

# Organic Gas Speciation Profiles for Biomass Burning (OG1471-1478)

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February 2, 2018

## 1 Introduction

Biomass burning is a significant global source of trace gases and aerosols. It is defined as open or quasi-open combustion of vegetative or organic fuel [1]. Wildfires and prescribed fires are the two major types of biomass burning. The organic gas emissions from wildfires and managed burning categories in CARB's emission inventory are assigned with Profile OG307 (Forest fire) [2], which was derived from US EPA Profile 0307 (Miscellaneous burning - forest fires) [3]. In OG307, the organic gases are exclusively characterized as hydrocarbon species, including alkanes, alkenes and alkynes; however, recent studies indicate that oxygenated species are emitted during the fires or burning and the emission factors of oxygenated compounds are even larger than those of hydrocarbons [4-6]. Examples of these oxygenates include aldehydes, organic acid, alcohols and ketones. Moreover, additional hydrocarbon species have been identified by advanced species identification processes in many recent laboratory-based fire studies. Therefore, it is necessary to develop new fire speciation profiles with the missing oxygenate species and the newly discovered hydrocarbon species using up-to-date measurement data. The new profiles will replace OG307 for various biomass burning categories to better represent the composition of the fire emissions. The profiles developed in this work include:

- OG1471: Savanna fires
- OG1472: Forest fires
- OG1473: Chaparral fires
- OG1474: Crop residue burning
- OG1475: Pasture maintenance burning
- OG1476: Garbage burning
- OG1477: Timber and brush fires
- OG1478: All vegetation burning

## 2 Methodology

Most biomass burning studies only measure emission factors of selected organic species [1, 7-15]. In order to make organic gas speciation profiles for the fires, comprehensive measurement data need to be summarized and compiled among the various studies. Akagi et al. [16] organized the available data into 3 major fire-type categories: vegetation, biofuel and agricultural/waste burning. The vegetation fires are classified into 6 broad types of vegetation susceptible to burning: tropical forest, savanna, boreal forest, temperate forest, peatlands, and chaparral; the biofuel burning has open cooking fires, dung burning, Patsari cooking stoves, charcoal making, and charcoal burning; and the agricultural/waste burning includes crop residue, pasture maintenance fires, and open burning of garbage. Among these types of burning, the ones most applicable to California vegetation are chosen for development of speciation profiles, including

savanna, temperate forest, chaparral, crop residue, pasture maintenance and garbage burning. There are over 90 chemical species identified from the various measurements of biomass burning [16]. Their emission factors are used for the new profile development. The species from biomass burning studies are usually summarized as follows:

- Non-methane hydrocarbons (NMHC): organic compounds excluding methane that contain only C and H, such as alkanes, alkenes, alkynes, aromatics and terpenes;
- Oxygenated volatile organic compounds (OVOC): organic compounds contain C, H and O, such as alcohols, aldehydes, ketones, and organic acids;
- Non-methane organic compounds (NMOC): organic compounds excluding methane. NMHC and OVOC can account for nearly all NMOC;
- Total organic gases (TOG): all gas phase organic compounds including methane and total NMOC.

Studies found that only half of the NMOC mass can be identified when the emissions are measured by FTIR, GC, and PTR-MS [4, 5]; therefore, for most fuel type fires, the emissions of total NMOC are estimated by multiplying the emissions of total identified NMOC by a factor of 2. The emissions of total identified NMOC are calculated by summing the individual average NMOC emission factors. The emissions of TOG are obtained by adding the emissions of methane to the emissions of total NMOC. Based on the emission factors of the species compiled in Akagi et al. [16], speciation profiles for the six burning categories are created by normalizing the emission factor of the individual species by their TOG, respectively. The new profiles are OG1471 for savanna fires, OG1472 for forest fires, OG1473 for chaparral fires, OG1474 for crop residue burning, OG1475 for pasture maintenance, and OG1476 for garbage burning.

In addition to the above six profiles, two composite profiles, OG1477 for timber and brush fires and OG1478 for all vegetation burning are also developed in this work to meet the needs for CARB's emission inventory. OG1477 is made by averaging the profiles for forest fires (OG1472) and chaparral fires (OG1473). OG1478 is created as a composite profile of 9.5% savanna fires (OG1471), 37.4% forest fires (OG1472), 41.1% chaparral fires (OG1473) and 12.0% crop residue burning (OG1474). The weighing factors used for making the composite profile reflect the distribution of the four major vegetation types in California, which is estimated based on a tabulation of vegetation types in the state represented by the Fuel Characteristic Classification System [17]. The details of the eight new speciation profiles (OG1471-1478) are tabulated in the Appendix (Table 1).

### **3 Results and Discussion**

Because only half of the NMOC species can be identified, the group of unidentified species is nearly 50% of the TOG and is the major component in all profiles. In most of the profiles, methane is the most abundant identified species. Its weight percentage of TOG varies from 7.3% in savanna fires (OG1471) to 17.2% in chaparral fires (OG1473). Acetic acid is the most abundant OVOC species, and it accounts for 7.1% of the TOG in forest fires (OG1472) to 13.3% in savanna fires (OG1471). Other OVOCs, such as methanol (3.6 to 7.0%) and formaldehyde (2.4 to 8.2%) are also important species of the emissions from wildfires and other types of biomass burning. The shorter-chained alkanes and alkenes (C2-C3) are the most abundant

NMHC species in the plumes; these include compounds such as ethylene, ethane and propylene. The ROG/TOG ratios of the new profiles vary in the range of 0.81 to 0.90. These values are much higher than the ratio of OG307 (0.63) due to the addition of the oxygenated species in the new profiles. The ozone forming potential of the new profile is estimated based on SAPRC07 and the range varies from 1.20 to 1.77 g O<sub>3</sub>/g ORG, much lower than that of OG307 (4.68 g O<sub>3</sub>/g ORG). This big drop is mainly because ethylene, with a relatively high MIR value (9 O<sub>3</sub>/g ORG), decreases from 35% of TOG in OG307 to less than 5% in most of the new profiles.

**Table 1. ROG/TOG ratios and ozone forming potentials of OG1471-1478**

<i>Profile Number</i>	<i>OG1471</i>	<i>OG1472</i>	<i>OG1473</i>	<i>OG1474</i>	<i>OG1475</i>	<i>OG1476</i>	<i>OG1477</i>	<i>OG1478</i>
ROG/TOG	0.90	0.82	0.80	0.87	0.89	0.86	0.81	0.83
Ozone forming potential (g O <sub>3</sub> /g ORG)	1.39	1.77	1.63	1.20	1.36	1.32	1.70	1.61

#### 4 Estimated Impacts of the Profile Update on the Emission Inventory

The newly-developed profiles OG1471-1478, will replace the current profile OG307 for the various biomass burning categories. The affected EIC/SCC categories and the assignment of the new profiles are summarized in the Appendix (Table 2).

The statewide annual average TOG emissions of biomass burning are about 35.30 tons/day based on CEPAM (version 1.05): 2016 SIP Baseline Emission Projection for year 2016 [18]. Using the new profiles, the corresponding ROG of these biomass burning emissions will be 30.00 tons/day, which is 34.1% higher than the ROG emissions estimated based on the current profile OG307. If the new profiles are applied to these categories, the calculated ozone forming potential will be 67.2% lower than the estimation using the current profile OG307. For toxic species, the emissions of benzene, formaldehyde, acetaldehyde and toluene will be increased with the application of the new profiles; while the emissions of 1,3-butadiene will be decreased compared to the values calculated based on OG307.

**Table 2. Changes on emissions of organic gas species for biomass burning related categories (2016)**

<i>Statewide Annual Ave. Emissions</i>		<i>Current OG307 (tons/day)</i>	<i>New OG1471-1478 (tons/day)</i>	<i>Change</i>	
				<i>Emissions (tons/day)</i>	<i>Percentage</i>
ROG		22.37	30.00	+7.63	+34.1%
Ozone forming potential (g O <sub>3</sub> )		165.2	54.17	-111.03	-67.2%
Toxics	Benzene	0	0.08	+0.08	NA
	Formaldehyde	0	1.96	+1.96	NA
	1,3-butadiene	0.33	0.02	-0.31	-93.9%
	Acetaldehyde	0	0.37	+0.37	NA
	Toluene	0	0.05	+0.05	NA

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## Appendix

**Table 1. OG speciation profiles for biomass burning (OG1471-1478)**

<i>Species</i>	<i>SAROAD</i>	<i>Weight Percentage (%)</i>							
		<i>OG1471</i> Savanna fires	<i>OG1472</i> Forest fires	<i>OG1473</i> Chaparral fires	<i>OG1474</i> Crop residue burning	<i>OG1475</i> Pasture maintenance burning	<i>OG1476</i> Garbage burning	<i>OG1477</i> Timber and brush fires	<i>OG1478</i> All vegetation burning
1,2-propadiene	43208	0.045124				0.020343			0.004287
1,3-butadiene	43218	0.195536			0.263913				0.050245
1-butene	43213	0.161693			0.234201	0.172916			0.043465
1-hydroxy-2-propanone	47048	1.692138			6.589078	6.286013			0.951442
2,3-butanedione	47033					1.607104			
2-butanone	43552					0.956125			
2-methyl-1-butene	43225	0.022186							0.002108
2-methyl-1-pentene	98040	0.013161							0.00125
2-methyl-2-butene	43228	0.018049							0.001715
2-methyl-2-propenal	43506					0.406862			
2-methylfuran	43327					0.203431			
2-methylpropanal	98036					0.335661			
2-pentanone	98160					0.172916			
3-methyl-1-butene	43223	0.019178							0.001822
3-methylfuran	43328					1.434187			
acetaldehyde	43503	2.143375			2.16723	2.44117			0.463688
acetic acid	43404	13.34909	7.144671	7.52909	9.770011	10.578404	9.215537	7.336881	8.207128
acetone	43551	0.601649			0.786495	1.068012			0.151536
acetonitrile	43702	0.413634			0.367031	0.559435			0.083339
acetylene	43206	0.902474	1.051754	1.368925	0.471897	0.213602	1.523229	1.21034	1.098347
acrylonitrile	43704	0.191776			0.052433				0.024511
benzene	45201	0.752062			0.262165	0.712008			0.102906
chloroform	43803	0.045124				0.006428			0.004287
cis-2-butene	43217	0.031587			0.075154	0.040686			0.012019
cis-2-pentene	43227	0.009401							0.000893

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crotonaldehyde	98156					0.610293			
cyclopentane	43242				0.003321				0.000399
diethyl ketone	98161					0.081372			
dimethyl sulfide	99278	0.004888							0.000464
ethane	43202	2.481803	4.061945	2.464066	1.590467	0.966296		3.263006	2.958526
ethylbenzene	45203	0.022562				0.068149			0.002143
ethylene	43203	3.083452	4.061945	5.13347	2.551738	1.301957	4.798172	4.597708	4.22816
formaldehyde	43502	2.745025	8.232691	5.68104	3.635353	1.932593	2.361005	6.956866	6.110954
formic acid	43403	0.789665	1.269358	0.410678	1.747766	0.203431	0.685453	0.840018	0.928279
furan	99902	0.639252	0.725347	1.232033	0.192254	1.037497		0.97869	0.861445
glycolaldehyde	47045	3.045849	0.906684	1.574264	3.513009			1.240474	1.697039
hexaldehyde	98159					0.034583			
hydrogen cyanide	43332	1.541726	2.647517	2.600958	0.506852	0.467891	1.789794	2.624238	2.266451
isobutane	43214	0.016169			0.043694	0.01424			0.006779
isobutylene	43215	0.090247			0.204489	0.111887			0.033112
isomers of xylene	45102	0.052644				0.111887			0.005001
isopentane	98132	0.008273			0.034955	0.007527			0.004981
isoprene	43243	0.146652			0.664151	0.122059			0.09363
methane	43201	7.294997	14.21681	17.18001	10.172	8.859413	13.93755	15.69841	14.29174
methanol	43301	4.437163	6.999601	5.475702	5.75015	5.940181	3.579589	6.237652	5.979913
methyl bromide	43819	0.003208				0.005808			0.000305
methyl chloride	43801	0.206817				0.294975			0.019648
methyl iodide	47051	0.001903				0.00354			0.000181
methyl nitrate	47053	0.001918							0.000182
methyl vinyl ether	47046	0.601649			0.139821				0.073935
methyl vinyl ketone	47047					1.017154			
n-butane	43212	0.060165	0.301019	0.958248	0.125839	0.040686		0.629634	0.527237
n-heptane	43232	0.026322							0.002501

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n-hexane	43231	0.048884							0.004644
n-pentane	43220	0.012033			0.043694	0.005696			0.006386
phenol	45300	1.95536	1.196823	3.080082	0.908838	1.708819		2.138453	2.008345
propanal	43504					0.162745			
propane	43204	0.376031	0.942951	1.300479	0.489374	0.223774		1.121715	0.981608
propanenitrile	47049	0.11657			0.104866				0.023658
propylene	43205	2.970643	3.445399	2.600958	1.188481	0.864581	4.798172	3.023179	2.782402
toluene	45202	0.300825			0.332076	0.345832			0.068427
trans-2-butene	43216	0.041363			0.099623	0.050858			0.015884
trans-2-pentene	43226	0.016921							0.001607
unidentified	99999	46.25178	42.79549	41.40999	44.91758	46.188973	57.3115	42.10274	42.80905
Total		<i>100.000000</i>	<i>100.000000</i>	<i>100.000000</i>	<i>100.000000</i>	<i>100.000000</i>	<i>100.000000</i>	<i>100.000000</i>	<i>100.000000</i>

**Table 2. Biomass burning related categories and profile assignment**

SCC/EIC	Category Name				New OG Profile
50200202	SOLID WASTE DISPL	COMMERCL/INSTITNL	OPEN BURNING	REFUSE	OG1476
50200207	SOLID WASTE DISPL	COMMERCL/INSTITNL	FOREST RESIDUES		OG1472
66065602000000	FIRES	STRUCTURAL FIRES	SOLID FUEL (UNSPECIFIED)	SUB-CATEGORY UNSPECIFIED	OG1476
66065802000000	FIRES	AUTOMOBILE FIRES	SOLID FUEL (UNSPECIFIED)	SUB-CATEGORY UNSPECIFIED	OG1476
67066002620000	MANAGED BURNING AND DISPOSAL	AGRICULTURAL BURNING - PRUNINGS	AGRICULTURAL WASTE	SUB-CATEGORY UNSPECIFIED	OG1474
67066002629842	MANAGED BURNING AND DISPOSAL	AGRICULTURAL BURNING - PRUNINGS	AGRICULTURAL WASTE	ATTRITION	OG1474
67066002629856	MANAGED BURNING AND DISPOSAL	AGRICULTURAL BURNING - PRUNINGS	AGRICULTURAL WASTE	GRAPE VINES/STUMPS	OG1472
67066002629862	MANAGED BURNING AND DISPOSAL	AGRICULTURAL BURNING - PRUNINGS	AGRICULTURAL WASTE	ORCHARD REMOVAL	OG1472
67066002629874	MANAGED BURNING AND DISPOSAL	AGRICULTURAL BURNING - PRUNINGS	AGRICULTURAL WASTE	RAISIN TRAYS	OG1472
67066002629884	MANAGED BURNING AND DISPOSAL	AGRICULTURAL BURNING - PRUNINGS	AGRICULTURAL WASTE	TREE PRUNINGS	OG1472
67066002629888	MANAGED BURNING AND DISPOSAL	AGRICULTURAL BURNING - PRUNINGS	AGRICULTURAL WASTE	UNTREATED GRAPE STAKES	OG1472
67066002629892	MANAGED BURNING AND DISPOSAL	AGRICULTURAL BURNING - PRUNINGS	AGRICULTURAL WASTE	VINEYARD REMOVAL	OG1472
67066202620000	MANAGED BURNING AND DISPOSAL	AGRICULTURAL BURNING - FIELD CROPS	AGRICULTURAL WASTE	SUB-CATEGORY UNSPECIFIED	OG1474
67066202629866	MANAGED BURNING AND DISPOSAL	AGRICULTURAL BURNING - FIELD CROPS	AGRICULTURAL WASTE	PAPER HOT CAPS	OG1474
67066202629878	MANAGED BURNING AND DISPOSAL	AGRICULTURAL BURNING - FIELD CROPS	AGRICULTURAL WASTE	RICE STUBBLE	OG1474

SCC/EIC	Category Name				New OG Profile
67066202629882	MANAGED BURNING AND DISPOSAL	AGRICULTURAL BURNING - FIELD CROPS	AGRICULTURAL WASTE	STUBBLE	OG1474
67066402000000	MANAGED BURNING AND DISPOSAL	RANGE IMPROVEMENT	SOLID FUEL (UNSPECIFIED)	SUB-CATEGORY UNSPECIFIED	OG1471
67066602000000	MANAGED BURNING AND DISPOSAL	FOREST MANAGEMENT	SOLID FUEL (UNSPECIFIED)	SUB-CATEGORY UNSPECIFIED	OG1472
67066702000000	MANAGED BURNING AND DISPOSAL	WILDLAND FIRE USE (WFU)	SOLID FUEL (UNSPECIFIED)	SUB-CATEGORY UNSPECIFIED	OG1472
67066802000000	MANAGED BURNING AND DISPOSAL	WEED ABATEMENT	SOLID FUEL (UNSPECIFIED)	SUB-CATEGORY UNSPECIFIED	OG1475
67066802009858	MANAGED BURNING AND DISPOSAL	WEED ABATEMENT	SOLID FUEL (UNSPECIFIED)	NOXIOUS WEEDS	OG1475
67066802009872	MANAGED BURNING AND DISPOSAL	WEED ABATEMENT	SOLID FUEL (UNSPECIFIED)	PONDING/LEVEE BANKS/DITCHBANK/CANAL	OG1475
67066802009886	MANAGED BURNING AND DISPOSAL	WEED ABATEMENT	SOLID FUEL (UNSPECIFIED)	TUMBLEWEEDS	OG1475
67066802009894	MANAGED BURNING AND DISPOSAL	WEED ABATEMENT	SOLID FUEL (UNSPECIFIED)	WEED ABATEMENT - OTHER	OG1475
93066702000000	WILDFIRES	WILDLAND FIRE USE (WFU)	SOLID FUEL (UNSPECIFIED)	SUB-CATEGORY UNSPECIFIED	OG1472
93093002000000	WILDFIRES	GRASS AND WOODLAND FIRES	SOLID FUEL (UNSPECIFIED)	SUB-CATEGORY UNSPECIFIED	OG1471
93093202000000	WILDFIRES	TIMBER AND BRUSH FIRES	SOLID FUEL (UNSPECIFIED)	SUB-CATEGORY UNSPECIFIED	OG1477
93093402000000	WILDFIRES	ALL VEGETATION	SOLID FUEL (UNSPECIFIED)	SUB-CATEGORY UNSPECIFIED	OG1478