528.0
	Ethylbenzene	2400.0
SVOC	1,2-Dichlorobenzene[a]	110.0
	Benzaldehyde[a]	1690.0
	Benzenebutanenitrile[a]	3340.0
	Biphenyl	330.0
	Bis(2-ethylhexyl)phthalate	2058.0
	Caprolactam	177.0
	Ethyltoluene[a]	140.0
	Ethynylbenzene[a]	460.0
	m/*p*-Xylene	1290.0
	Methylethylphenol[a]	260.0
	Phenol	990.0
	Phenylethanone[a]	1080.0
	Phthalicanhydride	230.0
	Quaterphenyl[a]	37.0
	Terphenyl[a]	40.0
	Trimethylbenzene[a]	140.0
PAH	Naphthylene	883.3
	Acenaphthylene	150.0
	Acenaphthene	13.3
	Fluorene	38.0
	Phenanthrene	231.3
	Anthracene	35.7
	Fluroanthene	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
PCDD/F	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 PCDD/F	4.45

Source. Ref. [18].

[b] Compound of interest not on HAP list.

Table 13
Emissions from open burning of fiberglass (mg/kg burned)

Class	Compound	Boating industry	Building industry
VOCs	Chloromethane	435.9	420.8
	Vinylchloride	0.8	
	Bromomethane	1.7	772.6
	Chloroethane	0.8	
	1,1-Dichloroethene[a]	0.8	
	Acetone[a]	155.6	158.0
	trans-1,2-Dichloroethene[a]	0.3	
	1,1-Dichloroethane[a]	0.8	
	Chloroform	36.9	23.9
	1,1,1-Trichloroethane[a]	0.5	
	Carbon tetrachloride	0.6	
	Benzene	5921.3	10,472.7
	1,2-Dichloroethane[a]	0.7	
	Trichloroethene	0.8	
	1,2-Dichloropropane[a]	1.0	
	Bromodichloromethane[a]	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[a]	0.9	
	Chlorobenzene	2.0	
	Ethylbenzene	700.7	2686.0
	m,*p*-Xylene	468.0	1523.2
	o-Xylene	4.5	8.1
	Styrene		9931.6
	Bromoform	0.9	
	1,1,2,2-Tetrachloroethane	2.6	
	1,2-Dichlorobenzene[a]	1.5	
	1,4-Dichlorobenzene	1.8	
	1,3-Dichlorobenzene	1.1	
SVOCs	Acetophenone	77.0	286.0
	Benzoic acid[a]	1288.0	781.0
	Biphenyl	689.0	1936.0
	Cumene[a]		251.0
	Dibenzofuran	105.0	945.0
	n,*n*-Diethylaniline		353.0
	Di-*n*-butylphthalate		24.0
	Bis(2-ethylhexyl)phthalate		60.0
	2-Methylnaphthalene[a]	89.0	516.0
	2-Cresol	125.0	400.0
	3/4-Cresol		1731.0
	Phenol	328.0	6830.0
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
	Dibenz[*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		

Source. Ref. [26].

[a] Compound of interest not on HAP list.

Table 14
Emissions from open burning of pesticide bags (mg/kg burned)

Class	Compound	Empty Thimet bags	Thimet bags	Empty Atrazine bags	Atrazine bags
VOCs	Acetone[a]	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
	Methylenechloride	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
	Xylenes	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[a]	12.0	30.0		
	2-Methylnaphthalene[a]	8.0	20.0		10.0
	Benzoic acid[a]				90.0
	Dibenzofuran	4.0	8.0		
	Diethylphthalate				3.0
	Bis(2-ethylhexyl)phthalate		8.0		
	Thimet[a]		180.0		
	Atrazine[a]				420.0
PAHs	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		
	Pyrene	3.0	6.0		
PCDD/F	TCDD				8.0×10^{-6}
	PeCDD				
	HxCDD				2.7×10^{-5}
	HpCDD				1.0×10^{-4}
	OCDD				4.0×10^{-5}
	TCDF				6.7×10^{-6}
	PeCDF				
	HxCDF				3.3×10^{-5}
	HpCDF				3.3×10^{-5}
	OCDF				
	TEQ				9.0×10^{-6}

Source. Ref. [27] (assuming each bag weighed 0.1 kg).
[a] Compound of interest not on HAP list.

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 [88,89]. Another study was performed to examine the mutagenicity of airborne particulates near an operation where copper wire was reclaimed by open burning [90]. Another article presented PCDD/F results from surface and ash sampling at a metal recovery facility where open burning was used [91] 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 US, 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 [92]. There have been several studies that attempted to estimate emissions due to fireworks. Dyke et al. [50] measured emissions during ‘bonfire night’ in England, which involves bonfires and

Table 15
Summary of available data

	Prescribed burning/ forest fires	Agricultural burning	Land clearing debris	Yard waste	Camp fires	Animal carcasses	Liquid fuels	Accidental fires	Backyard trash burning	Landfill fires and burning dumps	Tire fires	Automobile shredder residue	Fiberglass	Agricultural plastic	Structural fires	Vehicle fires	Construction debris	Grain silo fires	Copper wire reclamation	Fire works
VOCs	×	×	×				×		×		×	×	×	×						
SVOCs/PAHS	×	×	×	×			×		×		×	×	×	×						
Carbonyls	×	×					×		×											
Total PCDDs/Fs	×						×		×			×								
TEQ PCDDs/Fs	×	×							×											
Total PCBs									×											
TEQ PCBs									×											

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. [93] 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. [50] were probably due to the bonfires and not the fireworks. Another study on emissions from fireworks examined only metals [94].

4. Emissions analysis

Based on the data that were collected and presented in Section 3, Table 15 was constructed to visualize the completeness of the data set. As can be seen from Table 15, some sources are better-characterized than others, some are poorly characterized, and some are not characterized at all. If a source had data on any organic air toxics, PAHs were always part of the dataset, and VOC data are available for most of the sources. Non-PAH semi-volatile 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, showing the minimum and maximum reported values.

Of the VOCs, benzene, toluene, ethylbenzene, xylenes, and styrene were selected for comparison. They are commonly produced during combustion processes, and data are available for most of the sources. Fig. 6 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. The error bars

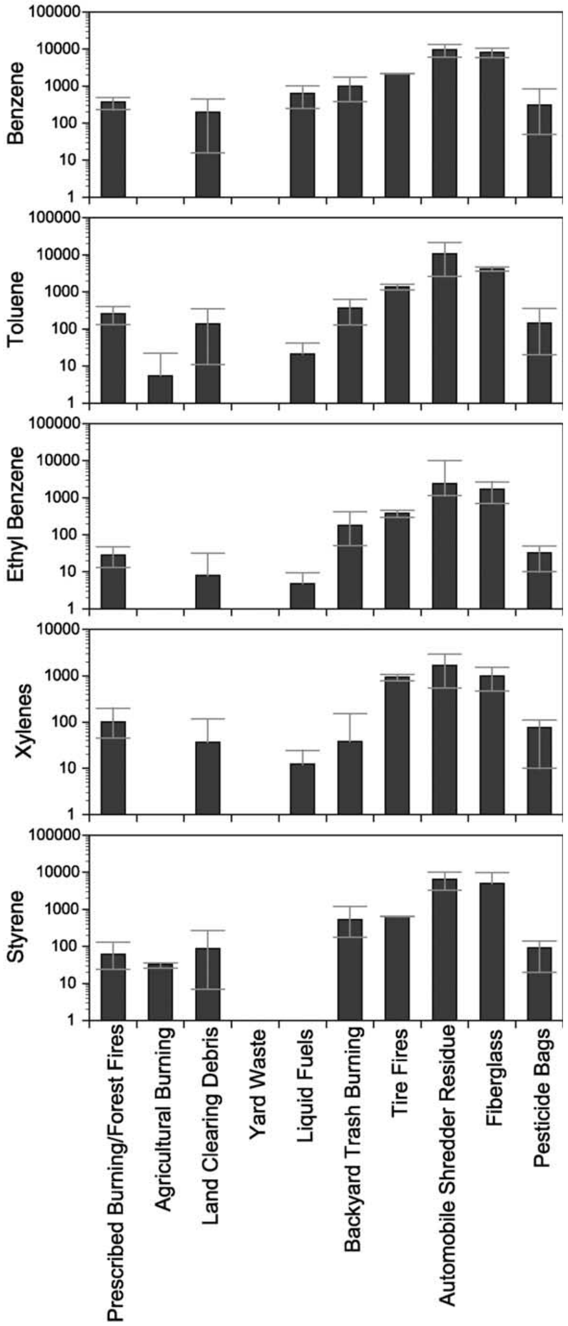

Fig. 6. VOCs from open burning sources (mg/kg burned).

on Figs. 6–9 represent the range of values for the data; 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. This is distinguished from plots where no bar is shown at all, which indicates that no data were available.

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. Fig. 7 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.

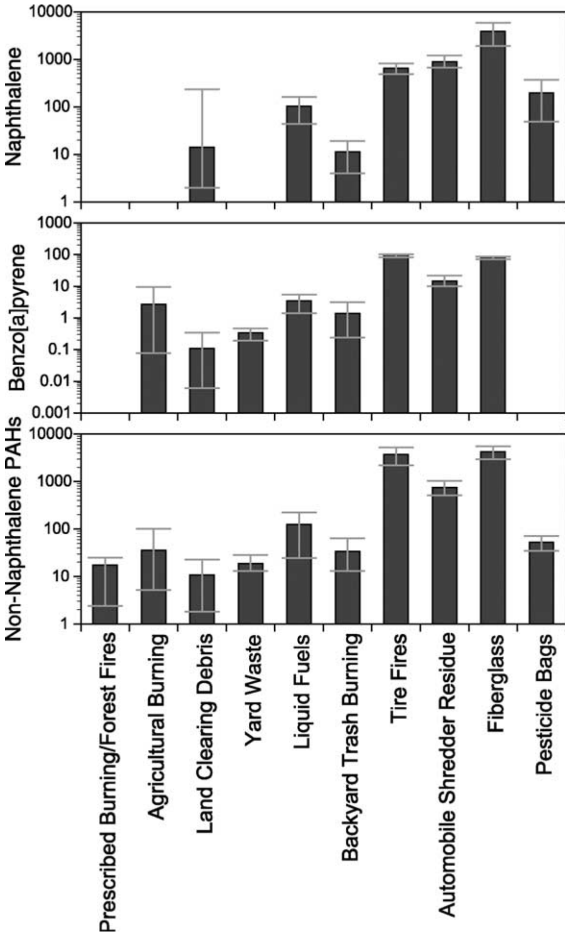

Fig. 7. SVOCs from open burning sources (mg/kg burned).

The available data for carbonyls is much more limited. For this analysis, formaldehyde was chosen as the compound for comparison between sources. Fig. 8 shows 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.

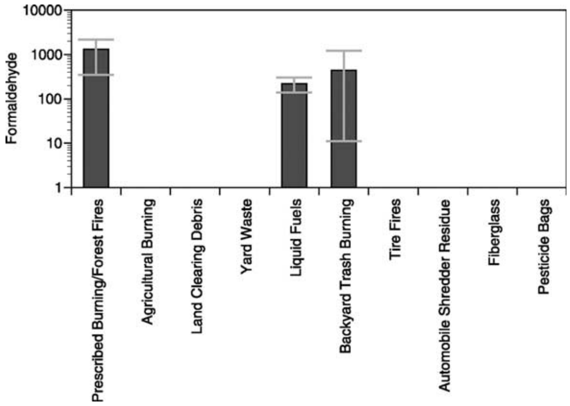

Fig. 8. Formaldehyde from open burning sources (mg/kg burned).

Emissions of PCDDs/Fs showed significant variation within a given source. This is likely due to several effects that to which PCDD/F formation is especially sensitive. PCDD/F formation is highly temperature sensitive, and is impacted by availability of catalytic sites for heterogeneous formation reactions [1]. Open burning situations exacerbate temperature gradients, oxygen transport issues, and local fuel composition variations. It is likely that any or all of these variables contribute the wide variations in PCDD/F emissions.

Emissions of PCDDs/Fs showed significant differences between somewhat similar sources. As can be seen in Fig. 9, 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 [18]. During the backyard burning experiments [37] 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 US (≈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:

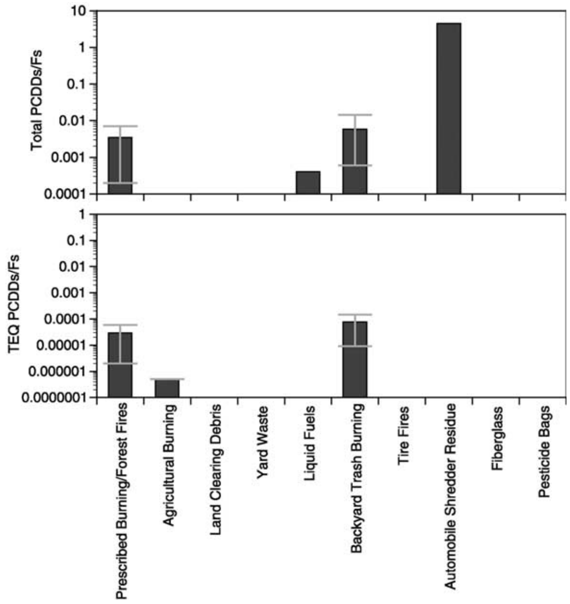

Fig. 9. PCDDs/Fs from open burning sources (mg/kg burned).

- Forest fires
- Land-clearing debris
- Construction debris

5. Conclusions

5.1. Purpose of review

The purpose of this review 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, research needs, 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;
- Structure fires;
- Vehicle fires;
- Copper wire reclamation.

Acknowledgements

The author would like to thank Dennis Tabor and Dr. Ram Hashmonay of ARCADIS G&M, and Satish Bhagat of the SEE program for their support in performing the literature search and in helping to prepare this document.

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