PM Speciation Profiles for Tire Burning

—PM1301 (Controlled Tire Combustion) & PM1302 (Uncontrolled Open Tire Fire)

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1. Introduction

More than 48 million reusable and waste tires are generated every year across California. Scrap tires represent both a resource opportunity and a disposal problem [1]. One of the major uses for scrap tires is fuel, or so-called tire-derived-fuel (TDF). Scrap tires are typically used as a supplement to traditional fuels such as coal, coke or woodchips. When the TDF is burned in combustors specifically designed for efficient combustion of solid fuel, such as kilns and boilers, the combustion is under control. The combustors are usually also equipped with add-on air pollution control devices for the control of particulate emissions. However, waste tires which remain in stockpiles pose a potential threat to public health, the environment, and safety. Open fires on stockpiled scrap tires are uncontrollable and hard to extinguish. The incomplete combustion during tire burning produces unhealthful emissions that are directly released to the atmosphere.

The current CARB speciation profile database lacks profiles for both controlled and uncontrolled tire burning. In this work, the following two particulate matter (PM) speciation profile are generated based on source testing data to fill the gap:

- PM1301: Controlled tire combustion
- PM1302: Uncontrolled open tire fire

2. Methodology

2.1 Controlled tire combustion

Scrap tires can be used to supplement fuel burning in combustors, such as kilns and boilers. The combustors are specifically designed for efficient combustion of solid fuel; therefore, the burning is well controlled. Several source tests were conducted on TDF combustion in California between 1996 and 1999, including the Mitsubishi Cement Plant test, the California Portland Cement Company test, the Kaiser Cement Corporation test, and the Stockton Cogen Inc. test. All of these tests focused on emission factors of AB2588 toxic species, such as polycyclic aromatic hydrocarbons (PAHs) and heavy metals. These studies are valuable data sources for generating emission factors of the toxic species as needed. However, the key components of PM speciation profiles, such as elemental carbon (EC), organic carbon (OC), and sulfate, are not the species of interest in these source tests. Therefore, the species measured in these source tests are not comprehensive enough to support speciation profile development.

Chow et al. performed source testing of TDF burning in a cement kiln during the 1999-2000 Big Bend National Park Regional Visibility Study (BRAVO). A variety of PM species were analyzed [2]. The emission samples of TDF combustion were collected from stacks of a cement kiln equipped with an electrostatic precipitator. The kiln was fueled by a mixture of 70% low sulfur Wyoming coal, 10% pet coke and 20% scrap tires. Six source tests were performed at different times, and $PM_{2.5}$ (particulate matter less than 2.5 µm in diameter) speciation profiles were generated based on the individual testing results. The six profiles were named as cement kiln profiles PM4323, 4324, 4325, 4326, 4327 and 4328 in the EPA SPECIATE 4.5 database [3]. The average of the six profiles is assigned as the composite cement kiln profile PM4376.

The 2016 Report on Air Emissions from Facilities Burning Waste Tires in California shows that the percentage of tires burned as part of the total fuel mix ranged from 10 to 44% for different facilities [4]. The 2015 report [5] and the 2014 report [6] both indicate that the total burned fuel consisted of 9 to 39% of scrap tires. Therefore 20% tires in the fuel mix as used in the BRAVO source tests, i.e. EPA-PM4376, is a reasonable composition that typifies TDF combustions in California.

Compared with the standard CARB PM profile format, some key species are missing from EPA-PM4376, and double-counting of species should be avoided. Thus, the following steps were carried out to convert the EPA composite profile to a CARB profile:

- NCOM (non-carbon organic matter): a factor of 1.4 was used to convert OC to OM (organic matter) [7]. NCOM is calculated by subtracting OC from OM, i.e., $[NCOM] = [OM] - [OC] = 1.4 \times [OC] - [OC] = 0.4 \times [OC]$.
- 'Others': this species group is created to capture the metal-bound oxygen by multiplying the five geological elements (i.e., Al, Si, Ca, Fe and Ti) by their oxygen-to-metal ratios. These ratios were based on the expected oxidation state of the metals in the atmosphere (i.e., Al_2O_3, SiO_2, CaO, Fe_2O_3 and TiO_2). The following equation is used to calculate "Others" [8]:

$$[\text{others}]=0.89\times[\text{Al}]+1.14\times[\text{Si}]+0.40\times[\text{Ca}]+0.43\times[\text{Fe}]+0.67\times[\text{Ti}]$$

- Double-counting species: because different analytical methods are performed on PM samples to determine more complete speciation information for multiple purposes, some species are often reported twice in the speciation profiles, such as K and K^+, Na and Na^+, total Cl and chloride (Cl^-), total S and sulfate (SO_4^{2-}). To avoid double counting in profiles, the overlap portion has to be eliminated. For example, non-sulfate sulfur, insoluble-Cl, insoluble-K and insoluble-Na are calculated and used to replace total S, total Cl, K and Na, respectively, if the values are greater than zero.

- Normalization: the weight percentages of all the species, including NCOM, ‘Others’, and the species created to avoid double counting, are added up to get a new total weight percentage for all the profile species; and then the weight percentage of each species is divided by the total percentage to get its normalized weight percentage for the new profile PM1301.

2.2 Uncontrolled open tire fire

Two recent field studies of tire fires, the Iowa City and the Spain fires, were used in this work for developing PM profiles for uncontrolled open tire burning. The field-based approach provides a real-world perspective on open tire fires.

In summer 2012, a landfill liner comprising an estimated 1.3 million shredded tires burned in Iowa City, Iowa. Downard et al. characterized the gas and particle emissions from the fire [9]. PM_{10} (particulate matter less than 10 µm in diameter) samples were collected with a PM_{10} air sampler on Teflon filters at 24-hour intervals, and the PM_{10} mass was measured. $PM_{2.5}$ samples were collected with a multi-volume sampling apparatus equipped with a Teflon-coated aluminum cyclone operating on quartz fiber filters. $PM_{2.5}$ mass was estimated and derived from particle number. EC/OC were analyzed by thermal-optical transmittance and inorganic ions were measured by ion chromatography (IC). The study of the Iowa City fire discovered that EC levels in fire emissions were well above background levels while OC was not significantly enhanced. With the enhanced EC and typical OC levels, fire-impacted samples had characteristically low OC: EC ratios ranging 3.6-7.4 (compared to a background ratio 9-46). The 24-hour average $PM_{2.5}$ sample consisted of 29% OC, 8% EC, 13% sulfate, 8% ammonium and 4% nitrate. Although EC, OC and inorganic ions were analyzed in this study, no detailed metal species were reported.

Meanwhile, a very comprehensive measurement for metal species was conducted during a large open fire at a tire landfill in Spain from May to June in 2016 [10]. Sampling was carried out approximately 700 m downwind of the burning tires. PM_{10} samples were collected on a quartz microfiber filter. Major species were analyzed by Inductively Coupled Plasma-Automatic Emission Spectrometry (ICP-AES) and trace elements were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The measurement indicated that sulfate accounted for 14.4% of the Spain fire PM_{10} [10], which is very close to the 13% sulfate content measured in the Iowa fire $PM_{2.5}$ [9]. Assuming the compositions of the Spain fire PM_{10} and Iowa fire $PM_{2.5}$ are comparable, then the weight percentage of each metal species in the Spain PM_{10} are combined with the weight percentage of EC, OC, sulfate, nitrate and ammonium in the Iowa $PM_{2.5}$ to obtain a full list of species that can be used to generate a PM speciation profile. As there is no concern for double-counting species in these two studies, three steps are carried out for the profile development, as follows:

- NCOM: an OM/OC ratio of 1.4 was used for the combustion source [7], so $[NCOM] = 0.4 \times [OC]$.

- 'Others': this species group is created to capture the metal-bound oxygen by multiplying the five geological elements (i.e., Al, Si, Ca, Fe and Ti) by their oxygen-to-metal ratios. The following equation is used to calculate "Others" [8]:

$$[\text{others}]=0.89\times[\text{Al}]+1.14\times[\text{Si}]+0.40\times[\text{Ca}]+0.43\times[\text{Fe}]+0.67\times[\text{Ti}]$$

- Normalization: the weight percentages of all the species, including NCOM and 'Others', are added to obtain a new total weight percentage for all the profile species; and then the weight percentage of each species is divided by the new total percentage to get its normalized weight percentage for the new profile PM1302.

3. Results and discussion

A few metal species in the newly developed profiles are not in the existing CARB CEIDARS (California Emission Inventory Development and Reporting System) pollutant table. Their names, CAS numbers, molecular weight and assigned ARB-SAROAD codes are listed in Table 1. The new additions will be added to the CEIDARS database.

Table 1. New ARB-SAROAD codes to be added to CEIDARS POLLUTANT table

ARB-SAROAD	*CAS*	*Chemical Name*	*Formula*	*Molecular Weight*
12138	7439-93-2	Lithium	Li	6.94
12125	7440-56-4	Germanium	Ge	72.61
12123	7440-54-2	Gadolinium	Gd	157.25
12121	7429-91-6	Dysprosium	Dy	162.50
12120	7440-52-0	Erbium	Er	167.26
12122	7440-64-4	Ytterbium	Yb	173.04
12127	7440-58-6	Hafnium	Hf	178.49
12174	7440-29-1	Thorium	Th	232.04

The details of the new profiles PM1301 (controlled tire combustion) and PM1302 (uncontrolled open tire fire) are listed in Appendix Table 1 and Table 2, respectively. Since particle-size-specific chemical composition data are not available, a homogeneous chemical composition is assumed for all PM size ranges. That is, the chemical speciation profiles of TPM, PM_{10} and $PM_{2.5}$ are assumed to be the same.

The speciation profiles show that sulfate, Ca, K, OC, and nitrate are major species in particles emitted from controlled tire combustion (PM1301); while OC, sulfate and Ca contribute more than other species in the particles produced from uncontrolled burning (PM1302). Among the heavy metal species analyzed, Zn was detected at significantly high levels. In PM1302, Zn is about 6.3% of the PM mass. Zn and S are often associated with tire wear emissions. This is because sulfur compound and oxides of Zn, Ca, Pb and Mg are added to accelerate vulcanization, yielding concentrations of S and Zn within 1-2% of total PM concentrations from bulk tire burning [11].

Figure 1 shows pie charts of the two profiles with their major species. Compared to PM1301 (controlled tire combustion), the contents of EC and OC in PM1302 (open tire fire) are 2 to 3 times higher. Sulfate is the most abundant species (26.5%) in PM1301, but it is less than half of that value in PM1302. On the other hand, PM1302 contains a very high content of Zn (6.3%) compared to PM1301 (0.2%). One factor causing the differences between PM1301 and PM1302 is that only 20% of the test fuel in the combustors is TDF while scrap tires were the sole fuel burned in the open fires. The combustion conditions, for example, complete vs. incomplete, and controlled vs. uncontrolled, also result in different emission compositions.

Because size distribution data are not available for the newly developed profiles, the size fractions of the existing PM130 (Solid material combustion) are used for PM1301 (Controlled tire combustion) and the size fractions of the existing PM462 (Waste burning) are used for PM1302 (Uncontrolled tire burning) as shown in Table 2.

Table 2. PM profile size fractions

	PM_{10}/TPM	*$PM_{2.5}$/TPM*
PM1301	0.997	0.927
PM1302	0.9825	0.9316

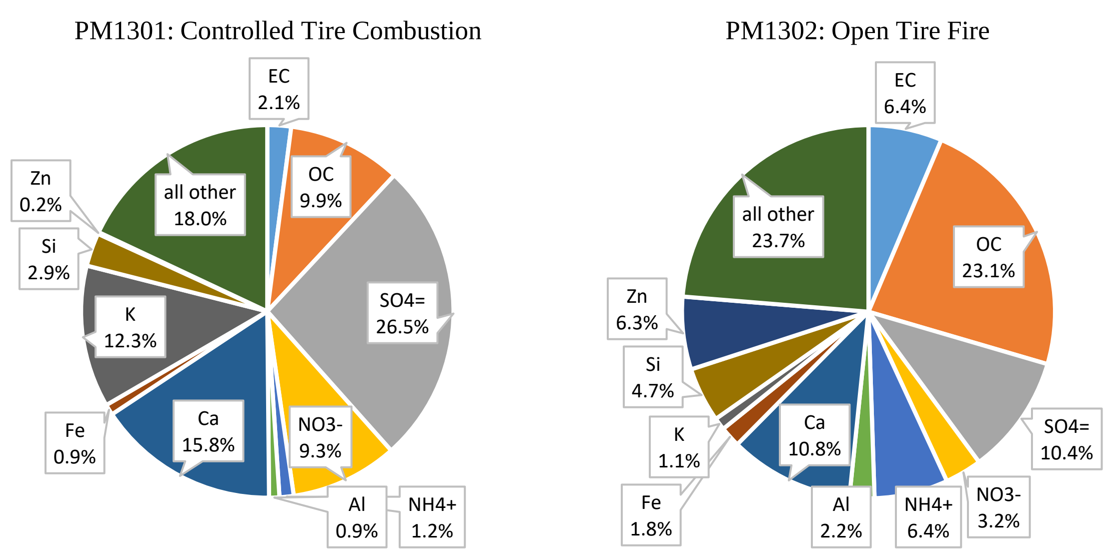

Figure 1. Major species in tire fire particles

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Appendix

Table 1. Profile PM1301: Controlled tire combustion

Species Name	*SAROAD*	*Weight Percentage (%)*		
		TPM	PM_{10}	$PM_{2.5}$
Aluminum	12101	0.893321	0.893321	0.893321
Ammonium	12301	1.230675	1.230675	1.230675
Antimony	12102	0.000842	0.000842	0.000842
Arsenic	12103	0.000589	0.000589	0.000589
Barium	12107	0.018863	0.018863	0.018863
Bromine	12109	0.037559	0.037559	0.037559
Cadmium	12110	0.000758	0.000758	0.000758
Calcium	12111	15.839273	15.839273	15.839273
Chloride	12203	0.739297	0.739297	0.739297
Chromium	12112	0.008000	0.008000	0.008000
Cobalt	42101	0.002021	0.002021	0.002021
Copper	12114	0.018442	0.018442	0.018442
Elemental Carbon	12116	2.056963	2.056963	2.056963
Indium	12131	0.007242	0.007242	0.007242
Iron	12126	0.928690	0.928690	0.928690
Lead	12128	0.023916	0.023916	0.023916
Magnesium	12140	0.030148	0.030148	0.030148
Manganese	12132	0.106276	0.106276	0.106276
Mercury	12142	0.000084	0.000084	0.000084
Molybdenum	12134	0.001600	0.001600	0.001600
Nickel	12136	0.012969	0.012969	0.012969
Nitrate	12306	9.306525	9.306525	9.306525
Organic Carbon	11102	9.892135	9.892135	9.892135
Non-carbon Organic Matter	11103	3.956854	3.956854	3.956854
Palladium	12151	0.000421	0.000421	0.000421
Potassium Ion	65312	10.565073	10.565073	10.565073
Potassium-insoluble	12182	1.768621	1.768621	1.768621
Rubidium	12176	0.070233	0.070233	0.070233
Selenium	12154	0.004632	0.004632	0.004632
Silicon	12165	2.885020	2.885020	2.885020
Silver	12166	0.002779	0.002779	0.002779
Sodium Ion	12181	1.323055	1.323055	1.323055
Sodium-insoluble	12186	0.308721	0.308721	0.308721

Species Name	*SAROAD*	*Weight Percentage (%)*		
		TPM	*PM_{10}*	*$PM_{2.5}$*
Strontium	12168	0.077391	0.077391	0.077391
Sulfate	12403	26.469442	26.469442	26.469442
Non-sulfate sulfur	12404	0.211541	0.211541	0.211541
Thallium	12173	0.002021	0.002021	0.002021
Tin	12160	0.005474	0.005474	0.005474
Titanium	12161	0.117560	0.117560	0.117560
Vanadium	12164	0.014232	0.014232	0.014232
Yttrium	12183	0.001432	0.001432	0.001432
Zinc	12167	0.154782	0.154782	0.154782
Zirconium	12185	0.006737	0.006737	0.006737
Others	12999	10.897791	10.897791	10.897791
Total		*100.000000*	*100.000000*	*100.000000*

Table 2. Profile PM1302: Open tire burning

Species Name	*SAROAD*	*Weight Percentage (%)*		
		TPM	*PM_{10}*	*$PM_{2.5}$*
Aluminum	12101	2.154441	2.154441	2.154441
Ammonium	12301	6.384877	6.384877	6.384877
Antimony	12102	0.002953	0.002953	0.002953
Arsenic	12103	0.001197	0.001197	0.001197
Barium	12107	0.034478	0.034478	0.034478
Beryllium	12105	0.000160	0.000160	0.000160
Bismuth	12106	0.000080	0.000080	0.000080
Cadmium	12110	0.000479	0.000479	0.000479
Calcium	12111	10.780729	10.780729	10.780729
Cerium	71111	0.002315	0.002315	0.002315
Cesium	12118	0.000399	0.000399	0.000399
Chromium	12112	0.005188	0.005188	0.005188
Cobalt	12113	0.108144	0.108144	0.108144
Copper	12114	0.050361	0.050361	0.050361
Dysprosium	12121	0.000160	0.000160	0.000160
Elemental Carbon	12116	6.384877	6.384877	6.384877
Erbium	12120	0.000080	0.000080	0.000080
Gadolinium	12123	0.000192	0.000192	0.000192
Gallium	12124	0.000559	0.000559	0.000559
Germanium	12125	0.001038	0.001038	0.001038
Hafnium	12127	0.000160	0.000160	0.000160
Iron	12126	1.786233	1.786233	1.786233
Lanthanum	12146	0.001437	0.001437	0.001437
Lead	12128	0.014765	0.014765	0.014765
Lithium	12138	0.002634	0.002634	0.002634
Magnesium	12140	0.818278	0.818278	0.818278
Manganese	12132	0.033361	0.033361	0.033361
Molybdenum	12134	0.018277	0.018277	0.018277
Neodymium	12144	0.003512	0.003512	0.003512
Nickel	12136	0.005108	0.005108	0.005108
Niobium	12147	0.000479	0.000479	0.000479
Nitrate	12306	3.192439	3.192439	3.192439
Organic Carbon	11102	23.145180	23.145180	23.145180
Non-carbon Organic Matter	11103	9.258072	9.258072	9.258072
Phosphorus	12152	0.174148	0.174148	0.174148
Potassium	12180	1.060017	1.060017	1.060017

Species Name	*SAROAD*	*Weight Percentage (%)*		
		TPM	*PM_{10}*	*$PM_{2.5}$*
Praseodymium	12155	0.000319	0.000319	0.000319
Rubidium	12176	0.007343	0.007343	0.007343
Samarium	12190	0.000239	0.000239	0.000239
Scandium	12104	0.000239	0.000239	0.000239
Selenium	12154	0.000160	0.000160	0.000160
Silicon	12165	4.738577	4.738577	4.738577
Sodium	12184	0.355223	0.355223	0.355223
Strontium	12168	0.068238	0.068238	0.068238
Sulfate	12403	10.375425	10.375425	10.375425
Thorium	12174	0.000431	0.000431	0.000431
Tin	12160	0.002953	0.002953	0.002953
Titanium	12161	0.191323	0.191323	0.191323
Tungsten	12119	0.000319	0.000319	0.000319
Uranium	12179	0.000231	0.000231	0.000231
Vanadium	12164	0.003033	0.003033	0.003033
Ytterbium	12122	0.000080	0.000080	0.000080
Yttrium	12183	0.000878	0.000878	0.000878
Zinc	12167	6.295728	6.295728	6.295728
Zirconium	12185	0.004469	0.004469	0.004469
Others	12999	12.527985	12.527985	12.527985
Total		*100.000000*	*100.000000*	*100.000000*