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DEVELOPMENT OF ORGANIC GAS EXHAUST SPECIATION PROFILES AND EMISSION FACTORS FOR NONROAD SPARK IGNITION AND COMPRESSION IGNITION ENGINES AND EQUIPMENT

Lawrence J. Reichle*
ORISE Fellow, hosted by the U.S. Environmental Protection Agency,
Office of Transportation and Air Quality, Ann Arbor, MI, USA

Catherine Yanca, Rich Cook, & Cheryl Caffery
U.S. Environmental Protection Agency,
Office of Transportation and Air Quality, Ann Arbor, MI, USA

1. INTRODUCTION

The composition of exhaust emissions from nonroad engines and equipment varies based on a number of parameters, including engine/equipment type, emission control technology, fuel composition, and operating conditions. Speciated emissions data which characterize the magnitude and chemical composition of these emissions are needed to develop chemical speciation profiles which are used for air quality modeling and development of air toxics inventories. In this paper, we present results of an extensive review and analysis of available speciation data for total organic gases (TOG). A key objective of this review was to identify speciation data for nonroad engines, with and without emission controls, running on diesel fuel or gasoline/ethanol blends now in widespread use. Improvements in the quality of these data will result in more accurate emissions and air quality modeling as well improved capability of EPA's MOVES (Motor Vehicle Emission Simulator) model to predict the emissions of in-use engines.

Our review concluded that the best available data sets for nonroad engines that had different levels of emission controls and were running on representative fuels were from two test programs conducted by Southwest Research Institute (SwRI), under contract to U.S. EPA. These data sets were used to create engine exhaust speciation profiles and emission factors for a variety of nonroad spark ignition (SI) engines (Carroll, 2010) and compression ignition (CI) engines (Starr, 2004a and 2004b).

In this paper, we discuss differences we have found in SI engine exhaust speciation profile chemical composition between 2-stroke and 4-stroke engines using E0 (0% ethanol) and E10 (10% ethanol) blends. We also discuss differences between CI engine exhaust speciation profiles resulting from different engine control tiers, horsepower, and engine test cycles. Moreover, we discuss potential implications for air quality modeling. Finally, we discuss limitations in these data, and identify additional data needs.

2. METHODS

2.1 SPARK IGNITION ENGINES

2-stroke and 4-stroke engine exhaust speciation profiles were very different in chemical composition. However, engine exhaust speciation profiles for different engines were similar if they shared the same number of strokes; thus engines were categorized according to stroke.

Seven small off-road engines (SOREs) were used to create E0 and E10 4-stroke uncatalyzed engine exhaust speciation profiles (Table 1).These engines include two mowers, two riding mowers, two generators, and a blower. Steady-state modal emissions tests were performed on these engines. Each type of equipment used different, weighted, steady-state engine operational modes for certification, listed in Table 18 of the test report (Carroll, 2010).

Four recreational equipment engines were used to create E0 and E10 2-stroke uncatalyzed engine exhaust speciation profiles (Table 2). These included two all-terrain vehicles (ATVs) and two non-road motor cycles (NRMCs). Each recreational equipment engine was tested on the Urban Dynamometer Drive Schedule (UDDS) transient test cycle from 40 CFR, Part 86, Appendix I.

**Corresponding author:* Lawrence J. Reichle, Office of Transportation and Air Quality, 2000 Traverwood Drive, Ann Arbor, MI 48105; e-mail: reichle.lawrence@epa.gov

Table 1. 4-Stroke Off-Road Spark-Ignition Test Equipment and Engines

Type	Year[1]	Equipment Make/Model	Engine Make/Model
22" Mower	2006	MTD 11A-084F229	Briggs & Stratton 10T502158
Mower	2007	Honda HRC 2163HXA	Honda GXV160
Riding Mower	2007	MTD 638RL Yard Machine 13A1762F229	Techumseh OV 358 EA
Riding Mower	2007	Snapper S150X	Kawasaki FH641V-ES25-R
Generator	2004	Briggs & Stratton Elite Series 6200 30386	Briggs & Stratton 1015499427
Generator	2006	Honda EB11000	Honda GX620KI
Blower	2007	Makita BHX2500	Makita EHO25

[1] California certification year

Table 2. 2-Stroke Spark-Ignition Recreational Equipment Engines

Type	Model Year	Engine Make/Model	Oil Lubrication
NRMC	2007	Honda CR125	Pre-mixed
NRMC	2002	Kawasaki KX250	Pre-mixed
ATV	2006	Yamaha Blaster	Injected
ATV	2005	Polaris Trailblazer	Injected

2.2 COMPRESSION IGNITION ENGINES

Seven engines were used to create CI engine exhaust speciation profiles and include construction equipment and engines, a forklift truck, and an agricultural tractor (Table 3). These engines were tested using transient and steady-state cycles. Transient cycles used were the U.S. on-highway heavy-duty Federal Test Procedure (FTP) and nonroad backhoe loader duty cycle (BHL). Steady-state engine tests were based on an 8-mode ISO Type-C1 weighting scheme. Calibration and sampling methods of the steady-state C1 test adhered to test procedures in CFR, Part 89, and generally satisfied ISO 8178-1 guidelines.

Table 3. Compression-Ignition Test Engines

Intended Application	Manufacturer	Year/ Model	Tier	hp
forklift truck	Kubota	1999 V2203E	1	50
construction equipment	Cummins	1999 QSL9	1	330
rubber-tired loader	Caterpillar	1999 3408	1	480
motor grader	Deere	1996 6068T	0	160
excavator	Cummins	1997 M11C	1	270
agricultural tractor	Caterpillar	2001 3196	2	420
telescoping boom excavator	Cummins	2001 ISB190	1	194

2.3 FUELS

Test fuels used with the SI engines included federal certification fuels (CERT1 and CERT2), California Air Resources Board (ARB) provided fuels (E10-7, E10-10, E0), and an EPA gasoline blend of E10. A brief description of the fuels is provided in Table 4 and the test properties of these fuels is included in Table 5.

Table 4. Fuel Used for SI Engine Testing

Fuels	Fuel description
CERT1	Federal Certification, non-oxygenated
CERT2	Federal Certification, non-oxygenated
ARB E0	Non-oxygenated gasoline
ARB E10-7	10% ethanol, RVP 7 psi
ARB E10-10	10% ethanol, RVP 10 psi by adding butane to ARB E10-7
EPA-E10	10% ethanol, RVP 9 psi

Fuels used with the CI test programs were an emissions certification test grade Type-2D diesel fuel and a high-sulfur Nonroad-2D diesel fuel. The Type-2D fuel had a sulfur level of 390 ppm with an API gravity of 36.1 and the Nonroad-2D had a sulfur level of 2570 ppm with an API gravity of 34.8. Additional fuel properties are described in Table 6.

Table 5. Select SI Test Fuel Properties

Test fuel	Ethanol (Wt%)	RVP (psi)	T50 (deg F)	T90 (deg F)	Aromatics (Vol%)	Benzene (Wt%)
ARB E0	<0.2	7.2	228	304	31.8	0.3
CERT1	<0.1	9.0	224	309	31.5	0.7*
CERT2	NP	9.2	223	318	27.9	NR
ARB E10-7a	9.7	7.0	214	315	22.1	1
ARB E10-7b	9.9	6.8	213	314	24.9	0.7*
ARB E10-10	9.7	9.8	207	313	22.7	0.7*
EPA-E10	9.4	9.0	211	319	24.7	0.7

NP = Not performed for this fuel
NR = Not reported
* Benzene content reported as volume %

Table 6. Select CI Test Fuel Properties

Test fuel	Type-2D	Nonroad-2D
Sulfur, ppm	390	2570
Cetane Number	48.0	46.1
T50 (deg F)	505	511
T90 (deg F)	618	613
Total Aromatics (Vol%)	32.15	31.9
Saturates (Vol%)	66.05	67.45
Specific Gravity	0.8444	0.8507
API Gravity	36.1	34.8

2.3 SAMPLE COLLECTION AND ANALYSIS

Exhaust samples were analyzed for the presence of more than 200 different species including hydrocarbons, aldehydes and ketones, and alcohols. Gas chromatography (GC) procedures similar to the Phase II Auto-Oil method were used to identify and quantify alcohols, select aromatics, and C_2-C_{12} hydrocarbons. A high performance liquid chromatography (HPLC) procedure was used for aldehydes and ketones.

One complete emission test was performed with each test fuel with the SI engines and multiple emission tests were performed with each test fuel with the CI engines. All engine exhaust emissions were measured using dilute exhaust test methodologies.

2.4 CO-ELUTED AND UNKNOWN COMPOUNDS

For some species that co-elute, the GC peak area was split equally between the two compounds by the contractor. For other species, co-elution was noted but only one of the co-eluted compounds was reported and all mass was assigned to that species. In such cases, the mass was subsequently split equally between the co-eluted compounds and the unreported species were added to the chemical list. The following were indicated as co-eluted species:

- 2,2-dimethylpentane and methylcyclopentane
- 3-methyl-3-ethyl-pentane and 3,4-dimethylhexane
- Cis-1,4-dimethylcyclohexane and trans-1,3-dimethylcyclohexane
- Propylcyclopentane and 2,6-dimethylheptane
- 2,5-dimethylheptane and 3,5-dimethylheptane
- Decane and isobutylbenzene
- n-butylbenzene and 1-methyl-4-n-propylbenzene
- Isobutyraldehyde and methyl ethyl ketone

Unknown hydrocarbons were reported by the lab according to carbon number, as unidentified C5, C6, C7, C8, and C9-C12+. Reported designations were maintained in assigning specie identification numbers instead of combining unknowns into one specie identification number.

3. SPECIATION PROFILE DEVELOPMENT

Profiles developed from the SI engine test program are:

- 4-stroke uncatalyzed engines running on E0
- 4-stroke uncatalyzed engines running on E10
- 2-stroke uncatalyzed engines running on E0
- 2-stroke uncatalyzed engines running on E10

A speciation profile comprised of weight percents of TOG for every compound was created for each individual test by dividing each compound's mass by the total mass of all the species. These individual test profiles were averaged within their respective engine/fuel categories to obtain a composite profile representing that particular engine/fuel combination. The number of tests for each composite profile are indicated in Table 7 (note that CERT1 and CERT2 test fuels are E0 fuels). Two tests, not shown in Table 7, were excluded from the 4-stroke profiles due to missing data: a Briggs and Stratton walk behind mower test (indicated as 1-E10-759 in the test report) was missing seven low weight paraffins and olefins, and a Honda walk behind mower test (2-E0-776) was missing all alcohol data. A standard deviation test was performed to identify potential outliers. No outliers were identified outside of 3.5 standard deviations of the mean profile value.

Table 7. Engine/Fuel Combinations Used for SI Engine Exhaust Speciation Profile Development

	Engines	Tests	Fuels
4 stroke, E0	SOREs	7	ARB E0
	SOREs	1	CERT2
4 stroke, E10	SOREs	6	ARB E10-7
	SOREs	1	EPA-E10
2 stroke, E0	ATV-Blaster	1	CERT1
	ATV-Polaris	1	CERT1
	NRMC-CR125	1	CERT1
	NRMC-Kawasaki	1	CERT1
2 stroke, E10	ATV-Blaster	1	ARB E10-10
		1	ARB E10-10
		1	ARB E10-7
	ATV-Polaris	1	ARB E10-7
		1	ARB E10-10
	NRMC-CR125	1	ARB E10-7
		1	ARB E10-10
	NRMC-Kawasaki	1	ARB E10-7
		1	ARB E10-10

While emissions test data from 2-stroke catalyst engines were available, we were unable to use these tests to create speciation profiles due to many inconsistencies and high values in the data.

Eight profiles were developed from the CI engine test program based on emission control tier and power rating. One set of steady state operations and another set of transient operations were categorized according to the following categories:

- Pre-Tier 1 engines
- Tier 1 engines with greater than 50 horsepower (hp)
- Tier 1 engines with less than 50 hp
- Tier 2 engines with greater than 50 hp

As with the SI engine profiles, a CI speciation profile was first created for each individual test by dividing each compound's mass by the total mass of the all species for that test. These profiles were averaged within their respective emission control/power categories to obtain a composite profile representing that particular control/power combination under steady state and transient operating conditions. The number of tests for each CI engine profile are indicated in Table 8. To increase the robustness of the composite profiles, we doubled the number of samples by including tests on both high and low sulfur fuel types after our analysis found that speciated compounds had similar weight percent values between high and low sulfur fuel tests (the correlation between the low and high sulfur species was R^2=0.97 for the pre-Tier 1 profile, R^2=0.85 for the Tier 1 < 50hp profile, R^2=0.98 for the Tier 1 > 50hp profile, and R^2=0.65 for the Tier 2 > 50hp profile). After incorporating both high and low sulfur fuels, a standard deviation test was performed to identify potential outliers. Outliers were identified outside of 3.5 standard deviations of the mean profile value for the Tier 1 > 50hp transient profile and were addressed.

Table 8. Engine Combinations Used for CI Engine Speciation Profile Development

	Transient/ Steady-State Tests	Rated Power (Hp)	Engines
Pre-Tier 1	6 / 2	160	Deere 6068T
Tier 1 >50 hp	28 / 8	270	Cummins M11C
		194	Cummins ISB190
		330	Cummins QSL9
		480	Caterpillar 3408
Tier 1 <50 hp	8 / 2	50	Kubota V2203E
Tier 2 >50 hp	6 / 2	420	Caterpillar 3196

4. RESULTS

Speciation of SI engines was compared across engines and between profiles using E0 and E10 fuel by compound class (Figure 1) and compounds which are large contributors to the profiles (Figure 2).

Percent composition of compound class were similar between E0 and E10 fuel, with the exception of oxygenates (ethanol) showing up in the exhaust of E10 fuel. SI engines were also compared by 2- and 4-stroke engine type. 4-stroke SI engines overall had a higher percentage of olefins than 2-stroke engines (mostly due to higher propylene, ethylene, and acetylene). 2-stroke engines had a higher percentage of paraffins than

4-stroke engines (mostly due to higher 2,2,4-trimethylpentane, 2-methylbutane, and 2-methylhexane). 4-stroke profiles have much higher methane than 2-stroke profiles. 2-stroke profiles have a higher percentage of unknowns which may be due to higher molecular weight compounds in the exhaust. Differences between ethanol blends were not as pronounced except for E10 blends having a higher oxygenate percentage due to ethanol. However, the weight percentage of acetaldehyde more than doubles with E10 fuel.

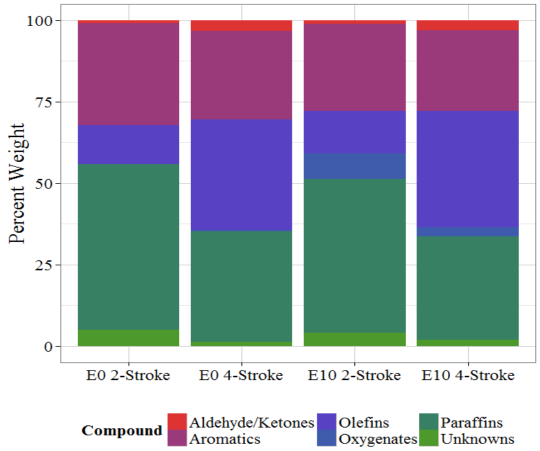

Fig 1. Comparison of SI profiles by compound class.

Figure 2 shows the contribution of highest emitted chemicals to SI engine exhaust speciation profiles. Chemical composition of these top compounds varied more between 2-stroke and 4-stroke engines than between fuel types. Methane, acetylene, ethylene, and toluene were the largest contributors to the 4-stroke profiles. 2-Methylbutane, 2,2,4-trimethylpentane, toluene, and ethanol were the largest contributors to the 2-stroke profiles. Note, toluene was highly variable across SI profiles. As a result, toluene values were replaced with pre-Tier 2 on-road vehicle profiles from SPECIATE4.4 profiles 8750a and 8751a (U.S. EPA, 2014).

Speciation of diesel engines was compared across CI engine control tier and power rating. Steady-state and transient tests were also compared between CI engine profiles. These comparisons were made by compound class (Figure 3) and by the largest contributors to the CI engine exhaust speciation profiles (Figure 4).

Aldehydes and ketones (27.5%-46.6%) make up a larger percentage of the CI engine exhaust speciation profiles than the SI engine exhaust speciation profiles. Tier 2 engines run on steady-state and transient cycles had the highest percent of paraffins compared to the other profiles.

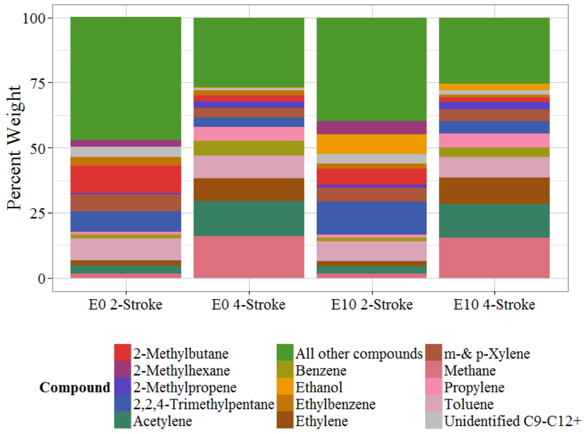

Fig 2. Composite compounds which are the largest contributors to SI profiles.

Formaldehyde (15.5%-26.6%) and ethylene (13.4%-22.9%) make up a large percentage of the CI engine exhaust speciation profiles. Formaldehyde and acetaldehyde increase going from pre-Tier 1 to Tier 2. Other large contributors include acetaldehyde, methane, and acetylene. 1-Butene and nonane were higher in the Tier 2 steady-state profile than other profiles.

There seemed to be more variation between engine control tier and power rating than between steady-state or transient test cycles. However, a few differences between test cycles were still present. For example, the Tier 1<50hp engine steady-state cycle profiles have the greatest percentage of olefins compared to the other profiles and Tier 2 steady-state profiles for ethane and propane are higher than most other profiles.

Tier 1 profiles had differing composition with horsepower across test cycles. These differences are indicated in Table 9.

Table 9. Tier 1 CI engine exhaust speciation profile percent differences in mass of emissions between greater than 50hp and less than 50 hp profiles [a]

Compound	% mass difference
Paraffins	42.2, 89.3
Olefins	8.3, 77.1
Aromatics	0.8, 83.9
Crotonaldehyde	35.2, 89.1
Methane	7.7, 100
Propionaldehyde	-48.7, 79.0
Ethylene	12.7, 80.2
Acetylene	-125.3, 41.7
Benzene	8.2, 72.9

[a] Values indicate the percent difference in mass of emissions between Tier 1 >50hp and Tier 1<50hp profiles on transient and steady-state tests, respectively

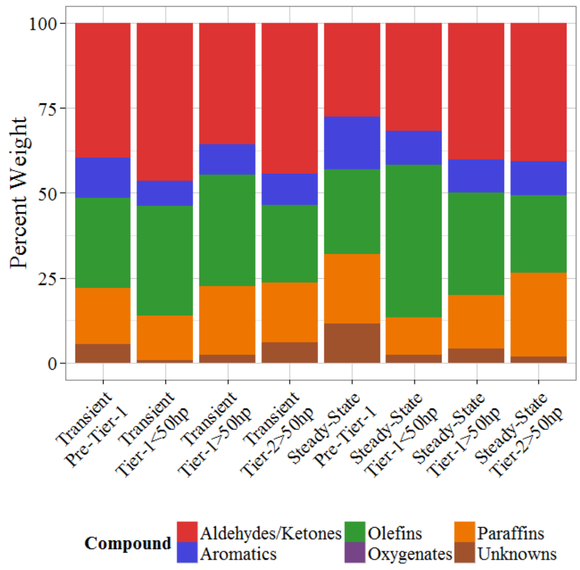

Fig 3. Comparison of CI profiles by compound class.

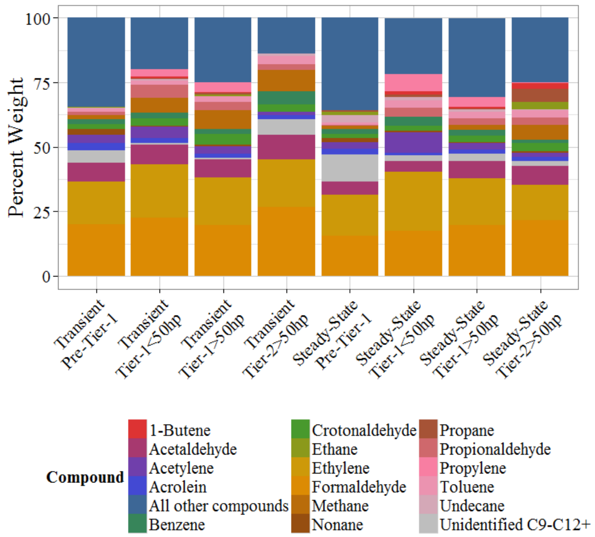

Fig 4. Composite compounds which are the largest contributors to CI profiles.

Volatile organic compound (VOC) profiles were created for SI and CI engines by removing the values for methane, ethane, and acetone from TOG profiles. Emission factors will be reported in fractions of individual species over total VOCs. The standard format for SPECIATE is VOC profiles.

5. APPLICATIONS

The nonroad engines and equipment TOG speciation profiles developed will be recommended for use in the SPECIATE4.4 database to feed air quality modeling. In addition, these profiles are being considered for incorporation into MOVES to speciate VOC in MOVES/NONROAD runs and for use as emission factors in the model.

6. LIMITATIONS AND DATA NEEDS

Organic gas exhaust chemical speciation is resource intensive and rarely done on nonroad engines or equipment. As a result, few test programs have included full exhaust speciation besides those cited in this paper performed by SwRI and EPA. Data cited in this paper is limited by a low number of tests and future test programs could include repeat tests and additional engines to bolster the accuracy of the data. Inventory projections suggest nonroad engines will become a larger contributor to the overall air toxics inventory in future years, due to control programs for on-road vehicles and point sources. Thus, robust detailed emissions characterization will become more important, and more speciation should be considered for future test programs.

There are many other types of engines and equipment that comprise the nonroad fleet which are not captured with the SI and CI test programs. We were unable to find recent or valid speciated emissions data on outboard and stern-drive marine engines. Other categories of nonroad engines for which speciation data is needed are catalyzed SI engines/equipment, CI Tier 3 and 4 engines, liquified petroleum gas (LPG) engines, and compressed natural gas (CNG) engines.

7. REFERENCES

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U.S. EPA (2014) SPECIATE4.4 is available online at: http://www.epa.gov/ttnchie1/software/speciate/