# New Insights to the Use of Ethanol in Automotive Fuels: A Stable Isotopic Tracer for Fossil- and Bio-Fuel Combustion Inputs to the Atmosphere

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Ⓢ *Supporting Information*

ABSTRACT: Ethanol is currently receiving increased attention because of its use as a biofuel or fuel additive and because of its influence on air quality. We used stable isotopic ratio measurements of $^{13}C/^{12}C$ in ethanol emitted from vehicles and a small group of tropical plants to establish ethanol's $\delta^{13}C$ end-member signatures. Ethanol emitted in exhaust is distinctly different from that emitted by tropical plants and can serve as a unique stable isotopic tracer for transportation-related inputs to the atmosphere. Ethanol's unique isotopic signature in fuel is

related to corn, a C4 plant and the primary source of ethanol in the U.S. We estimated a kinetic isotope effect (KIE) for ethanol's oxidative loss in the atmosphere and used previous assumptions with respect to the fractionation that may occur during wet and dry deposition. A small number of interpretive model calculations were used for source apportionment of ethanol and to understand the associated effects resulting from atmospheric removal. The models incorporated our end-member signatures and ambient measurements of ethanol, known or estimated source strengths and removal magnitudes, and estimated KIEs associated with atmospheric removal processes for ethanol. We compared transportation-related ethanol signatures to those from biogenic sources and used a set of ambient measurements to apportion each source contribution in Miami, Florida—a moderately polluted, but well ventilated urban location.
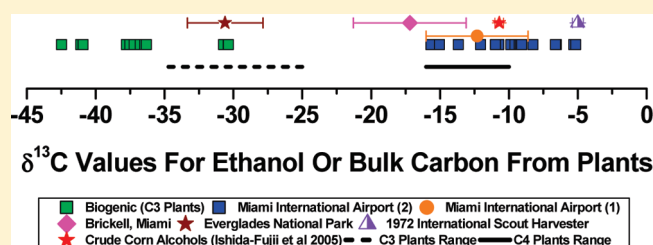
■ INTRODUCTION

The United States (U.S.) began using ethanol fuel mixtures containing up to 10% ethanol (v/v) in 1978 during President Carter's Administration and when the U.S. Congress passed the Energy Tax Act. The Act was designed to stimulate alternative fuel production to help decrease the country's future dependency on nonrenewable oil. Currently, there are ~190 biorefineries producing ethanol within the U.S. and greater than 90% of these use corn exclusively as feedstock.[1] Yearly production of "fuel ethanol" (intended for use in the transportation sector) within the U.S. has increased by a factor of 1300 between the years 1981 and 2009 when ~7.5 billion gallons were produced.[2] U.S. production of ethanol is expected to increase further as a result of the milestones set forth by the Energy Independence and Security Act 2007 (EISA07), which call for a total of 36 billion gallons of renewable fuel by year 2022.[3] Despite the nation's desire to scale-up ethanol production from cellulosic feedstock, careful inspection of EISA07 shows that greater than 50% of U.S ethanol will be derived from corn over the next decade. Today, ethanol penetrates 80% of the U.S. fuel supply, primarily as E10 (up to 10% ethanol by volume, 90% gasoline),[1] and the U.S. EPA recently increased the maximum allowable national limit to E15 (i.e., 15% ethanol by volume) for newer gasoline vehicles.[4]

Air quality studies related to ethanol fuel use within the U.S. have occurred in western states mandated to use oxygenated or reformulated gasoline blends to help attain National Air Quality Standards.[5] Most of these studies focused on measuring primary emissions of formaldehyde and acetaldehyde, which are derived from ethanol fuel combustion and are known carcinogens. However, acetaldehyde can also be formed as a secondary product; nearly 65% of ethanol in the atmosphere is directly converted to acetaldehyde when ethanol is oxidized by OH. Acetaldehyde's secondary production should be a concern to countries that are increasing the amount of ethanol used as fuel because studies in Brazil, a country that uses ethanol as its primary fuel, have observed unusually high ambient concentrations of ethanol that are expected to be a result of the fuels use.[6,7] Acetaldehyde also reacts photochemically to produce secondary pollutants such as peroxyacetyl nitrate (PAN) and has been shown to indirectly impact local and regional ozone production.[5,8−10]

Currently, studies of ethanol are increasing because of its use as an additive in vehicle fuels and its likely expanded use as an

alternative fuel. The impacts related to ethanol fuel use are not clear and the emission strengths of biogenic and anthropogenic sources of ethanol are not well characterized. In light of this, the need for better quantification and understanding of ethanol sources has been realized and a number of budget and modeling studies were published in the past three years.[11−13]

The work presented here used gas chromatography—isotope ratio mass spectrometry (GC-IRMS) to measure stable isotopic ratios ($^{13}C/^{12}C$) of gas-phase ethanol emitted directly from a small group of tropical plants, in vehicle exhaust, and in ambient air samples. Unlike radiocarbon measurements, which can distinguish anthropogenic from biogenic sources based on a compound's ^{14}C content, GC-IRMS is the only method capable of distinguishing ethanol emitted from fuel from that emitted by plants because in each case the ethanol is of a modern carbon source. Measured $\delta^{13}C$ values from vehicle exhaust and plant emissions were used as end-member signatures and anchored our observed $\delta^{13}C$ range during the study. The isotopic composition of ethanol emitted from vehicles was distinctly different from that emitted from tropical plants and can serve as a unique stable isotopic tracer for transportation-related inputs to the atmosphere. Unburned ethanol remaining in the exhaust gas was substantially enriched in ^{13}C compared to other gases found in the matrix and reflects ethanol's corn origins.

Owing to the absence of carbon isotopic data for ethanol we estimated the isotopic enrichment (ε) that would occur with ethanol's oxidative loss in the atmosphere using an approach founded on Atkinson's structure reactivity method.[14] Kwok and Atkinson have demonstrated that the structure reactivity method can reasonably estimate the hydrogen abstraction rate constant for gas-phase organic compounds with the hydroxyl radical based on a compound's molecular structure.[14,15] We also used previous assumptions with respect to the isotopic fractionation that may occur during dry and wet deposition events.[16,17] Three interpretive model calculations were used for source apportionment of ambient ethanol and to understand effects resulting from the alcohol's atmospheric removal.[18,19] The model calculations incorporated our end-member signatures and ambient measurements of ethanol, known or estimated source strengths and removal rates, and estimated KIEs associated with atmospheric removal processes for ethanol. We compared transportation-related ethanol signatures to those from biogenic sources and use a set of ambient measurements to apportion each source contribution in Miami, Florida—a moderately polluted, but well ventilated urban location.

■ EXPERIMENTAL SECTION

A detailed description of the GC-IRMS design and sampling procedures is available in a previous publication;[20] however, a review is included here. A custom two-stage preconcentration system, designed to concentrate and selectively separate ethanol and other hydrocarbons from gases such as H_2O, CO_2, and N_2, was connected to the inlet of a Hewlett-Packard 6890 gas chromatograph (GC). Chromatographic separation occurred on an Agilent DB-624 chromatography column (20 m × 0.18 mm I.D. × 1 μm film thickness, 6% cyanopropylphenyl/94% dimethyl polysiloxane). The GC operated in constant flow mode (0.7 cm^3 min^{-1}) and controlled the temperature programming during the analyses. A heated combustion column (900 °C) containing two catalytic wires was used to convert the hydrocarbons to CO_2 and H_2O; the latter of which was cryogenically removed ($\sim$ −60 °C)

from the sample stream while CO_2 was transferred through the open split to the ion source of a Europa Scientific Geo 20-20 isotope ratio mass spectrometer (IRMS). For carbon, the stable isotopic composition of a sample is expressed as a ratio (R) of $^{13}C/^{12}C$ and reported in delta (δ) notation as a per mil (‰) difference of the sample compared to a working reference gas calibrated to the international standard V-PDB: $\delta^{13}C$ (‰) = $((R_{SAMPLE}/R_{REFERENCE}) − 1) \times 10^3$.

A limited number of samples were also analyzed using a preconcentration cryogenic trapping gas chromatography with flame ionization detection (GC-FID) procedure[21,22] to determine the concentrations of acetylene and ethanol as well as their emission ratios, which allowed us to estimate the amount of U.S. fuel-derived ethanol emitted from "onroad" vehicles.

Sampling. In earlier work,[20] direct emission samples were collected from a small group of tropical plants and from the exhaust pipe of a 1972 International Scout; combined emissions of modern vehicles were collected at the lower-roadway of Miami International Airport. Ambient samples were collected from Everglades National Park and Brickell (Downtown), Miami during the same study to represent a rural and semiurban atmosphere, respectively. For additional details of the collection procedures used for both source and ambient samples, and for information on sample volumes used during analysis, please refer to the original publication.[20]

A second, larger set of samples was collected from Miami International Airport for this study. Sampling occurred on a Monday between 9 and 11 a.m. because it was identified as a high traffic period. The sampling site was located approximately halfway through the partially enclosed lower roadway and approximately 25 m away from a location where taxicabs departed for service. A DC-powered metal bellows pump (MB-302, Senior Flexonics, Sharon, MA) was used to draw tunnel air through $\sim$3 m stainless steel tubing which extended over the sidewalk curb and into the first traffic lane. Traffic cones surrounded the sampling area to divert traffic around the tube and prevent it from being crushed. The opening of the sampling tube was elevated over the roadway by $\sim$70 cm and fixed to the top of a traffic cone. The metal bellows pump was used to pressurize the sampled air into individual stainless steel canisters that were evacuated prior to use. The samples were returned to the laboratory and analyzed within 36−48 h.

■ RESULTS AND DISCUSSION

Sources of Ethanol. Plants are the largest known natural source of ethanol to the atmosphere, and emissions have been reported to range between 6 and 9 Tg yr^{-1}.[13,23] The carbon isotopic composition of plant material and the compounds they produce or emit are determined mainly by photosynthesis. Terrestrial plants fix atmospheric carbon using one of two pathways: the Calvin—Benson (C3 pathway), or the Hatch—Slack (C4 pathway). Approximately 85% of plants use C3 photosynthesis to meet their metabolic needs.[24] C4 plants, which account for $\sim$5% of all plant biodiversity, are more efficient at fixing carbon and less restrictive in their discrimination of ^{13}C during photosynthesis compared to C3 plants. As a result, C4 plants have more ^{13}C content. The typical ranges of $\delta^{13}C$ values for bulk plant material from C3 and C4 photosynthesizing plants are $\sim$−25 to −35‰ and $\sim$−10 to −18‰, respectively (see TOC graphic).[25] In the present work, we assumed that all

biogenic emissions to the atmosphere were from C3 plants based on plant biodiversity.[24]

Anthropogenic sources of ethanol are thought to mirror those of oxygenated volatile organic compounds (OVOCs) in general, with the largest known source being related to commercial and industrial production. Emissions from these sources were estimated to range between 2 and 3 Tg yr^{-1}.[13,23] A "biofuel" component with an emission strength of 1.8 Tg yr^{-1} was included in the global budget by Naik et al., but the term was defined as "biomass-derived fuel" that was intended for use as a fuel for cooking and heating, or a byproduct of agricultural waste burning in developing areas of the world and not as alternative vehicle fuel.[26] Ethanol is also formed during biomass burning events and as a secondary product in the atmosphere when higher order compounds are oxidized. According to the recent ethanol budget proposed by Naik et al., <1% and 3% of all ethanol in the atmosphere is derived from in situ production and biomass burning, respectively. For the purpose of this study, we do not include them in our discussion and analysis.

Ethanol released from fuels was included in the industrial source strength in the work of Singh et al.; however, it is uncertain if this refers to fuel evaporative emissions or direct vehicle exhaust.[23] Ethanol emissions from vehicles using fuels blended with ethanol have not been carefully quantified to date and little data currently exists.[27,28] However in 2007, Jacobson estimated that a U.S. switch to E85 fuel (85% ethanol by volume, 15% gasoline) would result in an additional 2 Tg yr^{-1} of ethanol to the atmosphere when only tailpipe emissions are considered. It seems plausible, then, that vehicle emissions can release an amount of ethanol similar to the total industrial source strength on a global level, especially if the U.S. and other areas of the world continue to rely on ethanol as an alternative fuel or if its addition is increasingly mixed with fossil fuel. It is important to mention that other minor sources of ethanol exist, please see Supporting Information for a brief discussion and additional details on these sources.

Biogenic End-Member (C3 Plants) $\delta^{13}C$ Signature. Ethanol emissions from C3 tropical plants were previously measured for their $\delta^{13}C$ values.[20] These values were shown to range between −30.3‰ and −42.5‰ and had a corresponding average of −36.5 ± 3.7‰ (±1σ, Table 1). The only known measurements to which our ethanol signature can be compared are to those of Keppler et al., who measured fresh ethanol emissions from a mix of C3 plants by detaching the leaves and placing them in sealed glass vials for up to 18 h at 25 °C. Their observations showed that emitted ethanol had an average $\delta^{13}C$ signature of −29.4 ± 2.6‰ (±SD).[29] The average ethanol signature obtained in this study was depleted by ∼6‰ compared to that presented by Keppler et al.; however, both measurements agree within their reported uncertainties. In the same work, Keppler et al. also measured fresh ethanol emission from corn leaves and obtained an average value of −15.2 ± 0.5‰ (±SD).[29]

Fossil- and Bio-Fuel Combustion End-Member $\delta^{13}C$ Signature. Samples (n = 5) collected during the first visit to Miami International Airport were used during method development to determine if the isotopic signature of OVOCs, including ethanol, emitted from vehicles could be distinguished from biogenic sources.[20] Ethanol in these samples had a $\delta^{13}C$ signature of −12.3 ± 3.7‰ (±1σ). The second sampling (n = 20) at the airport yielded similar results; ethanol's $\delta^{13}C$ signature was measured to be −10.4 ± 3.9‰ (±1σ) and remains within the measurement uncertainty of the initial set of airport samples.

Both airport data sets were combined (n = 25) and ethanol's transportation related source signature was −10.4 ± 3.6‰ (±1σ). The combined results were identical to that of the most recent sampling at the airport and the variation differed only by 0.3‰. All airport values are included in Table 1.

Observed $\delta^{13}C$ values for ethanol found in both sets of airport samples and the pooled results, in particular, are in close agreement with the $\delta^{13}C$ isotopic range (given earlier) for C4 photosynthesizing plants and nearly match the value given for crude corn-derived alcohols by Ishida-Fujii et al.[30] In that study, rectified and crude (industrial) alcohols with known botanical and geographical origins were analyzed for their $\delta^{13}C$ signature and alcohols derived from corn were found to have an average $\delta^{13}C$ = −10.7 ± 0.3‰ (see Table 1). The study did not list individual alcohols; however, if the trend is conserved across all corn-derived alcohols we can assume this to be true for corn-derived ethanol.

The 1972 Scout was not equipped with a catalytic converter, was operating with E10 fuel, and represents the assumed condition and age of similar vehicles operating in many developing countries of the world. Ethanol collected in the Scout's exhaust had an average $\delta^{13}C$ of −5.0 ± 0.4‰ (see Table 1) and was ∼5‰ enriched compared to both the bulk alcohols and the heaviest value given for the range of C4 plants. All automotive sources of ethanol in this study had distinct $\delta^{13}C$ values that were substantially enriched and aligned with the values given for C4 plants. Since the results for both source end-member signatures differed by ∼25−30‰ (see TOC graphic), each source's contribution was easily differentiated in ambient air samples collected in two South Florida locations.

South Florida Ethanol Budget. Using ambient air samples collected in Downtown Miami (n = 4) and Everglades National Park (n = 3) in conjunction with $\delta^{13}C$ end-member signatures for biogenic and transportation sources, it was possible to construct a simple budget for ambient ethanol in the South Florida metropolitan area, which is typically considered to span from Palm Beach County to Miami-Dade County. Making the assumption that emissions in the downtown area and Everglades National Park were fresh, and no loss has occurred, the contribution made from each source at each location was calculated using the following equation:

$$\delta^{13}C_{Ambient} = f(\delta^{13}C_{Biogenic}) + (1-f)(\delta^{13}C_{Anthropogenic}) \quad (1)$$

where the ambient signature ($\delta^{13}C_{Ambient}$) is related to both the biogenic and anthropogenic end-member signatures, $\delta^{13}C_{Biogenic}$ and $\delta^{13}C_{Anthropogenic}$, respectively.

Using this relationship, samples from Downtown Miami showed to be strongly influenced by ethanol blended fossil fuel emissions; nearly 73.9% (±7.4%, standard error of the mean (SEM); ± 20.4%, at 95% confidence level) of the ethanol present originated from anthropogenic sources. The remaining 26.1% (±7.4%, SEM; ± 20.4%, at 95% confidence level) of ethanol was of biogenic origin. The uncertainty estimate for the source apportionment accounts for the variability in the isotopic signatures for the end-members and the ambient mixture; the uncertainty was calculated using published formulas and an available Excel spreadsheet (ISOERROR version 1.04).[31−33]

Observation of a large anthropogenic source in Downtown Miami is consistent with ship-based measurements that have occurred off the coast of New England, where approximately 70% of the ethanol was thought to come from primary anthropogenic

Table 1. δ^{13}C Values (Mean $\pm 1\sigma$) for Ethanol Emitted from Various Samples and Locations[a]

	biogenic sources						anthropogenic sources			ambient location		
	clipped samples			intact samples			fossil fuel(E10)/alcohols					
species/vehicle/location	mean $\pm 1\sigma$ (‰)	95% confidence (±‰)	sample no.	mean $\pm 1\sigma$ (‰)	95% confidence (±‰)	sample no.	mean $\pm 1\sigma$ (‰)	95% confidence (±‰)	sample no.	mean $\pm 1\sigma$ (‰)	95% confidence (±‰)	sample no.
Citrus sinensis	−41.5 ± 0.8	1.0	n = 5									
Philodendron selloum	−37.5 ± 0.3	0.4	n = 5									
Coccoloba uvifera	−30.6 ± 0.2	0.2	n = 5	−36.5 ± 0.2	0.2	n = 5						
1972 International Scout							−5.0 ± 0.4	1.0	n = 3			
Miami Inter. Airport 1							−12.3 ± 3.7	4.6	n = 5			
Miami Inter. Airport 2							−10.4 ± 3.9	1.8	n = 20			
Everglades Nat. Park										−30.6 ± 2.75	6.8	n = 3
Miami Financial District										−17.2 ± 4.1	2.2	n = 5
combined end-member values for ethanol and previously published values for alcohols												
combined biogenic end-member	−36.5 ± 3.7	1.7	n = 20									
combined anthropogenic end-member							−10.4 ± 3.6	1.5	n = 25			
corn derived alcohols	−10.7 ± 0.3		n = 9									
industrial alcohols							≈ −28		n ≈ 3			

[a] All samples were collected in previous work,[1] however Miami International Airport 2 results are from the current study. Combined biogenic results represent the pooled values across each of the plants that emitted the alcohol. Combined anthropogenic results exclude the Scout samples. Corn and industrial alcohol values taken from Ishida-Fujii et al.[30] (see TOC graphic for a plot of similar data).

sources.[34] Our result is understandable; even though the downtown area is dominated by vehicle emissions it does receives a fair amount of biogenic emissions from pockets of dense, lush, tropical biomass located throughout the area. Additionally, many of the major roadways are lined with numerous palms, banyans, and other types of trees.

Samples from Everglades National Park exhibited an opposite trend, where biogenic emissions contributed 77.4% ($\pm$6.6%, SEM; + 22.6%, $-$ 28.3%, at 95% confidence level) of total ethanol within the park and automobiles contributed the remaining 22.6% ($\pm$6.6%, SEM; + 28.3%, $-$ 22.6%, at 95% confidence interval). Calculated confidence intervals are different because the upper and lower interval cannot be greater or less than 100% and 0%, respectively.[33] The area where the samples were collected was within a mahogany hammock forest located approximately 20 miles into the park's southern region and nearly 50$-$60 miles southwest of Miami International Airport. The roadway through the southern portion of the park is approximately 40 miles long and traveled mostly by car by an estimated 1 million people who visit the park each year. As a result, the park is influenced by some direct vehicle emissions. This area of the Everglades is also influenced by urban outflow emanating from Miami for large portions of the year. Because South Florida's prevailing boundary layer wind pattern is from the ENE, anthropogenic emissions including those from vehicles are continuously exported across southern Florida toward the sampling site.

The present study represents the first stable isotopic assessment of ethanol's budget in a local/regional area, was based on a moderate set of samples, and employed an interpretive calculation for source apportionment of ethanol. Despite these seeming limitations, the results obtained from Everglades National Park compare well to some of the models and budgets, which estimate biogenic emissions account for nearly 63$-$74% of ethanol's presence in a well-mixed atmosphere.[12,13]

Ethanol Sinks and Isotopic Fractionation. In the previous section, ambient isotopic signatures for ethanol were evaluated in terms of their source contribution. Such an approach is valid only if the emissions were fresh and experienced minimal to no atmospheric loss. However, atmospheric losses do occur and each can influence a compound's ambient isotopic signature. Three removal pathways exist for atmospheric ethanol; these include oxidation by OH, and a combination of wet and dry deposition. Nearly 65% of ambient ethanol is estimated to be lost through oxidation and is converted nearly quantitatively ($\sim$95%) to acetaldehyde. The two remaining pathways, wet and dry deposition, account for 10% and 25%, of ethanol's loss, respectively. Each depositional process and the chemical/physical properties that influence ethanol's deposition rates are poorly understood.

An atmospheric reaction between a hydrocarbon and OH is a unidirectional loss process, and a hydrocarbon consisting of ^{12}C atoms only will react faster than its heavier isotopologue (i.e., the same compound substituted with a single ^{13}C atom) because of the increased mass substitution. Therefore, an atmospheric reservoir of a hydrocarbon and its isotopologues are subjected to mass-dependent isotopic fractionations during oxidation. For CH_3CH_2OH + OH, the reactant (ethanol) and product (acetaldehyde) become enriched and depleted in the heavier isotope, respectively. This type of isotopic fractionation is referred to as a kinetic isotope effect (KIE) because the fractionation is dependent on two competing reaction rates among the two isotopologues. The KIE is a ratio of rate constants of the

isotopologue containing ^{12}C atoms exclusively to that of the isotopologue containing a ^{13}C atom:

$$KIE = \frac{k_{12}}{k_{13}} \qquad (2)$$

where k_{12} and k_{13} are the rate constants for the loss of the lighter and heavier isotopically substituted isotopologues, respectively.[14] However, direct measurements of KIEs rarely occur. Instead the δ^{13}C value of a given reactant is measured before and after a reaction occurs, and the observed change in the remaining reactants' isotopic composition is defined as an enrichment factor (ε)

$$\varepsilon = (KIE - 1) \times 10^3 \qquad (3)$$

The utility of eq 3 is 2-fold, ε and KIE can easily be interconverted if needed, and the enrichment factor is conveniently expressed in permil notation. For the remainder of this discussion, the term enrichment factor (or ε-factor) will be used, unless an actual rate or kinetic measurement was performed.

To date, isotopic fractionations associated with ethanol's atmospheric removal processes are not known, and this information is essential to properly evaluate the alcohol's isotopic budget. Even on a very basic level, knowledge of the fractionation that would occur with ethanol's major loss process, atmospheric oxidation, would greatly improve our understanding of the isotopic change that will accompany ethanol's removal from the atmosphere.

In 2004, Anderson et al. derived carbon isotope specific group rate constants for inclusion within Atkinson's well-known structure reactivity relationship.[14,15] In doing so, Anderson et al. reasonably estimated ε-factors for eleven alkanes within a factor of 2 of their experimentally determined values when they used published rate constants in their calculation. We estimated an ε-factor for the atmospheric oxidation of ethanol using the technique and carbon isotope specific group rate constants derived by Anderson et al. and used the same structure reactivity functional group values.[15] The estimated ε-factor associated with this atmospheric process is 6.2 $\pm$ 0.9‰.

In 2008, Feilberg et al. performed a relative rate kinetics experiment and measured the rates of reaction for CH_3OH and $^{13}CH_3OH$ with OH and obtained a KIE value (or what they defined as α) of 1.031 $\pm$ 0.020.[35] This result translates to an ε-factor of 31 $\pm$ 20‰ for methanol's atmospheric oxidation. The kinetic and fractionation data presented by Feilberg et al. allowed us to gauge the accuracy of ethanol's estimated ε-factor via comparison of an estimated ε-factor for methanol to the experimental results of Feilberg et al. Returning to the approach used by Anderson et al., we calculated a $\sim$10‰ enrichment in methanol after its atmospheric oxidation. Compared to the results of Feilberg et al., the calculated ε-factor for methanol appears to be a reasonable first approximation, even if the estimate is toward the lower limit of their experimental results.

Methanol is the only OVOC that has had its KIE measured to date; however much of what is known about KIEs and isotopic fractionations associated with atmospheric loss processes has come from studying alkanes and alkenes.[36] Our estimated ε-factors for methanol and ethanol are intermediate of those measured for alkanes and alkenes.

Currently, there is a lack of information on isotopic fractionations related to wet and dry deposition for OVOCs like ethanol. In 1993, Johnson and Dawson examined the ^{13}C isotopic content

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of gaseous formic acid and estimated the fractionation that would occur during its dry deposition to the earth's surface by using a reduced mass, molecular weight technique for CO_2 that was first presented by Craig.[16,17] As a result of the lighter isotope's (^{12}C) greater diffusional flux through a stagnant air layer surrounding a collection surface, the residual atmospheric pool was enriched in ^{13}C by 4‰. The pair also investigated vapor−liquid transitions of formic acid and used a statistical thermodynamic approach to estimate the ^{13}C signature of ionized formic acid within aqueous phase. This approach led to a calculated enrichment in ^{13}C of <1‰. However, ethanol has a lower Henry's Law constant and higher vapor pressure than that of formic acid, which suggests that it is more likely to exist in gas phase compared to formic acid. It is reasonable to assume that wet deposition may influence ethanol's ambient isotopic signature to some degree, but considering that the process accounts for only 10% of ethanol's loss, that the effect seems to be minor, and that there is a lack of data to constrain it, we chose to not include it for the purposes of this analysis.

Plume Tracking and Identification. Estimating how ethanol's isotopic signature changes as a result of atmospheric removal allowed us to simulate the change that would be observed for an aging atmospheric plume leaving the Middle Atlantic and Northeast region of the U.S. These regions were chosen as the backdrop of this hypothetical discussion because they contain five major U.S. cities that are heavily influenced by vehicle emissions and at the same time surrounded by rural locations to their North and West, which contribute substantial amounts of biogenic emissions. The same areas are adjacent to the North Atlantic Ocean and no known oceanic sources of ethanol currently exist. Therefore, it is reasonable to assume that the physical loss and isotopic change of ethanol occurring over the ocean would not be influenced by fresh emissions and can be used as a means for identifying and tracking a plume leaving the East coast.

The concomitant isotopic change observed with ethanol's loss was simulated using a mathematical approach.[18,37] The ratio between ethanol's isotopologues ($^{12}EtOH = {}^{12}CH_3{}^{12}CH_2OH$ and $^{13}EtOH = {}^{12}CH_3{}^{13}CH_2OH + {}^{13}CH_3{}^{12}CH_2OH$) for any time ($t$) was calculated using the mean photochemical age equation as presented by Rice and Quay (eq 4).[18]

$$\frac{[^{13}EtoH]_t}{[^{12}EtOH]_t} = \frac{[^{13}EtOH]_o}{[^{12}EtOH]_o} exp\left[\frac{t\Delta\tau}{\tau_{12_{EtOH}}^2 + \tau_{12_{EtOH}}\Delta\tau}\right] \quad (4)$$

The loss and concurrent isotopic enrichment of ethanol was modeled as a direct result of the gas' primary loss mechanism, oxidation, using the estimated enrichment (ε) factor that was determined earlier. Depositional losses were not included because the physical mechanisms and parameters controlling ethanol's dry/wet depositional rates and lifetimes have not been clearly identified, and as a result could not be included into an expression such as eq 4.

Because the initial concentration ratio of the isotopologues $[^{13}EtOH]_0/[^{12}EtOH]_0$ in eq 4 is a ratio (R) of their masses ($^{13}C/^{12}C$), the concentration ratio term can be related to ethanol's isotopic signature ($\delta^{13}C$), and isotopic ratio ($^{13}C/^{12}C$), relative to the isotopic ratio of the V-PDB reference material ($R = 0.0112372$). Therefore, to begin the evolution of ethanol's isotopic signature in an aging atmospheric plume, the initial concentration ratio was set to ethanol's average isotopic ratio ($^{13}C/^{12}C$) for source and ambient samples.

The simulated isotopic enrichment of ethanol from its initial value is a function of ethanol's chemical lifetime (τ), the difference between chemical lifetimes ($\Delta\tau$) of each isotopologue, and related to ethanol's reaction rate against OH (k_{OH}) and the radical's concentration in the atmosphere. The second-order reaction between ethanol and the hydroxyl radical is identical for both isotopologues

$$\tau_{*EtOH} = \frac{1}{k_{*EtOH}^{OH}[OH]} \quad (5)$$

where *EtOH denotes the ^{12}C or ^{13}C isotopologue. For the case of $^{12}EtOH$, the rate constant (k_{12}^{OH}) was taken from the literature as 3.1×10^{-12} cm^3 molecule^{-1} s^{-1} and consistent with the rate used earlier to derive ethanol's enrichment factor.[38,39] The rate (k_{13}^{OH}) for $^{13}EtOH$ was derived using the estimated ε-factor, k_{12}^{OH}, and the following relationship.

$$\left(\frac{\varepsilon}{10^3}\right) + 1 = KIE = \frac{k_{12}}{k_{13}} \quad (6)$$

With k_{13}^{OH} (3.08×10^{-12} cm^3 molecule^{-1} s^{-1}) identified, the lifetime of $^{13}EtOH$ against OH and $\Delta\tau$ was calculated and used in eq 4.

Ethanol's isotopic transformation was initiated using the $\delta^{13}C$ average values from the urban and rural samples (i.e., Downtown, Miami and Everglades National Park) and each end-member (i.e., biogenic C3 plants and transportation) over a period of 30 days using eq 4. Results can be seen in Figure 1A. The ambient values were simulated under average high (1.0×10^6 molecules cm^{-3}; red lines) and low (5.0×10^5 molecules cm^{-3}; blue lines) OH concentrations to account for seasonal and geographical variations in the radical; whereas the anthropogenic and biogenic end-member signatures were forecasted under average high and low OH concentrations only, respectively. Evaluating the ^{13}C-enriched transportation end-member under high OH only and the ^{13}C-depleted biogenic end-member (black lines) under low OH only, created an envelope around the ambient data. The envelope is assumed to include all theoretically possible $\delta^{13}C$ values for ethanol that could be found in the atmosphere.

The decline in ethanol's mixing ratio that occurs when it is oxidized by OH is included in Figure 1B. Similar to the $\delta^{13}C$ simulation, both high and low OH concentrations were used to replicate the loss of ethanol from a plume assumed to contain 10 ppbv ethanol. Similar mixing ratios have been observed in Los Angeles, CA and its suburbs by Colon et al. and references therein.[6] The plot shows that 75% of the original ethanol present will be removed from the plume in 5 and 11 days under high and low OH conditions, respectively. In the absence of additional ethanol sources, 90% of the original ethanol present will be removed between 9 and 17 days for high and low OH conditions, respectively. The decline in ethanol concentrations limit the time scale over which it can be studied in a plume. However the results displayed in Figure 1B suggest that $\delta^{13}C$ and mixing ratio measurements of ethanol can be made for at least 7−14 days while remaining useful for source apportionment and plume identification purposes.

Most studies photochemically age or date air parcels using the more conventional hydrocarbon clock method which is based on a pseudo-first-order decay and concentration ratio change of two hydrocarbons (i.e., n-butane/ethane or toluene/CO) with differing OH rate constants.[40,41] This method has been identified to have significant drawbacks that are related to the difference in
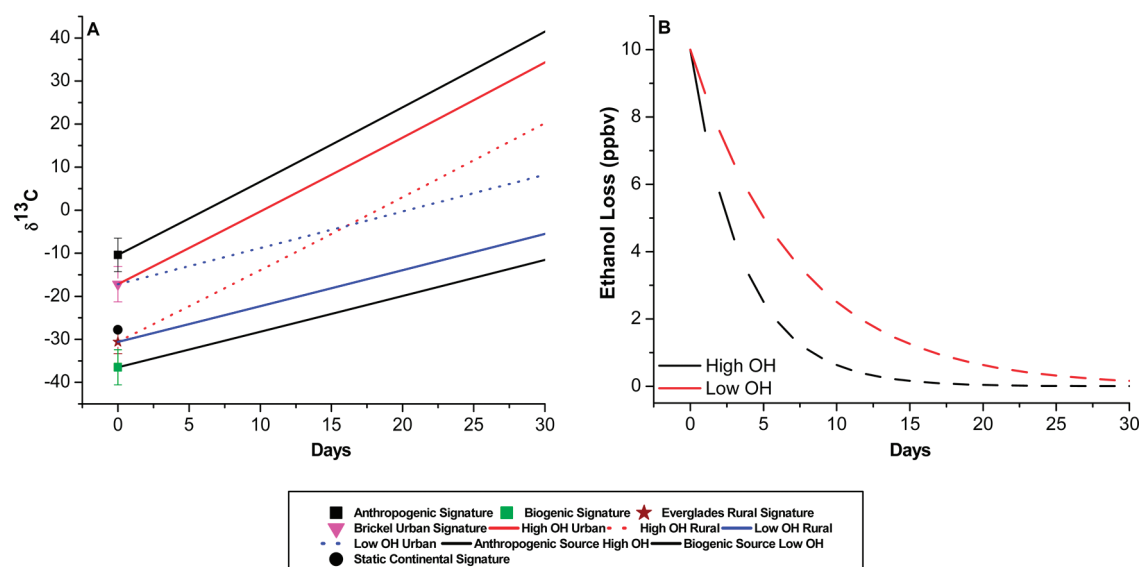
Figure 1. (A) Isotopic enrichment of ethanol associated with its chemical oxidation in the atmosphere under high and low OH conditions. The biogenic and anthropogenic end-members, simulated under low and high OH, respectively (black lines), bound all possible isotopic values that should exist for ethanol in the atmosphere. A static isotopic continental signature for ethanol is also included. Also shown (B) is the concentration loss of ethanol. Both plots are simulated over 30 days.

reactivity of the two hydrocarbons studied.[41] The less reactive hydrocarbon in the pair will make a stronger contribution to the concentration ratio and the overall determined age of the air parcel. As a result this method was shown to underestimate the age of an air mass. Similarly related to the reactivity differences, the hydrocarbon clock method was shown to be biased against mixing air masses and limited to a single isolated air mass.

Unlike the hydrocarbon clock method, using $\delta^{13}C$ values to calculate photochemical age provides certain strengths and advantages. Isotopic data are compound specific, eliminate the need and complication of using hydrocarbon pairs, and can be obtained independently of concentration measurements. Stable isotopic dating methods are also impervious to mixing air masses because of the similar lifetime that exists between isotopologues (i.e., $^{12}EtOH$ and $^{13}EtOH$); as a final added benefit, this method provides a linearly weighted average photochemical age of the studied compound.

Estimate of U.S. Fuel-Derived Ethanol. One of the goals of this work was to estimate the amount of ethanol released from vehicles that are assumed to be using E10 fuel, which accounts for ~90% of the alternative fuel market. E85 accounts for ~1% of the alternative fuel market.[42] GC-FID analyses of lower-roadway samples from Miami International Airport allowed us to identify an emission ratio for acetylene/ethanol based on peak area. Using this ratio, and a published ratio for CO/acetylene obtained from many urban cities dominated by vehicle emissions in the U.S.,[43] we determined an emission ratio for CO/ethanol and used EPA CO emissions to calculate the amount of ethanol released from "onroad" vehicles. Our results suggest that between ~0.35 and 0.7 Tg yr^{-1} of ethanol may be released to the atmosphere as a result of E10 fuel use in the U.S. and seems appropriate when compared to Jacobson's future emission estimate for a complete transition to E85 (i.e., 2 Tg yr^{-1} ethanol).[11] For a further description of the procedures used, please see the Supporting Information and Table S1.

Continental Signature for Ethanol. In 2002, Thompson et al. developed an atmospheric budget for chloromethane using stable carbon isotope measurements and a weighted average of the halocarbon's source emissions and removal mechanisms.[19]

$$\delta_{obs} = \frac{\sum\limits_{AllSources} \delta_i * S_i}{\sum\limits_{AllSources} S_i} + \frac{\sum\limits_{AllLosses} \varepsilon_J * L_J}{\sum\limits_{AllLosses} L_J} \quad (7)$$

We used eq 7 and generated a "static" isotopic signature for ethanol over the U.S. continental region (see Figure 1A) where biogenic and anthropogenic emissions and loss processes are expected to coexist in close equilibrium due to ethanol's moderate lifetime. Equation 7 reports the average isotopic value for ethanol (δ_{obs}) as a sum of all ethanol sources, loss processes, and their respective isotopic/fractionation values (δ/ε) and source/loss magnitudes (S/L).

The cumulative effort of this work resulted in a value of $-27.8‰$; for additional details on the calculation please see the Supporting Information and Table S2. We assume this value to be representative of ethanol over the continental U.S. where all sources and all losses are expected to be in equilibrium. The number presented here falls within the envelope of theoretically possible $\delta^{13}C$ values for ethanol in the atmosphere (Figure 1A). That earlier simulation accounted for only two source end-members (biogenic and fossil- or biofuel) and a single removal process (chemical oxidation). This calculation accounts for an additional source end-member (industrial) as well as an additional two removal processes (wet/dry deposition). Irrespective of these additions, the calculated static signature still falls within the envelope of all ethanol values.

With the expected increased use of ethanol as a fuel additive or alternative fuel and the uncertain emissions and environmental impacts associated with its use, it is clear that more studies of ethanol are warranted. Specifically, ethanol emissions from current vehicles, including new "flex-fuel" vehicles (those with the ability to run on ethanol blends between 10 and 85%) need to be tested to better quantify their emissions with more certainty. The current work has identified a unique $^{13}C/^{12}C$ ratio for

ethanol emitted in vehicle exhaust and used it for source apportionment purposes in two South Florida locations. The study has also demonstrated the utility of using ethanol's isotopic signature as a tracer for urban continental emissions; ethanol can serve this function for ~5–11 days. These results suggest that the stable isotopic signature of ethanol emitted in vehicle exhaust can be exploited as a tracer for biofuel inputs to the atmosphere on local and regional scales and can be incorporated into atmospheric chemistry models for isotopic fingerprinting and source apportionment purposes.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Additional information as noted in text. This information is available free of charge via the Internet at http://pubs.acs.org/.

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