

Isotopic Tracing of Bio-Derived Carbon from Ethanol-in-Diesel Blends in the Emissions of a Diesel Engine

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ABSTRACT

The addition of oxygenates to diesel fuel reduces particulate emissions, but the mechanisms responsible for the reductions are not well understood. Measurement of particulate matter (PM), unburned hydrocarbons (HC), and carbon monoxide (CO) are routine, but determining the origin of the carbon atoms that make up these undesired emissions is difficult. The sub-attomole ($<6 \times 10^5$ atoms) sensitivity of accelerator mass spectrometry (AMS) for measuring carbon-14 (^{14}C) allows tracing the carbon atoms from specific fuel components to soot or gaseous emissions. Radioactive materials are not required because contemporary carbon (e.g., ethanol from grain) has 1000 times more ^{14}C than petroleum-derived fuels. The specificity of the ^{14}C tracer and the sensitivity of AMS were exploited to investigate the relative contribution to diesel engine PM, CO, and CO_2 from ethanol and diesel fractions of blended fuels. The test engine, a 1993 Cummins B5.9 diesel rated at 175 hp 2500 rpm, was operated at steady-state conditions of 1600 rpm and 210 ft-lbs. PM was collected on quartz filters following a mini-dilution tunnel. The limited solubility of ethanol in diesel fuel required either an emulsifier (Span 85) or cosolvent (n-butanol) to prepare 10, 20, and 40% ethanol-in-diesel blends. An ignition improver, di-tert-butyl peroxide (DTBP), was added to give all blends the same autoignition properties as the baseline diesel. PM was separated into volatile and non-volatile organic fractions (VOF and NVOF) for AMS analysis. The homogeneous cosolvent blends were more effective in reducing total PM mass, but the heterogeneous emulsified blends yielded larger VOF that are easily treated by exhaust catalysts. Ethanol derived carbon tended to reside in the NVOF, especially for the cosolvent blends.

INTRODUCTION

Environmental and human health concerns over emissions from internal combustion engines continue to bring about increasingly stringent emissions standards

and drive research into the use of non-conventional, cleaner-burning fuels. For compression-ignition (diesel) engines, oxygenated fuels have been shown to dramatically reduce particulate matter (PM) while also improving or maintaining acceptable levels of other regulated emissions (NO_x , HC and CO) [1-14]. The mechanisms through which oxygenates reduce PM, however, are unclear. In addition to changes in combustion chemistry, the influence of thermophysical properties on fuel injection and fuel-air mixing can play a significant role.

Researchers in the mid-1980s labeled fuel components with ^{14}C and traced the radioisotope to PM or soot from a diesel engine [15] or diffusion flame [15,16] using a decay-counting technique. These experiments required special radioactive test facilities to contain the large amounts of volatile radioactive compounds needed for decay counting and housing a radioactive engine. In addition to generating a significant amount of radioactive and mixed wastes, high level radioactive tracing can never be used in a realistic engine environment. The high sensitivity of accelerator mass spectrometry (AMS) allows the specificity of the ^{14}C atom to be used while avoiding radioactive waste issues. Furthermore, AMS detection permits tracing with road vehicles in conventional dynamometer facilities or on the open road.

Radioisotopes are specific and distinctive because they are extremely rare in natural materials. A radioisotope-labeled compound has a very high abundance-to-background ratio in natural systems, but poor signal-to-noise in the isotope detector may obscure this property. For example, the natural level abundance of ^{14}C due to cosmic radiation is 1.2 parts in 10^{12} . The rare stable isotope of carbon, ^{13}C , is naturally 1.1%. A one ppm concentration of a ^{13}C -labelled compound (assume formula weight 200 g/mol) will change the ^{13}C concentration by only 0.3 per 1000, measurable under good conditions using an excellent mass spectrometer. The same material labeled with ^{14}C changes the

concentration of that isotope in a contemporary biological sample by a factor of 3 million. Efficient detection of radioisotopes is a key to using this specificity.

Short-lived isotopes can be efficiently detected by their decay but produce high radiation hazards in the laboratory. Radioisotopes that have longer half lives (e.g., ^{14}C half life = 5730 y) are inefficiently detected by measuring decays. Measuring only 0.1% of the ^{14}C decays in a sample requires uninterrupted counting for 8.3 years ($0.1\% \times 5730 \text{ y} / \ln(2)$). The sensitivity and specificity of the radioisotope label are wasted in detecting decays. Accelerator mass spectrometry (AMS) is an isotope-ratio measurement technique developed in the late 1970s as a powerful tool for tracing long-lived radioisotopes in chronometry in the earth sciences and archaeology [17]. Samples prepared for ^{14}C analysis are combusted to CO_2 and then reduced to graphite for use in the AMS ion source. The technique counts individual nuclei rather than waiting for their radioactive decay, allowing measurement of more than 100 ^{14}C samples per day.

The contemporary quantity of ^{14}C in living things (1.2 parts in 10^{12} or 110 fmol ^{14}C / g C) is highly elevated compared to the quantity of ^{14}C in petroleum-derived products. Accordingly, components of bio-derived fuels contain elevated ^{14}C as compared to fossil fuels. This isotopic elevation is sufficient to trace the fate of bio-derived fuel components in the emissions of an engine without the use of radioactive materials. The complications of licensing and radioactive waste disposal are completely avoided. Some petroleum-derived components can be synthesized from biological sources. If synthesis of a fuel component from biologically-derived source material is not feasible, another approach is to purchase ^{14}C -labeled material and dilute it with petroleum-derived material to yield a contemporary level of ^{14}C . In each case, the virtual absence of ^{14}C in petroleum based fuels gives a very low ^{14}C background that makes this approach to tracing fuel components practical.

Regulatory pressure to significantly reduce the particulate emissions from heavy-, medium- and light-duty diesel engines is driving research into understanding mechanisms of soot formation. If mechanisms are understood, then combustion modeling can be used to evaluate possible changes in fuel formulation and suggest possible fuel components that can improve combustion and reduce PM and other emissions. The current combustion paradigm assumes that large molecules break down into small components and then build up again during soot formation. If all fuel components are broken down into 1- or 2-carbon species, then there should be no difference in the contribution of carbon from aromatics, alkanes or oxygenates in the PM emissions. AMS allows the labeling of specific carbon atoms within fuel

components, tracing the carbon atoms, and testing this combustion modeling paradigm.

Volatile and non-volatile organic fractions (VOF, NVOF) in the PM can be further separated. Researchers at Southwest Research Institute (SwRI) showed that the addition of the oxygenate dimethoxymethane to diesel fuel not only reduced total PM emissions, but also increased the proportion of VOF in the PM [18,19]. The VOF of the PM can be oxidized in the exhaust stream to further decrease PM. A fuel formulation that significantly shifts PM to the VOF can be more valuable in reducing emissions than a variation that merely drops total PM.

The methods described below for tracing fuel components in the emissions of diesel engines can be applied to any engine or combustion system. Any molecule containing carbon can be labeled with ^{14}C . Techniques for measuring the ^{14}C concentrations by AMS are straightforward and routine. Knowing the chemical identity and carbon inventory of a sample is the key to exploiting the power of ^{14}C -AMS.

Meeting future emission requirements will likely require modification of existing diesel fuel and exhaust treatment to reduce NO_x and oxidize PM. The decisions which drive approaches to satisfying pending emission regulations must balance engine and emission performance, cost, fuel compatibility with the existing vehicle fleet, national security, and fuel supply. If reducing dependence on imported oil becomes a priority, use of bio-derived fuels will probably be required. Bio-diesel and ethanol are obvious options, each with its own features. Bio-diesel is immediately usable but production capacity is limited. Ethanol has a much larger production capacity, but it is not a good diesel fuel. The ease of tracing bio-derived ethanol against a petroleum background and the simplicity of the molecule influenced our decision to demonstrate the power of AMS to trace fuel component carbon in PM and gaseous emission from a variety of ethanol-in-diesel blends.

OBJECTIVE

Our goal was to demonstrate methods for tracing bio-derived carbon from fuel components in the emissions from a diesel engine. In addition to demonstrating methods, we present preliminary data showing the partitioning of labeled oxygenates in various fractions of particulate and gaseous emissions.

FACILITIES

ENGINE FACILITY – Emission samples were collected from a 1993 Cummins B5.9 engine at the Combustion Analysis Laboratory at the University of California at Berkeley (UCB). Figure 1 shows the engine installed at UCB and detailed specifications are listed in Table 1. Fuel injection is achieved with a Bosch P7100 PE type

inline pump capable of injection pressures of up to 115 MPa. No modifications were made to the engine or fuel injection system to optimize for operation on the test fuels.

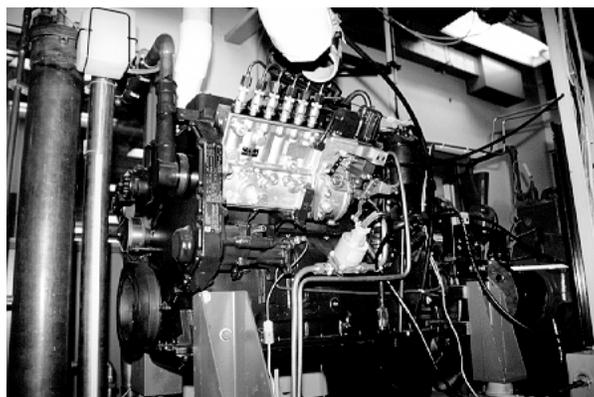


Figure 1. Cummins B5.9 Engine installed at UC Berkeley's Combustion Analysis Laboratory.

Table 1. Cummins B5.9 engine specifications

Model year	1993
Displacement	5.88 liters (359 in ³)
Configuration	6 cylinder inline
Bore	102 mm (4.02 in)
Stroke	120 mm (4.72 in)
Compression ratio	17.6:1
Horsepower rating	175 hp @ 2500 rpm
Torque rating	420 ft-lb @ 1600 rpm
Aspiration	turbocharged and aftercooled
Injection timing	11.5° BTDC

Fuel consumption was determined using a Micro Motion R025 coriolis flow meter. Modifications to the fuel return system were made to eliminate fuel return to the storage tank. The return line is instead routed back into the fuel delivery line and a shell-and-tube heat exchanger was installed to prevent overheating of the fuel in the short-circuited system.

Gaseous emissions were monitored using Horiba gas analyzers as listed in Table 2. Measurements of PM were made via a mini-dilution tunnel designed and constructed by UCB.

Table 2. Equipment for gaseous emissions measurements

HC	Horiba Instruments FMA-220 flame ionization analyzer
CO, CO ₂	Horiba Instruments AIA-220 infrared analyzer
NO _x	Horiba Instruments CLA-220 chemiluminescent analyzer

AMS FACILITY – The Center for AMS at LLNL houses four accelerators with different analysis capabilities [20-24]. The samples in this study were analyzed with the HVEE FN system operating at 6.5 MV (Fig. 2). All samples were prepared in the LLNL natural carbon prep lab using established methods [25]. The AMS sample prep method accommodates samples containing between 0.05 and 10 mg carbon. Samples containing 0.2-2 mg carbon are preferred for obtaining higher measurement precision and lower systemic backgrounds. Approximately 15000 ¹⁴C-AMS samples are measured annually at LLNL with 2-3 measurement days per week.

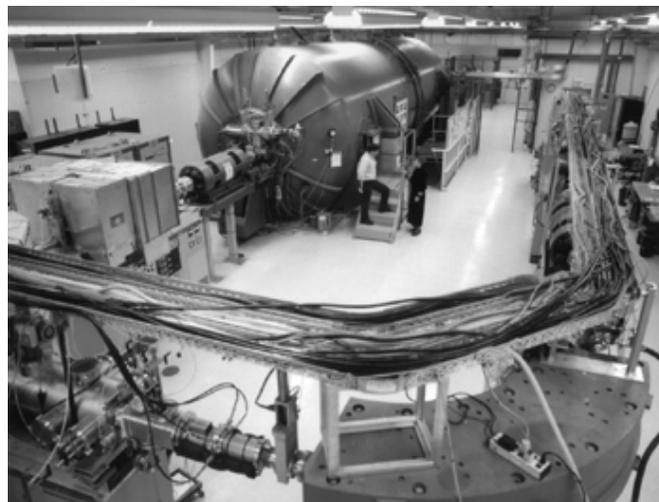


Figure 2. LLNL HVEE FN accelerator system viewed from the high energy end looking toward the ion source on the far side of the accelerator tank.

MATERIALS AND METHODS

TEST FUELS - All major fuel components and lubrication oils were checked for ¹⁴C content prior to use in the engine. Diesel fuel was not separated into components, its isotopic content was measured with any additives or detergents added by the manufacturer. Baseline diesel from two production lots were used. The test fuels included baseline diesel fuel and blends of baseline diesel with various amounts of bio-derived ethanol. Because ethanol is soluble in diesel fuel in only small quantities, either an emulsifier (Span 85, i.e., sorbitan trioleate) or a cosolvent (n-butanol) was used to prepare the ethanol-in-diesel blends. An ignition improver, di-tert-butyl peroxide (DTBP), was also used to compensate for the low cetane number of ethanol and to give all blends the same cetane number (49.2) as the baseline diesel. Table 3 lists fuel blends and ¹⁴C content of the major constituents in the fuels. The ¹⁴C content of diesel fuel is higher than expected for a petroleum product. The addition of small amounts of contemporary carbon detergents are likely responsible for the elevation. The isotopic content of the lubrication oil was at instrumental background. The contemporary carbon from the ethanol is the tracer in these fuels. Since the

Table 3. UCB test fuel blends (components listed in volume percent except for oxygen which is mass percent) and ^{14}C content of components (amol ^{14}C / mg C).

Fuel Component	Blend 10E	Blend 10C	Blend 20E	Blend 20C	Blend 40E	Blend 40C	^{14}C Content
Diesel A	88.0	88.5	76.0	77.0			0.33
Diesel B					52.0	54.0	0.23
Ethanol	9.5	9.0	18.5	18.0	37.0	36.0	107
SPAN 85	2.0		4.0	-	8.0		110
n-butanol		2.0	-	3.5		7.0	0.09
DTBP	0.5	0.5	1.5	1.5	3.0	3.0	0.01
Oxygen	3.5	3.5	7.0	7.0	13.9	13.9	NA

ethanol is bio-derived, each carbon atom in the ethanol is equally labeled with ^{14}C .

FILTER HANDLING AND LOADING – All PM samples were collected on 47 mm Gelman Sciences PALLFLEX tissuquartz 2500QAT-UP membrane filters. These quartz filters were pre-combusted at 1173 K for 3 h to remove all carbon residue and allowed to cool to 300 K in the furnace before removal. Blank filters were first conditioned to temperature and humidity overnight in petri dishes and then individually weighed with a Mettler UM 3 microbalance. Before sampling, the dilution ratio was adjusted to yield temperatures of the diluted exhaust below the required 325 K; resulting dilution ratios ranged between approximately 6 and 14. Diluted exhaust was drawn through each filter for 10 minutes and the filters were then removed, placed in petri dishes and once again conditioned overnight before weighing (see Figure 3). Three to five separate samples were taken for each point in the test matrix. A series blank was collected for each set of filters.

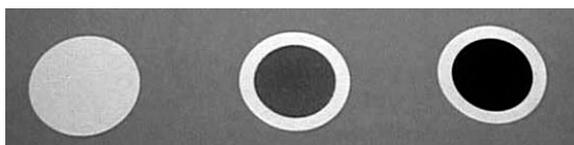


Figure 3. Filters loaded with PM from UCB engine. The filters from left to right are a blank control, a collection with 20% ethanol, and a collection with baseline diesel.

GAS SAMPLE COLLECTION AND PROCESSING – For each fuel used, three gas samples were collected in 3.0 L Tedlar bags placed after the filter holder in the exhaust line. Each bag had a conventional fill valve and second septa seal port. The septa port was used to remove gas for AMS sample preparation. Gas samples were processed within several days of collection. The bags were maintained at temperatures between 290 and 300 K and retained gas for weeks.

The diluted exhaust gases contained ~6% CO_2 and very low levels of CO. Approximately 40 mL of exhaust gas at

atmospheric pressure was transferred to an evacuated stainless steel AMS graphitization line. The transfer volume was selected to produce an AMS sample containing approximately 1 mg carbon. Water was removed using a dry ice/ isopropanol cold trap. The CO_2 was then cryogenically condensed in a liquid nitrogen (LN) cold trap and non-condensable gases were removed. The CO_2 was then moved to a graphitization head [25] for conversion to an AMS graphite sample.

CO cannot easily be removed from gas by cryogenic methods because its condensation temperature is below that of LN, 78K. CO can be removed from a gas on 3A molecular sieve (MS) material (Sigma Chemical, St. Louis, MO). The MS was pre-combusted at 1173 K for 3-h to remove all residual carbon, allowed to cool to 300 K, and then stored in a tightly sealed glass bottle with a teflon lined top prior to use. Approximately 600 mg MS was used to capture a <0.1 mg CO sample. The same 40 mL volume used to produce CO_2 samples was used in preparing CO samples. Dry ice/alcohol and LN cold traps removed water, CO_2 , HC, and SO_2 from the 40 mL volume. It was then allowed to contact MS in a quartz tube partially submersed in LN for several minutes. The residual gases were then removed and the process was repeated twice. The quartz tube containing the MS and about 20 mg copper oxide (CuO) was evacuated, sealed with a torch fueled with hydrogen and oxygen, and combusted like a typical AMS sample. After combustion, the sample was converted to graphite using the standard AMS procedure [25]. Typical CO samples contained 40-70 μg carbon. Process blanks prepared on the rig contained <10 μg carbon, too little to make graphite.

AMS FILTER PREPARATION – Beyond measuring total PM emissions, we sought to determine the susceptibility of PM to exhaust oxidation treatment to reduce mass. In practice, the criteria for this separation are operationally defined by the investigator. Depending on the field of the investigator, the separation of PM carbon is commonly described by the following pairs: elemental and organic carbon, soluble organic fraction (SOF) and insoluble organic fraction (IOF), or volatile organic fraction

(VOF) and non-volatile organic fraction (NVOF). We prefer the VOF/NVOF nomenclature because it reflects the process we use and the physical properties employed in any realistic exhaust treatment scheme.

Loaded filters are cut in half with a clean stainless steel surgical scissors. One half is cut into strips and placed in a quartz combustion tube with CuO oxidizer and converted to an AMS graphite sample [25]. This measurement is of the total carbon in the PM. The other half filter is heated to 613K for 2 h in a furnace and then allowed to cool to room temperature. This procedure to remove the VOF was developed using National Institute of Standards and Technology (NIST) standard reference material (SRM) to obtain consistent isotope ratios and mass fraction of the NVOF. NIST SRM 2975 (diesel soot) and SRM 1649a (urban dust) are the closest NIST SRMs to exhaust PM. The diesel soot SRM 2975 had only 7% VOF with this procedure, much less than observed with PM from a typical diesel. The filters loaded with PM lose mass during the thermal separation and the soot deposits are noticeably lighter. The remaining carbon is the NVOF. The filters with NVOF are then prepared as AMS samples with the usual procedure [25].

Gravimetric measurement of PM deposited on filters can be unreliable if the PM mass is small (100 µg) and the filter mass is large (100 mg). During the AMS sample preparation method we measure the CO₂ pressure from the completely combusted sample. The VOF is estimated by difference in mass of the two half filters.

AMS MEASUREMENT AND ANALYSIS - AMS is an isotope ratio mass spectrometry technique where ¹⁴C/¹³C ratios of the unknowns are normalized to measurements of 4-6 identically prepared standards of known isotope concentration. Typical samples are placed in quartz combustion tubes with excess copper oxide (CuO), evacuated and combusted to CO₂. The evolved CO₂ is purified, trapped, and converted to graphite in the presence of cobalt or iron catalyst in individual reactors [25]. Large CO₂ samples (> 500 µg) can be split for additional ¹³C measurement by stable isotope ratio mass spectrometry. Identified fuel components were measured for ¹³C and gave δ¹³C corrections of -27 per 1000. All graphite targets were measured at the Center for AMS at LLNL.

The measured ratio of ¹⁴C to total C for each sample, R_{sample}, is described in Eq. 1. The concentration of the ¹⁴C labeled fuel component is ¹⁴C_{tracer}/C_{tracer}. The contributions from the fuel and additives to the measured ratio are ¹⁴C_{fuel}/C_{fuel} and ¹⁴C_{add}/C_{add}, respectively. The background contribution is ¹⁴C_{bk}/C_{bk} and the possibility of contamination to the sample is indicated as ¹⁴C_{uk}/C_{uk}.

$$R_{\text{sample}} = \frac{{}^{14}\text{C}_{\text{tracer}} + {}^{14}\text{C}_{\text{fuel}} + {}^{14}\text{C}_{\text{add}} + {}^{14}\text{C}_{\text{bk}} + {}^{14}\text{C}_{\text{uk}}}{\text{C}_{\text{tracer}} + \text{C}_{\text{fuel}} + \text{C}_{\text{add}} + \text{C}_{\text{bk}} + \text{C}_{\text{uk}}} \quad (1)$$

In theory, all the components in Eq. 1 need to be determined by a series of control experiments. In practice some components can be minimized by experimental design. In the case of PM samples, the ¹⁴C terms of petroleum derived fuel components are insignificant, only a biologically-derived additive (e.g., Span 85) contributes to the ¹⁴C content. The ¹⁴C_{bk} component is a systemic background of ambient CO₂ absorbed by the deposited PM. It is hoped that C_{uk} is eliminated and C_{bk} is consistently measured in blanks and baseline diesel samples.

The isotope ratio of the sample, R_{sample}, is calculated from the measured isotope ratios of the sample, R_{sample(meas)}, the average of the measured standards, R_{stand(meas)}, and the known isotope ratio of the standard, R_{stand}, shown in Eq. 2.

$$R_{\text{sample}} = \frac{R_{\text{sample(meas)}}}{R_{\text{stand(meas)}}} R_{\text{stand}} \quad (2)$$

Traditional tracer experiments generally depend on radioactive decay and are dominated by a highly labeled tracer with very small mass. In our case, the tracer was not radioactive and contributed a significant amount of carbon to the measured isotope ratio. The denominator of the Eq. 1 is an expression for the total carbon mass of the sample. The product of the isotope ratio and carbon mass is the quantity of ¹⁴C in the sample. The ¹⁴C in the measured sample comes from the fuel components (see Eq. 3), whose isotope ratios we measure.

$${}^{14}\text{C}_{\text{sample}} = {}^{14}\text{C}_{\text{tracer}} + {}^{14}\text{C}_{\text{fuel}} + {}^{14}\text{C}_{\text{add}} + {}^{14}\text{C}_{\text{bk}} \quad (3)$$

The relative contribution of the tracer to the PM ¹⁴C content then be calculated by solving Eq. 3 for the ¹⁴C_{tracer} term. The carbon mass of the tracer, C_{tracer}, in the PM is determined by dividing the tracer ¹⁴C content, ¹⁴C_{tracer}, by the tracer ¹⁴C concentration, R_{tracer}, as in Eq. 4.

$$\text{C}_{\text{tracer}} = \frac{{}^{14}\text{C}_{\text{tracer}}}{R_{\text{tracer}}} \quad (4)$$

The fraction of PM mass attributable to the tracer, F_{tracer}, is then the ratio of C_{tracer} to sample carbon mass, C_{sample}, as shown in Eq. 5.

$$F_{\text{tracer}} = \frac{\text{C}_{\text{tracer}}}{\text{C}_{\text{sample}}} \quad (5)$$

RESULTS AND DISCUSSION

Brake-specific emissions and fuel consumption results from the baseline diesel fuel and the six test fuel blends are shown in Table 4. Since the different production lots of baseline diesel fuel used had different brake-specific emissions, comparison of the blends is also presented as a percentage of baseline diesel emissions in Table 5.

Table 4. Brake-specific emissions and fuel consumption of baseline diesel and ethanol-in-diesel blends in g/kW-hr.

Fuel	Diesel A	Diesel B	Blend 10E	Blend 10C	Blend 20E	Blend 20C	Blend 40E	Blend 40C
PM	0.038	0.0221	0.0323	0.0302	0.044	0.027	0.0184	0.0457
NO _x	5.50	4.23	5.04	5.09	4.89	4.87	4.40	4.76
HC	0.097	0.114	0.132	0.147	0.155	0.155	0.291	0.310
CO	0.400	0.407	0.453	0.449	0.496	0.484	1.703	2.121
Fuel Consumption	185	184	201	207	206	208	227	225

Table 5. Brake-specific emissions and fuel consumption of ethanol-diesel blends expressed as percent of baseline diesel.

Fuel	Blend 10E	Blend 10C	Blend 20E	Blend 20C	Blend 40E	Blend 40C
PM	85%	79%	119%	71%	206%	83%
NO _x	91%	92%	87%	89%	104%	112%
HC	136%	151%	155%	160%	255%	271%
CO	112%	111%	120%	121%	419%	522%
Fuel Consumption	109%	112%	111%	112%	124%	123%

The homogeneous cosolvent blends (Blends 10C, 20C, and 40C in Tables 4 and 5) reduced total gravimetric PM emissions in each case. The heterogeneous emulsified blends (Blends 10E, 20E and 40E) actually experienced an increase in total PM mass for the 20 and 40% ethanol blends. The loaded filters did not appear darker however, suggesting that additional mass may have been due to increased water or unburned fuel absorption on the PM. NO_x emissions from the 10 and 20% blends were 90% that of the baseline diesel, probably due to lower combustion temperature. Emissions of both HC and CO increased for 10 and 20% blends, but remained very low as is typical with diesel engine combustion. Fuel consumption was higher with the test fuel blends due to the lower energy density of ethanol. The Cummins engine ran poorly with the 40% ethanol blends and emissions were unusually high for a diesel.

VOF/NVOF PARTITIONING – The CO₂ pressures measured from half filters during the production of graphite for AMS analysis provide an accurate measure of carbon mass. Traditional gravimetric measurements of filters can be misleading. It is difficult to measure 100 µg variations in a 100 mg filter. Furthermore, the filters are fragile and it is easy to lose small pieces on the soot-free border when handling with forceps. The PM deposited on quartz filters has very high specific surface area and readily absorbs water and other molecules from the vapor phase.

The partitioning of carbon in the VOF and NVOF for the different fuel blends is shown in Figure 4. The baseline diesel fuels, DA and DB, had NVOF/VOF splits of roughly 55/45 ± 1% and 48/52 ± 6%. The DB filters had significantly more variation. Partitioning of NVOF/VOF from the 10 and 20% ethanol cosolvent blends (10C and 20C) was essentially the same as the baseline fuels. The 10 and 20% ethanol emulsified blends (10E and 20E) had much higher VOF than baseline fuels, but samples were more variable (±10%). Both 40% ethanol blends produced low NVOF, but the engine ran poorly. Only the 10 or 20% ethanol blends are viable fleet fuels.

When viewed in conjunction with the brake-specific emissions, the large VOF of the 20% ethanol emulsified blend yields a brake-specific PM NVOF only 23% that of diesel assuming a 20-80 NVOF-VOF partition. The cosolvent blend yields a brake-specific PM NVOF 32% that of diesel assuming a 45-55 NVOF-VOF partition. The NVOF PM is more resistant to exhaust oxidation, so driving more PM into the VOF may be more effective in reducing emissions.

ETHANOL CONTRIBUTION TO PM – The ¹⁴C signal from the bio-derived ethanol in the PM was easily measured above the isotope level of the baseline diesel. Blank filters used to measure the carbon mass and isotopic content of the ambient environment absorbed approximately 25 µg carbon with a ¹⁴C content about 50% of contemporary plants. In a half filter this background accounted for 0.5 amol of ¹⁴C. Filters

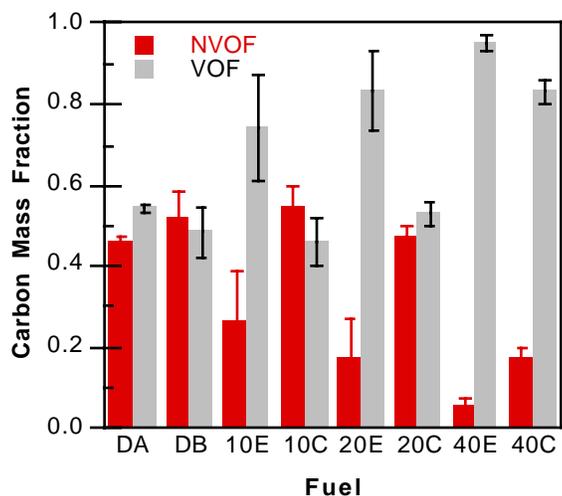


Figure 4. Partitioning of carbon between VOF and NVOF on filters loaded with PM from both baseline diesel fuels (DA and DB), emulsified blends containing 10, 20 and 40% ethanol (10E, 20E, and 40E) and cosolvent blends containing 10, 20 and 40% ethanol (10C, 20C, and 40C). Error bars represent standard deviation of 3-5 measurements.

loaded with PM from running baseline diesel absorbed ^{14}C between loading and AMS sample processing. Since fresh soot is more absorbent than aged soot, it is reasonable to assume most of this ^{14}C was absorbed in the engine lab where the ambient ^{14}C content is 50% that of contemporary plants. This absorbed mass is approximately 10 μg . Finally, the ^{14}C content of the diesel fuel is 0.3 amol / mg C. This level is higher than expected for a petroleum-derived material. Commercial diesel fuel contains a variety of additives, some of which may have bio-derived carbon, that slightly elevate the ^{14}C above a single petroleum derived molecule (e.g. n-butanol in this study). The PM collected from the baseline diesel fuels contained about 2.0 amol ^{14}C / mg C. The thermal treatment to remove the VOF cut this background level to 1.3 amol ^{14}C / mg C. The absorbed background depends on surface area which depends on the mass of PM deposited. Scaling the background as a function of sample mass is achieved by combining the fuel and background contributions and expressing them as a ratio of ^{14}C to PM sample mass.

The contributions of ethanol to the carbon in PM is listed in Table 6. The fraction of carbon mass contributed by ethanol varies slightly between emulsified and cosolvent blends so that the same oxygen content was achieved by each blending method. The ethanol carbon mass percentage was calculated from knowledge of the mixture components. The total and NVOF PM ethanol carbon mass percentage are averages of measurements from 2-5 samples. Uncertainties were driven by scatter among samples rather than measurement precision and typically ranged 0.2-0.7%.

Table 6. Distribution of ethanol-derived carbon in total and NVOF PM.

Fuel Blend	Ethanol Vol %	Fuel Ethanol C Mass %	Total PM Ethanol C Mass %	NVOF PM Ethanol C Mass %
10E	9.5	5.7	2.4	3.4
10C	9.0	5.4	0.8	2.7
20E	18.5	11.7	3.7	10.8
20C	18.0	11.4	2.9	6.7
40E	37.0	26.2	20.9	24.2
40C	36.0	25.2	3.7	15.0

The following trends were observed during the study of blended fuels:

- Carbon masses of the PM generated by the cosolvent and emulsified blends were almost identical.
- PM from the cosolvent blend had a lower ^{14}C concentration than that of the emulsified blend.
- Ethanol-derived carbon residing in PM is more likely to be NVOF.
- The ^{14}C concentrations of the PM were below those of the CO_2 for the 10% and 20% blends.

The trend that ethanol-derived carbon was less likely to be found in the PM is not surprising. Carbon mass measured by CO_2 pressure from combusted half filters was the same for cosolvent and emulsified blends. The emulsified blend produced PM with higher mass but did not contain more carbon. Furthermore, much of this larger mass was volatile. The combination of no carbon and volatility of the PM and the possibility of unburned emulsifier in the PM suggest that the higher PM mass is due to absorbed water. In the case of the cosolvent blends, it appears that the ethanol-derived carbon resides primarily in the building blocks of soot rather than in condensed volatiles on the surface of the PM. Ethanol produces some acetylene and other soot precursors during combustion which contribute to soot formation. Although its contribution to soot is less than diesel fuel, the oxygenate does participate in soot formation. Some of the loss of ^{14}C to the VOF for the emulsified blend appears to be associated with the emulsifier. Control experiments in which emulsifier was added to diesel without ethanol indicated that emulsifier-derived carbon resided mostly in the VOF.

AMS GAS ANALYSIS – Since the majority of the carbon from the fuel is fully combusted, the isotope ratio of the collected CO_2 reflects the isotopic content of the fuel. The CO_2 from the emulsified blend has more ^{14}C than the cosolvent blend as expected due to use of a

contemporary emulsifier. The ^{14}C content of fuels and collected CO_2 is listed in Table 7. The collected CO_2 samples had more ^{14}C than the fuel average in all cases. A small elevation is due to the small amount of atmospheric CO_2 drawn through the engine and possible migration through the collection bag. Additionally, the ethanol in the blends is more likely to reach CO_2 than the diesel fuel, slightly increasing the measured ^{14}C content of the combusted gas.

The CO samples were so small that high precision measurement of ^{14}C content was impossible. Some CO samples had slight isotopic elevation compared to CO_2 , indicating that the ethanol may not have combusted as fully as the diesel fuel. In general, however, isotopic measurements of separated CO were the same as the CO_2 within measurement uncertainties.

Table 7. Comparison of fuel and combusted gas CO_2 ^{14}C content for baseline diesel A and fuel blends.

Fuel	Fuel (amol ^{14}C / mg C)	CO_2 (amol ^{14}C / mg C)
Diesel	0.33	0.86
10E	8.10	8.63
10C	6.12	6.55
20E	16.3	17.4
20C	12.5	13.5
40E	35.9	37.7
40C	27.2	28.1

CONCLUSION

AMS provides a means of following the fate of carbon in specific compounds from the fuel to the emissions from diesel engines. Selective labeling of specific carbon atoms within a fuel component provides direct experimental evidence of the behavior of different chemical groups during combustion. In addition to providing data validation to combustion modelers, the data provides insights into which chemical structures within fuels and additives most greatly influence emissions.

Solubility issues and extremely low cetane number limit the likelihood that ethanol would be used routinely as a diesel oxygenate. The ease of using the contemporary tracer carbon demonstrated the simple application to tracing bio-derived components of blended fuels. Despite being partially oxidized, ethanol-derived carbon contributed significantly to PM. The relatively large amounts of ethanol-derived carbon in the PM points to potential problems of using oxygenates which form unsaturated C2 fragments during combustion. The heterogeneous emulsified blends had larger VOF than the homogeneous cosolvent blends. The differences in the PM produced with cosolvent and emulsified blends

indicates that the distribution of oxygen in the fuel, not just its content, significantly affects PM production.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

¹⁴C: carbon-14, long-lived naturally occurring radioisotope of carbon

AMS: accelerator mass spectrometry

amol: attomole, 1x10⁻¹⁸ mole, ~6x10⁵ atoms

DTBP: ditertiarybutyl peroxide

HC: hydrocarbons

LLNL: Lawrence Livermore National Laboratory

LN: liquid nitrogen

MS: molecular sieve

NVOF: non-volatile organic fraction

PM: particulate matter

UCB: University of California at Berkeley

VOF: volatile organic fraction