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Isotopes of Volatile Organic Compounds: An Emerging Approach for Studying Atmospheric Budgets and Chemistry

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1. Introduction

1.1. Scope of Review

Knowledge of the isotopic composition of a variety of atmospheric trace gases, particularly methane and

CO₂, has proven to be useful for elucidating information on their atmospheric budgets and biogeochemistry that could not be determined from concentration measurements alone. Until recently, isotopic measurements of non-methane volatile organic compounds (VOCs) in ambient atmospheric samples had not been achieved. Advances in measurement techniques for the compound-specific isotopic composition (¹³C/¹²C) of VOCs were first applied to atmospheric samples by Rudolph et al.¹ The ability to measure stable isotope ratios of specific VOCs in atmospheric samples with concentrations down to the tens of parts per trillion (ppt) range has stimulated research on potential applications of this information for increasing our understanding of their atmospheric budgets and chemistry. For example, the kinetic isotope effect of atmospheric photochemical loss processes of non-methane hydrocarbons (NMHCs) has been exploited to estimate their photochemical age from atmospheric measurements.^{2,3} In another example, an isotope mass-balance approach has been explored for reducing the large uncertainties in the atmospheric budgets for methyl halides, whose sources and loss processes have distinctly different isotopic signatures.^{4,5}

So far, ¹³C/¹²C is the only stable isotope system which has been used in published studies of VOCs in the ambient atmosphere.^{1,3,5–14} However, source or sink characterizations have been done for a wider set of isotope pairs, including ²H/¹H and ³⁷Cl/³⁵Cl. Although the radioactive isotopes, including ¹⁴C and ³H, are much less abundant than the stable isotopes, they can still provide useful information if enough sample is available. For example, Currie et al.¹⁵ pioneered the use of ¹⁴C to differentiate between natural and anthropogenic sources of carbonaceous particles. This technique has since been applied to VOCs such as formaldehyde, other aldehydes, acetone,^{7,9,16} formic and acetic acids,^{12,13} and the total atmospheric burden of VOCs.^{17,18} This technique may prove to be particularly useful in studying the budgets for compounds with a combination of primary and secondary (photochemical) sources where the relative importance of contributions from biogenic and anthropogenic emissions is highly uncertain.

This review focuses specifically on the use of isotopes to study gas-phase atmospheric VOCs including NMHCs, oxygenated VOCs, and halogenated VOCs. Research on the isotopic composition of atmospheric VOCs is still relatively limited, but much

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Allen H. Goldstein was born in Santa Clara, California (1966). He received his B.S. in chemistry and B.A. in politics from the University of California at Santa Cruz (1989), and his M.S. (1991) and Ph.D. (1994) in chemistry from Harvard University. He joined the faculty at the University of California at Berkeley in 1995, and is currently an associate professor of biogeochemistry in the Department of Environmental Science, Policy, and Management. He leads a research group addressing interactions between atmospheric chemistry, terrestrial biogeochemistry, and human activity, and how these interactions determine atmospheric composition. His work focuses on volatile organic compounds and their photochemistry in the troposphere. In recent years he has been investigating the use of stable isotopes to study atmospheric budgets and chemistry of reactive trace gases.



Stephanie L. Shaw is a NOAA Postdoctoral Fellow in Climate and Global Change, working at the University of California, Berkeley. Her research interest is trace gas biogeochemistry, and she is currently studying the use of isotopes as tracers of microbial methyl halide production. She obtained her S.B. (1995) in chemical engineering and Ph.D. (2001) in atmospheric chemistry from the Massachusetts Institute of Technology. Her Ph.D. research investigated oceanic microbial cycling of isoprene and other non-methane hydrocarbons.

innovative work has been published since 1997. Additionally, many compounds of interest to atmospheric chemists have been extensively studied for several decades as tracers of fossil fuel well signatures, bioremediation processes, biomedical applications, biosynthesis processes, and extraterrestrial chemistry, among other applications. This review provides a comprehensive summary of recent measurement and theoretical advances in the use of stable isotopes to study field measurements of atmospheric VOCs' isotopic composition, measurements of atmospheric source signatures, kinetic isotope effects associated with atmospheric loss processes, and application of this new information for exploring atmospheric VOCs' budgets and photochemical processing. A separate review in this issue by Brenninkmeijer

et al. focuses on the use of isotopes in studying less reactive atmospheric trace gases, including CO, CH₄, and N₂O. Previous reviews that have included a limited amount of isotopic information on a variety of individual VOCs sources to the atmosphere,¹⁹ the range of isotopic values observed in natural gas deposits,²⁰ or general isotopic techniques^{21,22} will be referenced here, but not reviewed in detail.

1.2. Brief Overview of Atmospheric VOCs

Atmospheric VOCs including NMHCs, oxygenated VOCs, and halogenated VOCs are ubiquitous trace gases that have important impacts on atmospheric chemistry in both the troposphere and the stratosphere. VOCs combine with oxides of nitrogen to produce O₃, contribute to aerosol growth and thus impact atmospheric radiative processes and visibility, substantially control the oxidative capacity of the troposphere in polluted and forested regions, and strongly influence OH cycling, even in remote regions of the troposphere. Halogenated VOCs are important because they contribute to stratospheric ozone depletion. Biogenic as well as anthropogenic sources release VOCs to the atmosphere, where their primary loss reactions are with the major oxidants hydroxyl radical (OH), ozone (O₃), and nitrate (NO₃). Some are also lost by photolysis. To set the stage for our discussion of the use of isotopes to study these compounds, we provide a brief summary of the major source categories, loss processes, atmospheric lifetimes, and budget uncertainties for NMHCs, oxygenated VOCs, and halogenated VOCs.

Specific NMHCs can typically be classified as dominantly biogenic or dominantly anthropogenic. Biogenic NMHC emissions are in turn dominated by terrestrial plants, with forested ecosystems being the largest source category. Thus, their source distributions are linked to the distribution of the emitting vegetation. Globally, biogenic emissions of NMHCs are roughly an order of magnitude larger than anthropogenic emissions of NMHCs, and outside of urban and industrial centers with little vegetation, the biogenic compounds have a much larger impact on atmospheric photochemical processes. Terpenoid compounds including isoprene, monoterpenes, and sesquiterpenes are the major biogenic NMHCs. These compounds are highly reactive due to their double carbon bonds and are removed from the atmosphere mainly by reaction with OH, and to a lesser degree by reaction with O₃ and NO₃. Their atmospheric lifetimes are typically a few hours or less during the day. Several thorough reviews have been published recently covering biogenic VOCs including NMHCs, their sources, loss processes, and impacts on atmospheric chemistry.^{23–25}

Anthropogenic NMHCs include a wide array of species, and the most commonly measured are C₂–C₁₀ alkanes, alkenes, alkynes, and aromatics. Major source categories for anthropogenic NMHCs include vehicle emissions, solvent evaporation, and fuel combustion. Burning biomass also emits substantial quantities of a wide range of NMHCs. Atmospheric lifetimes of these compounds are mostly determined by their rate of reaction with OH, with lifetimes

covering the full range from minutes to months. The literature on anthropogenic NMHCs in the atmosphere is vast and is covered well by several books.^{26,27} While the major source categories for biogenic and anthropogenic NMHCs are well known, the range of compounds emitted, their absolute emission rates, their chemical transformations in the atmosphere, and their impact on atmospheric photochemical processes are all active areas of research.

Oxygenated VOCs are a class of compounds including alcohols, aldehydes, ketones, and acids. They generally have a more diverse array of sources than NMHCs. Major source categories of OVOCs include natural emissions from plants, soils, and the ocean, anthropogenic emissions from combustion and solvent evaporation, biomass burning, and photochemical production in the atmosphere through oxidation of both biogenic and anthropogenic precursors. Their loss processes are also significantly more complex than those of NMHCs because, in addition to atmospheric oxidation, some of these compounds are quite soluble (i.e., acids), and others can be broken down by photolysis (i.e., aldehydes). Specific oxygenated VOCs may have a substantially less complicated set of sources and sinks, but the few compounds in this class which have been studied using isotopic techniques, such as formaldehyde and organic acids, have complicated budgets which remain highly uncertain. Furthermore, the atmospheric budgets of alcohols, ketones, and aldehydes are currently poorly constrained.^{28–31}

Halogenated VOCs include compounds whose origin is completely anthropogenic, such as chlorofluorocarbons (CFCs), halons, and hydrochlorofluorocarbons (HCFCs), compounds whose relative contributions from biogenic and anthropogenic sources are highly uncertain, such as methyl bromide (CH₃Br), compounds whose sources are dominantly natural, such as methyl chloride (CH₃Cl), and a series of less abundant compounds (e.g., methylene chloride, chloroform, and bromoform). The budgets of CFCs in the atmosphere are relatively simple because their source is purely anthropogenic, and their dominant atmospheric loss process is photolysis in the stratosphere, resulting in long atmospheric lifetimes of order 50–100 years. HCFCs are similar to CFCs, except that they contain HC bonds and their removal from the atmosphere is dominated by reaction with OH, resulting in atmospheric lifetimes of order 5–20 years. CFC and HCFC budgets in the atmosphere are fairly well known, and thus these gases have been used to elucidate quantities like atmospheric mixing times and global average OH concentrations.^{32,33} Methyl halides have significant anthropogenic sources, as well as terrestrial and oceanic sources and sinks. Their atmospheric lifetimes are of order 1 year, and their atmospheric budgets remain highly uncertain. An authoritative review of current knowledge regarding atmospheric concentrations, sources, and sinks of these halogenated VOCs can be found in the Scientific Assessment of Ozone Depletion published by the World Meteorological Organization.³⁴

1.3. Summary of Isotope Equations

The stable isotopic abundance of a specific element in a sample is measured as a ratio of the rare isotope to the abundant isotope. This ratio is then compared to that from a known standard. For carbon, the natural abundance ¹³C/¹²C ratio (*R*) is commonly compared to Vienna Pee Dee Belemnite (V-PDB), a virtual scale identical to an internationally accepted standard CaCO₃ deposit from the Pee Dee formation of South Carolina³⁵ with *R* = 0.0112372. The largest deviation in ¹³C/¹²C observed in naturally occurring molecules is of order 10%,^{36–38} but is typically much smaller, with meaningful and measurable changes occurring in the fourth significant digit. These small differences in C isotopic composition are conveniently expressed using delta notation as the per mil (‰) difference of the sample compared to a known standard:

$$\delta(\text{‰}) = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right] \times 10^3$$

A positive $\delta^{13}\text{C}$ value indicates that the sample has more ¹³C than the standard, or is “enriched”. Negative values indicate “depletion” of ¹³C in the sample. This delta notation equation is also used to define the isotopic composition of hydrogen (δD), oxygen ($\delta^{18}\text{O}$), and nitrogen ($\delta^{15}\text{N}$). The commonly accepted standard for hydrogen and oxygen is Standard Mean Ocean Water (V-SMOW³⁹), and the standard for N is atmospheric N₂.⁴⁰ All isotope data presented in this review are referenced to these commonly accepted standards unless otherwise noted.

The isotopic composition of a chemical element in a molecule can vary according to the element's source and the mechanism of the molecule's production. The element can also be fractionated by physical, chemical, or biological loss processes. Isotope fractionation occurs because the bond energy of each isotope is slightly different, with heavier isotopes having stronger bonds and typically slower reaction rates. This favors loss of the lighter isotope over the heavier isotope in a given process. The bonding energy difference is proportional to the relative mass difference between isotopes. Due to the much larger relative difference in mass between the two stable hydrogen isotopes (50%) as compared to the stable carbon isotopes (8%), we expect a priori that the natural variability between various fractionating processes involving ²H/¹H should be larger than that for ¹³C/¹²C in a given molecule, such as atmospheric VOCs. The isotopic variability of elements with smaller relative mass differences, such as ³⁷Cl/³⁵Cl or ⁸¹Br/⁷⁹Br in methyl halides, should be even smaller than for ¹³C/¹²C. For example, observed variations for ³⁷Cl/³⁵Cl fall within $\pm 3.5\text{‰}$ for groundwater and rock systems,⁴¹ but observed variations for ¹³C/¹²C in ambient NMHCs varied from -15 to -35‰ (see Figure 2).

Equilibrium fractionations can occur during the exchange of a molecule between two different phases (or compounds) at a rate that maintains equilibrium. Although the overall process is in equilibrium, the rate of these exchanges is different for each isotope

because of their intrinsic relative mass differences. Thus, a different isotope becomes enriched in each phase (or compound). Typically, the heavier isotope is preferentially incorporated into the phase (or compound) where it is most strongly bound. Equilibrium fractionation is not likely to be important for atmospheric VOCs because typically the lifetimes of these compounds are short compared to equilibrium times. Kinetic fractionations occur due to differences in reaction rates of different isotopes in irreversible physical, chemical, or biological processes. The resulting kinetic isotope effect (KIE) associated with a loss process is defined as

$$\text{KIE} = \frac{k_{\text{isotope1}}}{k_{\text{isotope2}}}$$

where k_{isotope1} and k_{isotope2} are the rate constants for loss of the lighter isotope-containing and heavier isotope-containing molecules, respectively. The KIE is typically expressed as a fractionation factor (ϵ) in delta notation:

$$\epsilon(\text{‰}) = (\text{KIE} - 1) \times 10^3$$

where a positive ϵ indicates that loss causes the remaining sample to be enriched in the heavier isotope.

The isotopic composition of atmospheric VOCs will reflect the weighted average isotopic signature of all the sources, and the weighted average of kinetic isotope effects of all the loss mechanisms, contributing to the measured sample:

$$\delta_{\text{atmosphere}}(\text{‰}) = \sum_i \delta_i S_i + \sum_j \epsilon_j L_j$$

where δ_i is the isotopic composition of each source i , S_i is the fractional flux contribution of i to the total sources, ϵ_j is the fractionation factor associated with each loss process j , and L_j is the fractional flux contribution of j to the total loss processes.

The radiocarbon ($^{14}\text{C}/^{12}\text{C}$) content or activity (A) of a sample is typically reported as a percentage of modern carbon (pMC) relative to a standard material containing carbon of modern origin:

$$A(\%) = \left[\frac{(^{14}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{14}\text{C}/^{12}\text{C})_{\text{standard}}} \right] \times 100$$

Radiocarbon activity may also be reported using the ($^{14}\text{C}/^{13}\text{C}$) ratios rather than the ($^{14}\text{C}/^{12}\text{C}$) ratios. The commonly accepted standard is oxalic acid (NIST SRM 4990B) extracted from 1890 wood. This standard is used because the release of radiogenic carbon from nuclear weapons and nuclear power generation has increased the ratio of $^{14}\text{C}/^{12}\text{C}$ in wood grown since World War II.

2. Measurement Techniques

2.1. Historical Perspective

Determination of the stable isotopic composition of VOCs requires complete separation of the individual

compounds to be analyzed, quantitative conversion of each compound to gases whose isotopic composition can be measured directly (e.g., CO_2 , H_2 , N_2),⁴² and subsequent analysis using a mass spectrometer. Complete separation of the compound of interest and quantitative conversion to the analyzed form of its elements is critical to ensure that no isotopic fractionation occurs in the analytical procedure.

Early efforts to quantify the isotopic composition of individual VOCs relied on obtaining pure samples of a specific gas. Sample combustion of the pure gas was performed offline in closed tubes at high temperatures with catalysts such as CuO to convert the carbon to CO_2 following procedures used for petroleum or organic matter samples.³⁵ The CO_2 was then cryogenically separated from other combustion products, collected, and introduced directly into a dual-inlet isotope ratio mass spectrometer. Dual-inlet mass spectrometers allow for precise isotope ratio determination by repeatedly alternating between measurements of a sample gas and a reference gas. The sample and reference gas reservoirs are maintained at precisely the same pressure to maintain constant flow through capillary tubes connecting the reservoirs to the mass spectrometer in order to match potential isotopic fractionations between sample and standard. The basic design has not changed significantly since 1950,⁴³ and its fundamental advantage is the high measurement precision of approximately 0.01‰ for $\delta^{13}\text{C}$, due to the multiple comparisons between the sample and reference gases. This time-consuming technique is still routinely used as the standard against which the accuracy of newer techniques for individual compounds must be tested.⁴

The first approaches for isotope measurements of individual VOCs separated from a mixture of gases utilized preparative gas chromatography, where compounds were isolated using a multiport valve as they eluted from a chromatography column. The separated compounds were then individually combusted to CO_2 and H_2O offline, and the products were separated and analyzed individually. The collected products would later be analyzed individually on a dual-inlet mass spectrometer, directly for $\delta^{13}\text{C}$ in CO_2 , or following reduction of H_2O to H_2 (e.g., on zinc or uranium) for δD .⁴⁴

The amount of sample required to maintain the needed flow for a dual-inlet mass spectrometer and achieve a precision of 0.01‰ is approximately 200 nmol of pure gas,²¹ but can vary significantly with the specific instrumentation and methods used, and will likely continue to decrease with improving technology. This approach has been successful for high-concentration samples such as natural gas or sediment gas, but the required sample size is quite large when considering the low concentrations of most VOCs in the atmosphere. To analyze a compound whose atmospheric concentration is 1 ppbC by dual-inlet mass spectrometry would require quantitative separation from approximately 4500 L(STP) of air.

The ability to measure compound-specific isotope ratios on smaller samples of complex mixtures without manual offline combustion of each compound was

developed by Sano et al. in 1976,⁴⁵ and Mathews and Hayes in 1978.⁴² Their approach was to separate individual compounds by gas chromatography, combust or reduce the eluting compounds to N₂, H₂O, or CO₂, and continuously analyze each chromatographically separated peak using a conventional sector mass spectrometer with a single collector alternating between stable isotopes. Mathews and Hayes used a selective trap to remove products other than those of interest and measured the ¹⁵N/¹⁴N (*m/z* 29 and 28) or ¹³C/¹²C (*m/z* 45 and 44) ratios. This allowed for continuous monitoring of the combustion effluent, and thus continuous, online, compound-specific isotope measurements. They named the technique "isotope-ratio-monitoring gas chromatography–mass spectrometry" (IRM-GCMS) and showed that directly comparable isotopic analyses could be accomplished for all eluting compounds with a precision of 0.5% relative standard deviation or better on samples of 20 nmol of CO₂ or 100 nmol of N₂. This method represented a significant breakthrough in terms of approach and sample size, but the precision using a single collector mass spectrometer was still not adequate for studying the variation of natural isotope abundances in atmospheric VOCs.⁴⁶

2.2. Measurement Advances in GC–C–IRMS

Coupling a GC and combustion chamber directly to a continuous-flow isotope ratio mass spectrometer was first achieved by Barrie et al. in 1984.⁴⁶ This was a multicollector mass spectrometer that could continuously monitor several mass-to-charge ratios. Their work demonstrated the feasibility of measuring $\delta^{13}\text{C}$ for individual organic compounds separated from complex mixtures with a precision of 1‰ at sample sizes of 8 nmol of C, and led to the first commercially available instrumentation being introduced in 1988²¹ (referred to from here forward as GC–C–IRMS). Keys to the development of GC–C–IRMS instruments included (1) modification of the IRMS vacuum pumping system to allow a continuous flow of carrier gas into the instrument, (2) improvements in the linearity of response of the IRMS to allow isotopic composition to be analyzed across a reasonable size range of chromatographically separated peaks, and (3) new approaches for comparing the sample isotope ratios to those of a standard.

The continuous-flow GC–C–IRMS instrument drastically reduced the minimum sample size which could be measured compared to a dual-inlet system, but the analysis of effluent from a GC column posed several challenges. Chromatographic separation has high enough resolution to also cause significant *isotopic* separation for individual compounds. This is due to slightly different vibrational energy effects for different isotopes during distribution between the stationary and mobile phases in the chromatography column.⁴⁷ The isotopic composition of eluting peaks is thus not homogeneous, with lighter isotopes favored in the leading edge and heavier isotopes favored in the trailing edge of each peak. Therefore, the isotopic ratio must be integrated from measurements over the whole chromatographic peak. The resulting requirements for baseline peak separation

are much more stringent than for most other GC detectors. Another analytical limitation is that the relative concentrations of different compounds to be measured in each sample cannot exceed the linearity range of the IRMS. A useful working range is typically 1 order of magnitude. Algorithms have been developed to correct for nonlinear detector responses over a response range up to 2 orders of magnitude,⁴⁸ although they have rarely been utilized in analyses of complex environmental samples. Standard reference gases for stable isotopes are typically introduced into the helium carrier gas stream downstream of the combustion oven during periods when the chromatographic baseline is constant before and/or after each sample analysis. Alternatively, reference compounds with known isotopic composition can be added to the sample, or run between samples, in amounts that mimic the magnitude range of chromatographic peaks being measured.

Development of the GC–C–IRMS technique was achieved by scientists who needed a tool to obtain isotope information for specific organic molecules in fields ranging from analysis of aspirin and its metabolites⁴⁵ to measuring the N isotope composition of individual amino acids.⁴² The measurement technique was first applied to ambient measurements of atmospheric VOCs by Rudolph et al. in 1997,¹ followed by Tsunogai et al. in 1999,¹¹ approximately one decade after commercial instrumentation was first available. This breakthrough coupled traditional cryogenic preconcentration of VOCs from ambient air (e.g., Greenberg and Zimmerman⁴⁹) with a GC–C–IRMS system. The focus was exclusively on measurement of $\delta^{13}\text{C}$, which allowed precision of 0.7‰ to be achieved for compounds containing 1 ng of C.¹ The typical atmospheric VOCs measurement setup consists of a canister for collecting ambient air samples and a two-stage cryogenic concentration and focusing system connected through a gas-sampling valve to the GC–combustion–IRMS instrument. In the example shown in Figure 1, samples are drawn from the canister at a controlled rate using a diaphragm vacuum pump and a mass flow controller through a chemical trap for removal of H₂O and CO₂ (typically magnesium perchlorate or Drierite, and Ascarite II or Carbosorb, respectively), then through a cryogenically cooled trap filled with glass beads. The primary trap is then heated and flushed with ultrapure He through another H₂O and CO₂ trap, and the sample is cryofocused onto a smaller trap. Injection into the GC is achieved by switching the six-port gas-sampling valve and heating the focusing trap.

Following GC separation, the column effluent passes through a combustion chamber filled with CuO (or similar catalyst) at approximately 850 °C to convert the individual VOCs to CO₂ and H₂O, then through a water trap before entering the IRMS. An open split is installed between the water trap and IRMS to allow a fraction of the effluent from the combustion chamber to be vented, while the rest enters the IRMS at a constant pressure. A reference gas with known CO₂ isotopic composition can then be routinely added for an interval equivalent to a

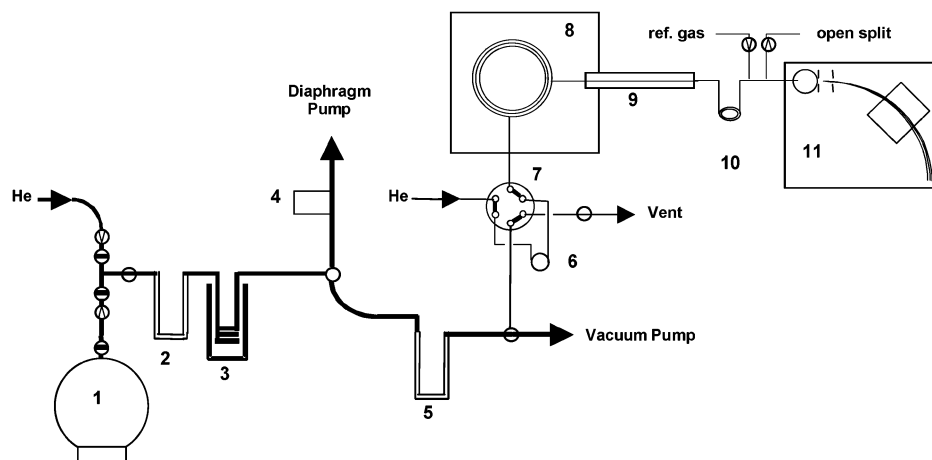


Figure 1. GC-C-IRMS instrument configuration for measurements of VOCs from canister samples. 1, Sample canister; 2 and 5, H₂O and CO₂ removal traps (typically magnesium perchlorate and ascarite II); 3, cryogenic preconcentration trap, typically packed with glass beads, used for initial concentration step; 4, flow controller; 6, cryofocusing trap; 7, six-port valve for loading trap and then injecting samples; 8, gas chromatograph; 9, combustion (or reduction) reactor; 10, water trap; 11, isotope ratio mass spectrometer. Adapted with permission from ref 95. Copyright 2002 American Geophysical Union.

chromatographic peak width in order to calibrate the $\delta^{13}\text{C}$ measurement.

Significant refinements in instrumentation and methods have occurred since the initial introduction of GC-C-IRMS in the 1980s. The combustion furnace can be followed by a reduction furnace to reduce NO_x to N₂ for analysis of $\delta^{15}\text{N}$, such as in the early design by Mathews and Hayes.⁴² The hydrogen in organic molecules can be analyzed by quantitatively converting it to H₂ using a higher temperature oven (>1400 °C) set for pyrolysis.⁵⁰ These or similar methods have been incorporated into commercially available instrumentation for compound-specific stable isotope measurements of $\delta^{13}\text{C}$, δD , $\delta^{15}\text{N}$, and $\delta^{18}\text{O}$, although only $\delta^{13}\text{C}$ measurements have thus far been reported for atmospheric VOCs. Several investigators also now split the effluent from the GC, sending only a fraction of it through the combustion furnace to the IRMS for stable isotope measurements. The other fraction is sent to another detector, such as a quadrupole or ion-trap mass spectrometer, for simultaneous measurements of mass spectra that can be used for compound identification and quantification.^{48,51}

2.3. Other Measurement Techniques

Sampling air in canisters can place significant limitations on the volume of air or the number of samples which can be collected and brought back to a laboratory for analysis. In addition, some compounds of interest, such as certain light alkenes and oxygenated VOCs, are not stable in many canisters, and this instability could cause a shift in isotopic composition. Yet, this is the main sample collection technique which has been utilized to date for atmospheric measurements. Alternative approaches for collecting the large-volume air samples needed for stable isotope analyses of atmospheric VOCs at low concentrations (e.g., ppt levels) include direct cryoconcentration of samples from the ambient atmosphere or collection on solid-phase adsorbents.

However, care must be taken to ensure that any sample treatment processes prior to isotopic analysis do not affect the measured isotopic composition.

Solid-phase microextraction (SPME) is a sampling technique for organic compounds that involves exposing an adsorbent fiber coated with a liquid polymer to the sample of interest. Analytes partition from the sample to the fiber, which can be thermally desorbed into a gas chromatograph. SPME can be used directly in a liquid organic phase, or by exposure to the headspace of a sealed sample. Dias and Freeman⁵² used SPME to measure the carbon isotope fractionation during headspace extraction of aqueous mixtures of various semivolatile organics, including toluene. Hydrophobic compounds were enriched by $\leq +0.5\text{‰}$ in ^{13}C when extracted with a nonpolar phase, and organic acids were depleted by $\leq +1.5\text{‰}$ when extracted with a polar phase. The authors determined that these are not kinetic effects, but rather are due to mass-dependent energy shifts and electrostatic effects during the partitioning process. These fractionations are quite small but can cause systematic measurement errors if not taken into account. The use of solid-phase carbon-based adsorbents has become routine for sampling and concentrating VOCs in ambient air for concentration measurements.⁵³ This approach may provide an attractive alternative for sampling atmospheric VOCs for stable isotope analysis, but there have been no measurements published to date utilizing this approach. It would be critical during method development to determine collection and desorption efficiencies and to ensure that no isotopic fractionation occurs during the procedure.

Carbon isotopic analysis of formic and acetic acids has been achieved by chemically selective oxidation to CO₂.^{12,13} For these measurements, formic and acetic acids were sampled on sodium carbonate (Na₂CO₃)-coated cellulose filters with a high-volume sampler at 50 m³/h for 2–9 days, while particles were excluded using an upstream quartz filter. After the

organic acids were extracted from the filter with distilled water, samples were acidified with sulfuric acid to remove carbonate as CO_2 , and then volatile acids were isolated by vacuum distillation. These acids were also collected in rainwater and concentrated by rotary evaporation following adjustment of the pH to alkaline conditions. Formic acid was selectively oxidized to CO_2 by reaction with HgCl_2 in perchloric acid solution, and then acetic acid was isolated from the remaining solution. The acetic acid was combusted in a closed tube containing CuO as described previously for other organic compounds. CO_2 from each selective oxidation was then analyzed using a dual-inlet IRMS. It is important to note that, with this technique, there was incomplete recovery of formic and acetic acids, so care must be taken to determine whether isotopic fractionations in the sample collection or analytical procedure compromised the measured isotopic composition.

Carbon isotopic analysis of formaldehyde has been achieved by selectively collecting milligram quantities of formaldehyde from air onto dry sulfite-treated glass substrates.^{6,7} The major limitation to this approach was reported to be the adsorption of atmospheric water onto the sulfite surface, causing formation of bisulfite, which then reacts with formaldehyde to form hydroxymethanesulfonate. Under favorable low-humidity conditions, they achieved collection efficiencies of $>90\%$, and they suggested that the selectivity for formaldehyde is high and the possibility of artifact formation is minimal. Variations of this approach have been used by de Andr   and Tanner⁵⁴ and Tanner et al.⁹

Klouda et al. developed a method to quantify the biogenic contribution to total atmospheric VOCs using ^{14}C measurements.^{17,18} Air samples were collected through a LiOH -packed column (to remove CO_2 without loss of VOCs) into 32-L SUMMA passivated canisters up to pressures of 3.1 bar. VOCs were then separated from residual CO_2 , H_2O vapor, carbon monoxide, methane, and noncondensable major gases (N_2/O_2). The total VOCs were oxidized to CO_2 and then reduced to graphitic carbon for ^{14}C analysis.

Analytical protocols have been developed for measuring $\delta^{37}\text{Cl}$ and $\delta^{13}\text{C}$ in micromolar quantities of chlorinated solvents for application to studying natural attenuation of contamination in groundwater plumes. For example, van Warmerdam et al.⁵⁵ and Holt et al.⁵⁶ combusted chlorinated solvents (e.g., chloroform, methyl chloride, methylene chloride) in closed tubes to convert C to CO_2 , precipitated the Cl to AgCl or CuCl , and then converted the Cl into CH_3Cl by reaction with CH_3I . Isotopic compositions of the purified CO_2 and CH_3Cl were then measured using a dual-inlet IRMS with 0.1% precision. This approach would be difficult for use with atmospheric samples because of the large volume of air required to obtain purified micromolar quantities of chlorinated compounds. However, coupling a GC with a continuous-flow IRMS, but *without* a combustion chamber, may provide another alternative for directly measuring the halogen isotopic composition of atmo-

spheric gases following sample preconcentration to low nanomolar quantities.

3. Atmospheric Measurements

Numerous measurements of VOCs concentrations have been performed over the past 30 years that demonstrate significant seasonal, hemispheric, vertical, and geographic variability of both biogenic and anthropogenic compounds. In comparison, very few ambient measurements are available for the *isotopic composition* of these gases. These published isotopic composition measurements are summarized in Figure 2. All of the research done thus far has focused on the stable carbon isotopes. Measurements of the isotopes of hydrogen and other elements have not been reported for atmospheric VOCs, but new commercially available measurement capabilities for isotopes of H, N, and O by GC-C-IRMS provide the opportunity to change this in the near future.

3.1. Carbon Isotopes

The majority of stable carbon isotope measurements of ambient VOCs have been performed on NMHCs and halogenated hydrocarbons. The first reported values were measured by Rudolph et al.¹ on air from Baring Head, New Zealand, that was not contaminated by local emissions. The $\delta^{13}\text{C}$ values were found to range from -22 to -29.7% for ethane, ethene, and propene, -6.7% for propane, and -43.5% for CH_3Cl . Czuba measured stable carbon isotope ratios for propene in Toronto during the summer.^{2,10} Daytime $\delta^{13}\text{C}$ values averaged $-19.8 \pm 2\%$ and were more variable than nighttime values, which averaged $-23.8 \pm 0.8\%$. The significant diurnal difference was attributed to a KIE associated with loss by reaction with OH. They also reported the first KIE measurements for propene at $11.7 \pm 0.3\%$. The nighttime values were noted to be similar to those from the automobile source of propene, which was assumed to be close to values from tunnel ($-25.2 \pm 0.6\%$) and garage ($-25.1 \pm 1.1\%$) measurements.

Tsunogai et al.¹¹ measured $\delta^{13}\text{C}$ of atmospheric C_2 – C_5 NMHCs and methyl chloride in the remote western North Pacific, coastal, and polluted urban regions. In general, the alkanes demonstrated very little variability, with an average $\delta^{13}\text{C}$ of $-27 \pm 2\%$ for C_3 – C_5 compounds. The exception was ethane, which was systematically more enriched in ^{13}C (-28 to -22%) as mixing ratios decreased (from 5 to 1 ppb) from urban to marine air samples. This trend was consistent with a possible fractionation due to OH oxidation in the atmosphere from urban NMHC emissions that is larger for ethane than for the other alkanes (see section 5.1.2). Alkene $\delta^{13}\text{C}$ signatures were more variable, ranging from -37 to -12% for ethene and from -27 to -14% for propene. Both compounds had $\delta^{13}\text{C}$ values that were systematically lower in the marine, as compared to urban, air samples. This may indicate different sources, or atmospheric processing of alkenes vs alkanes, but could also be due to artifacts in the alkene measurements due to interactions in the canisters. Despite a wide range of $\delta^{13}\text{C}$ values for methyl chloride (-44

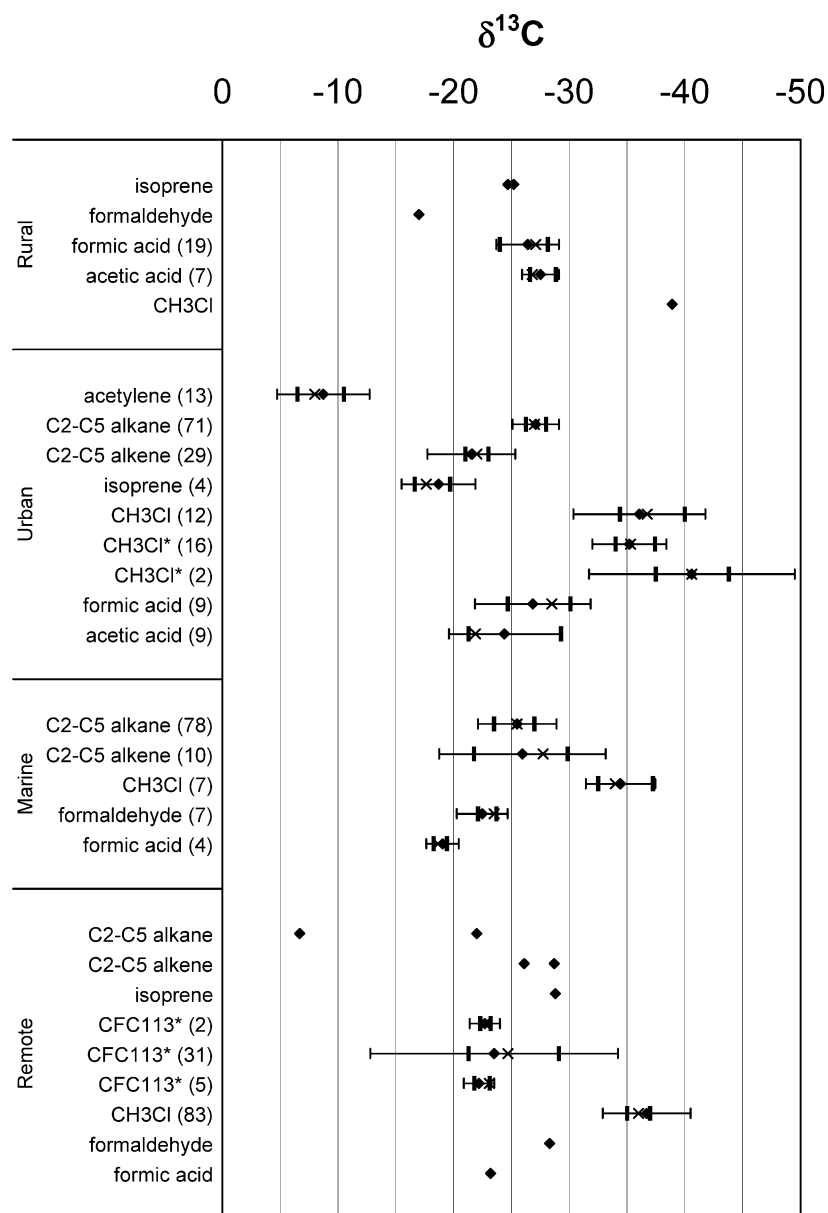


Figure 2. Carbon isotopic signatures for VOCs in atmospheric samples. Symbols are as follows: diamond, mean; ×, median; horizontal and thin vertical bars, standard deviation; and wide vertical bars, 25th and 75th percentiles. Number of samples is reported in parentheses. If only one or two values are reported, they are plotted directly, and no statistics are calculated. An asterisk signifies that data are reported as means and standard deviations of multiple treatments (see Appendix). References used, in same order as listed in figure: rural (refs 14; 6; 7,12,13; 13; 5), urban (refs 11; 1,10,11; 1,11; 14; 1,5,11; 5; 5; 7,8,13; 8,13), marine (refs 3,11; 11; 11; 9; 7), and remote (refs 1; 1; 14; 5; 5; 5; 1,5; 6; 13).

to -30‰), there was no significant difference between urban and marine air samples. The $\delta^{13}\text{C}$ ranges for all compounds were consistent with previously reported values from C_3 biomass burning and urban samples.¹

Rudolph, Czuba, and Huang⁵⁷ reported additional measurements in Toronto, focusing this time on diurnal cycles of $\delta^{13}\text{C}$ for propane, butane, pentane, propene, and benzene. Signatures for the three alkanes ranged from maximum values near -25.5‰ during the day to minimum values near -32‰ at night. The alkenes reached more enriched values (up to -12‰) during the day but had approximately the same values as the alkanes at night (minimum value -29.5‰). These minimum values were similar to carbon isotopic signatures of known transportation-

related sources of NMHCs (see section 4.1.2). The higher maximum values for alkenes as compared to alkanes is consistent with a daytime oxidation of the NMHCs by OH, with an associated KIE that is higher for alkenes than for alkanes (see section 5.1.2). In general, there were no obvious correlations between carbon isotopic signatures and mixing ratios in this dataset.

Saito et al.³ also measured $\delta^{13}\text{C}$ values for NMHCs in the western North Pacific. Ethane ranged from -26 to -19‰ , isobutane from -37 to -16‰ , and *n*-butane from -37 to -21‰ . Signatures for the latter two compounds reached far more depleted values than had been previously reported.¹¹ Samples taken during a frontal passage exhibited an inverse relationship between $\delta^{13}\text{C}$ value and mixing ratio for

ethane, as previously reported;¹¹ this was not observed for the other NMHCs, possibly because of air parcel mixing effects. This ethane trend was similar to a calculated estimate of the KIE due to oxidation by OH. However, observed ethane $\delta^{13}\text{C}$ values were slightly more enriched than calculated values; it was proposed that this was due to uncertainty in the KIE.

Despite the recent increase in the number of atmospheric NMHC isotope measurements, spatial and temporal coverage is still virtually nonexistent. To address this, Thompson et al.⁵⁸ calculated a global distribution of stable carbon isotope ratios and mean photochemical ages for ethane and benzene by incorporating known atmospheric and source signatures and sink KIEs into a chemical tracer model. Ethane $\delta^{13}\text{C}$ signatures were predicted to be higher in remote regions than over the continents and heavier during summer than winter, due to atmospheric photochemical processing. Photochemical losses were predicted to dominate other factors, such as emissions and transport, in controlling ethane signatures from spring to summer, while mixing became most important from fall to winter. Similar results were found for benzene, although the variability was significantly higher due to a more variable reaction rate with OH and associated fractionation. Additionally, photochemical loss during the transition from spring to summer was a less dominant factor for benzene than for ethane.

Isoprene is the dominant naturally produced VOC emitted to the atmosphere. It is biogenically produced by a variety of organisms, but the highest emissions are from vascular photosynthetic plants. Rudolph et al.¹⁴ made several measurements of the $\delta^{13}\text{C}$ of ambient isoprene in rural (−25 to −29‰) and urban (−16 to −23‰) locales. These values were similar, or enriched by up to 10‰, to laboratory cuvette measurements of direct emissions from a velvet bean plant (−27.7‰). This is consistent with a vegetative source of isoprene in rural areas and a chemical loss of isoprene to OH during transport to urban areas, with an associated KIE of $\sim 7\text{‰}$ ^{14,57} (see sections 5.1.2 and 6.2).

Thompson et al.⁵ reported stable carbon isotope signatures of CH_3Cl and CFC113 in remote air from both the Northern and Southern hemispheres. The average CH_3Cl $\delta^{13}\text{C}$ values were $-36.1 \pm 0.3\text{‰}$ in the Northern hemisphere and $-42.1 \pm 1.9\text{‰}$ in the Southern hemisphere. The Southern hemisphere values were likely impacted by local emissions, resulting in high variability and a skewed frequency distribution. Samples from suburban New Zealand had $\delta^{13}\text{C}$ for CH_3Cl of $-46.9 \pm 0.5\text{‰}$ and $-34.4 \pm 0.5\text{‰}$. In the Northern hemisphere, no relationship was observed between isotopic ratio and concentration, and no significant difference was observed in $\delta^{13}\text{C}$ for remote air at various latitudes. Additionally, the stable carbon isotope ratios at Alert research station were not significantly different for summer and winter. The global average $\delta^{13}\text{C}$ value for CFC113 was $-23.3 \pm 1.6\text{‰}$, with no significant interhemispheric difference.

Several studies have reported stable and radiocarbon isotope measurements of oxygenated VOCs

(OVOCs). Formaldehyde is directly emitted by automobiles, building materials, and vegetation, and is also produced by photochemical oxidation of both biogenic and anthropogenic VOCs. Johnson and Dawson⁶ collected ambient formaldehyde on sulfite-impregnated filters, which were then extracted and oxidized to CO_2 before mass spectrometric analysis. Samples from Baring Head, New Zealand (clean, remote site), had a mean $\delta^{13}\text{C}$ of -17.0‰ , while samples taken at Mt. Lemmon, Arizona (remote continental site), had a mean of -28.3‰ . The values are both more enriched than ambient methane ($-47.2 \pm 0.13\text{‰}$ ⁵⁹) and many NMHCs, which are the dominant photochemical precursors of formaldehyde. Tanner et al.⁹ also used this method to collect ambient formaldehyde at Nova Scotia during NOAA's North Atlantic Regional Experiment. IRMS analysis revealed an average $\delta^{13}\text{C}$ of $-22.8 \pm 2.1\text{‰}$ for seven samples, each collected over a minimum of 24 h. It should be noted that these reported values were not corrected for effects due to collection efficiencies of $<100\%$, which were assumed by the authors to have only a small fractionation effect. The ^{14}C content of these samples indicated a high percent of "modern" carbon ($78 \pm 8\%$). This implies that the primary source of formaldehyde at that location was from oxidation of biogenic, and not anthropogenic, hydrocarbon emissions.

The major organic acids in the gas phase are formic and acetic acids. They are found in both tropospheric air and rainwater and contribute substantially to precipitation acidity.⁶⁰ They are photochemical oxidation products of VOCs, and can also be directly emitted from biogenic or combustion processes.²⁶ Stable carbon isotope ratios of these compounds have been made with the goal of correcting ^{14}C measurements for isotopic fractionation, differentiating their biogenic versus anthropogenic sources,^{12,13} and possibly differentiating between methane and VOCs as the photochemical production sources of formaldehyde.⁶ Glasius et al.¹² trapped these acids on sodium carbonate (Na_2CO_3)-coated filters and purified them. After selective oxidation and isotopic analysis, the resulting $\delta^{13}\text{C}$ values for formic acid in Denmark ranged only from -28.6 to -27.1‰ for winter and spring. Johnson and Dawson⁷ collected formic acid on calcium dihydroxide ($\text{Ca}(\text{OH})_2$)-coated filters and then oxidized it by reaction with mercuric chloride. The average signature from 36 measurements at a remote Arizona mountain site was $-23 \pm 1.5\text{‰}$, while those from various urban and rural western U.S. sites ranged from -18 to -25‰ , respectively.⁷ Glasius et al.¹³ measured a range of $\delta^{13}\text{C}$ values for formic acid (-28.7 to -23.2‰) for various rural to remote sites across northwest Europe, while acetic acid $\delta^{13}\text{C}$ values were slightly more depleted, at -29.7 to -25.3‰ . Sakagawa and Kaplan⁸ isolated formic and acetic acids from atmospheric rain samples by ion chromatography before analysis with IRMS. In contrast to Glasius et al.,¹³ they measured average $\delta^{13}\text{C}$ values of -30.1‰ for formic acid, while acetic acid was more enriched, at -20.5‰ . As radiocarbon data have typically demonstrated a predominantly biogenic source for these acids, it was suggested that

Table 1. Known Hydrogen and Chlorine Isotopic Signatures and KIE

element	process and compound			refs	
hydrogen	sources	petroleum		δD	
		natural gas	ethane, propane	$-120.4 \pm 37.4\text{‰}$ (104) ^a	61
				$-120.8 \pm 5.7\text{‰}$ (4)	44
	KIE	OH oxidation	ethane	€	
			propane	$2070 \pm 1030\text{‰}$ (6)	67
			butane	$1030 \pm 420\text{‰}$ (8)	64
			isobutane	$530 \pm 350\text{‰}$ (3)	65
			cyclopentane	$1230 \pm 250\text{‰}$ (5)	68
			cyclohexane	$1330 \pm 340\text{‰}$ (4)	66
				$1220 \pm 310\text{‰}$ (4)	66
			bacterial uptake	toluene	$12-69\text{‰}$ ^b
		MTBE	$43.3 \pm 19.9\text{‰}$ (3)	63	
chlorine	sources	industrial	$\delta^{37}\text{Cl}$		
			CH_3Cl	$-6.4, -0.3\text{‰}$	69, 56
			chloroform	-1.5‰	56

^a Number of samples is reported in parentheses. ^b Non-Rayleigh fractionation with variable ϵ for one treatment. Maximum and minimum values are reported.

the $\delta^{13}\text{C}$ signature of terrestrial plants (typically -22 to -30‰)²⁰ was being reflected in most of these measurements.^{7,13} However, no studies of the $\delta^{13}\text{C}$ of formaldehyde, acetic acid, or formic acid produced from photochemical processes in the atmosphere have been published, and Johnson and Dawson⁷ estimated that there may be significant fractionations associated with dry deposition. Without more information it is very difficult to draw firm conclusions about sources from field measurements because we do not know if the various formaldehyde and organic acid source signatures would be distinguishable from each other or from the KIE of the loss processes.

3.2. Other Isotopes

We are not aware of any isotope measurements of atmospheric VOCs for elements other than carbon. Available data for stable H isotopes is thus far restricted to analyses of source signatures, including fossil fuels, natural gases, and industrial chemical production, and loss KIE, including microbial degradation processes and loss KIE of deuterated VOCs due to reaction with OH.^{44,61–68} Similarly, reported information on stable chlorine isotopes is restricted to industrial sources and microbial degradation processes.^{56,69}

4. Isotopic Source Signatures

The grouping of so many compounds with varying chemical structures and properties under the umbrella term “VOCs” means that there is a wide range of sources that need to be considered for this group of compounds. Anthropogenic sources dominate the emissions for some compounds, such as alkanes and aromatic species, while biogenic sources dominate the budget for isoprenoid species (isoprene, monoterpenes, sesquiterpenes). Many compounds have both biogenic and anthropogenic sources that are significant, such as oxygenated compounds which are emitted by both primary emissions (anthropogenic and biogenic) and secondary photochemical production from primary emissions. As a result, these budgets are quite complex and are discussed in detail elsewhere.^{23–25,27–31,34,70}

Most of the work that has been done on isotopic compositions of atmospheric VOCs has focused on measuring source signatures. This is likely because sufficient sample concentrations of the VOCs of interest can be more easily achieved than those for ambient samples. The known C, H, and Cl isotopic signatures for various sources to the atmosphere are summarized in Table 1 and Figure 3.

4.1. Anthropogenic Emissions

4.1.1. Fossil Fuels

Fossil fuels, including coal, petroleum, and natural gas, are derived from the transformation of sediments formed by deposition and burial of biogenic materials. Fossil fuels are of interest when considering the atmosphere because combustion and evaporation of such material is the basis for most anthropogenic sources of NMHCs. There is a rich history of research on the isotopic signatures of fossil fuel components for use in petroleum exploration. These data have been applied to investigate potential sources and formation processes of these fuels, source maturity, and subsequent chemical or physical alterations.^{20,61,71–76} This work will only be mentioned here briefly; the reader is referred to previous reviews on this topic for more detailed information.²⁰

Petroleum, or oil, is composed of many fractions with widely varying chemical and physical properties, such as gasoline ($\text{C}_5\text{--C}_{10}$), kerosene ($\text{C}_{11}\text{--C}_{13}$), diesel ($\text{C}_{14}\text{--C}_{18}$), heavy gas ($\text{C}_{19}\text{--C}_{25}$), and lubricating oil ($\text{C}_{26}\text{--C}_{40}$).⁷⁷ Due to this complexity, and the subsequent analytical difficulties involved in separating out individual components, isotopic signatures are typically measured for these or other grouped (e.g., saturated, aromatic) fractions. A range of $\sim 15\text{‰}$ in the stable carbon isotope ratio has been observed for oils worldwide (-20 to -35‰), and internal fractions for a given oil typically differ from each other by only $\sim 2\text{‰}$.²⁰ Few fractionation effects are observed for oils, so the resulting $\delta^{13}\text{C}$ values are fairly stable and very similar to those of the source rocks. Far fewer data are available for stable hydrogen isotope ratios of oils, but existing δD values range from -85 to -181‰ with rare exceptions, and differences between oil

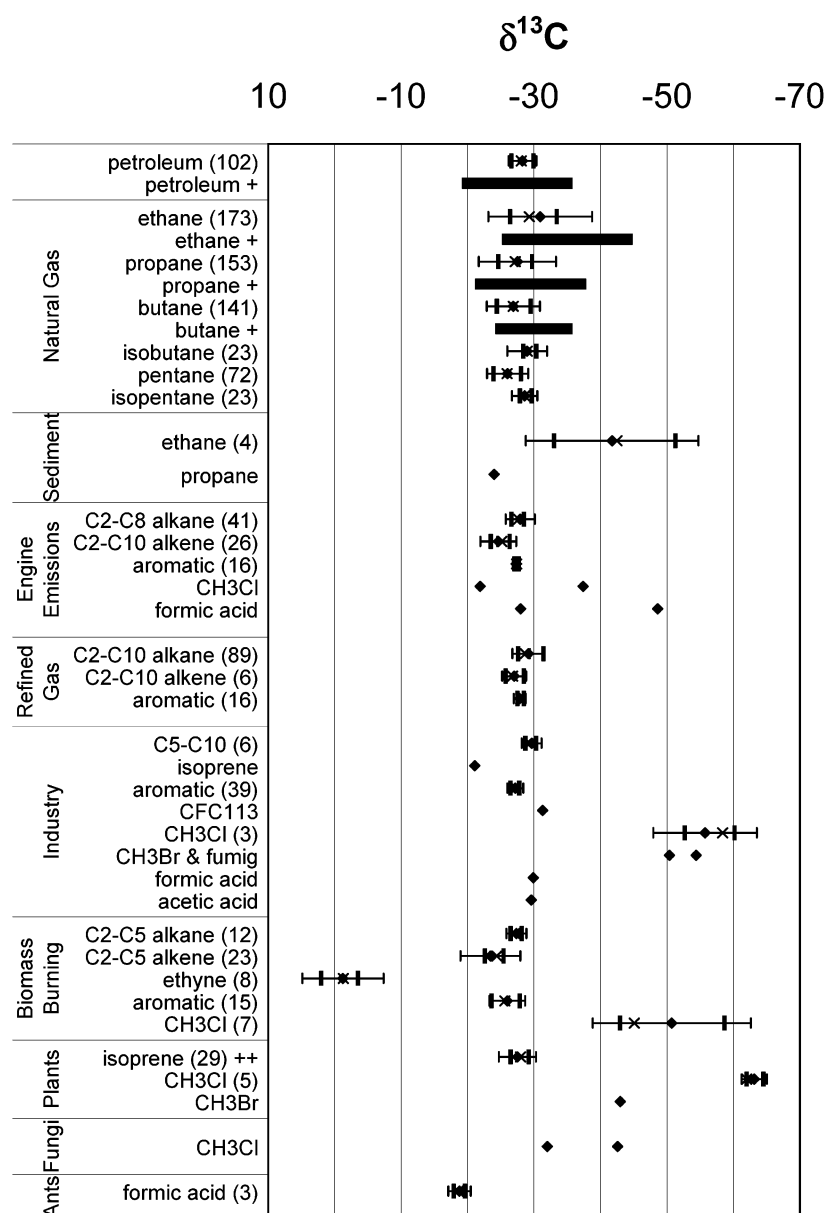


Figure 3. Carbon isotopic signatures for VOCs sources. Symbols and calculations as in Figure 2. Number of samples is reported in parentheses. A plus sign signifies that only ranges were reported. A double plus sign signifies that only measurements taken using near-ambient $\delta^{13}\text{C}$ CO_2 were used. References used, in same order as listed in figure: petroleum (refs 61; 20), natural gas (refs 44,71,74–76,79; 20; 44,71,74–76; 20; 71,74–76; 20; 74; 74,75; 74), sediment (refs 81,92; 81), engine emissions (refs 1,10,83; 1,83; 83; 1; 7), refined gas (refs 77,83; 83; 77,83), industry (refs 48,77; 14; 77,84; 5; 56,85; 4,86; 8; 8), biomass burning (1,87; 1,87; 1,87; 87; 1,87), plants (refs 14,89,90; 85,95; 95), fungi (refs 85,96), and ants (7).

fractions are only $\sim 3\%$.⁶¹ Oil δD values appear not to be a function of maturity and thus also simply reflect the isotopic composition of their source.⁶¹

The origin of many geothermal NMHC gases has been shown to be due to thermal decomposition of higher molecular weight organic matter (i.e., thermogenesis).^{71,75,76} This results in more depleted $\delta^{13}\text{C}$ values for the lower molecular weight NMHCs, as the lighter isotopes are preferentially removed from the source material. Indeed, observations of various components of natural gas are typically more depleted in $\delta^{13}\text{C}$ and δD than any associated petroleum.^{20,61} Additionally, most carbon and hydrogen isotope ratios of NMHCs in natural gas are more enriched than those of methane.^{20,71,74–76,78,79} In his review, Fuex²⁰ reported a range of ethane $\delta^{13}\text{C}$ values

from -26 to -44% , but since then values have been reported from -10 to -51.4% .^{74,75} Ranges for higher carbon number NMHCs tend to be smaller²⁰ (see Figure 3), such as -36.3 to -4.8% for propane, -30.6 to -14.6% for butane, -35.9 to -22.9 for isobutane, -30.6 to -17.2% for pentane, and -32.2 to -21.3 for isopentane $\delta^{13}\text{C}$,^{44,74,75} with most values falling in even tighter ranges^{20,77,80} (see Figure 3). Dumke et al.⁴⁴ measured δD values from -114 to -126% for ethane and propane in natural gas standards from the International Atomic Energy Agency in Vienna.

Other NMHC formation and destruction mechanisms will have different controls on isotope selectivity, and thus result in different signatures. For example, Rowe and Muehlenbachs⁷⁶ measured $\delta^{13}\text{C}$ values of ethane, propane, and butane in western

Canadian oil reservoirs and found that the signatures of gases in known thermogenic reservoirs were 13–22‰ more depleted in ^{13}C as compared to those in other locations. The more enriched signatures were attributed to partial biological degradation of the reservoir gases subsequent to their thermogenic formation. Biological processes preferentially use lighter isotopes; thus, any residual gas in the reservoir becomes more enriched in the heavier isotopes. Depending on the organisms present and their choice of substrate, this can also result in reversals of the trends of $\delta^{13}\text{C}$ versus compound carbon number.^{74–76} NMHCs can also be created from methane. This results in the trend in $\delta^{13}\text{C}$ values versus molecular weight being opposite to that for thermal decomposition.⁷¹ This has been observed for various situations, including natural gas formations, methane spark discharge experiments, and meteorites.^{71,72,75} Stable carbon isotope ratios for the 14 VOCs detected in this meteorite were also unusual, as they were almost all positive, ranging from $1.2 \pm 0.1\text{‰}$ for propane to $4.4 \pm 0.1\text{‰}$ for isobutene.⁷¹ Only benzene ($-28.7 \pm 0.2\text{‰}$) and ethene ($-0.1 \pm 0.4\text{‰}$) had negative values. While interesting in terms of historical VOC isotope measurements and their applications, these situations have little to no direct application for isotope studies in the Earth's atmosphere.

Oremland and Des Marais⁸¹ measured $\delta^{13}\text{C}$ values of ethane ($-27 \pm 0.3\text{‰}$) and propane ($-24 \pm 0.5\text{‰}$) observed in the monimolimnion of Big Soda Lake, an alkaline, hypersaline, meromictic lake. This area was thought to be similar to early depositional stages of oil and gas formation. These stable carbon isotope ratios were similar to those observed in areas of thermogenic hydrocarbon production.⁷¹ However, no origin could be confirmed for these gases because no $\delta^{13}\text{C}$ values were known for hydrocarbons of microbial origin.

4.1.2. Transportation

Approximately 20–25% of the total global anthropogenic VOCs emitted, and almost 50% of those in the United States, are due to vehicles with combustion engines, or other transportation-related sources.^{70,82} Rudolph et al.¹ first sampled air from a roadway tunnel near Wellington, New Zealand, and found $\delta^{13}\text{C}$ values for several NMHCs ranging from -21.9 to -31.3‰ . Samples taken near the Wellington waterfront and shipyards encompassed a larger range (-15.8 to -37.4‰).

Due to the importance of this source, further investigation was warranted. The stable carbon isotope ratios in 36 NMHCs emitted from transportation-related sources such as a gasoline refinery, evaporative emissions from gas stations, and engine combustion and evaporation were also measured by Rudolph and colleagues.⁸³ The average $\delta^{13}\text{C}$ of all compounds at all locations was $-27.1 \pm 2.1\text{‰}$, which was within the range expected for hydrocarbons derived from crude oil (-23 to -33‰).⁶¹ Differences in the $\delta^{13}\text{C}$ between the various sources were rarely significant and almost always $<2\text{‰}$. The alkene average $\delta^{13}\text{C}$ of $-25.3 \pm 1.9\text{‰}$ was statistically different from, but only slightly larger than, that of

the alkane + aromatic average of $-27.7 \pm 1.7\text{‰}$. The carbon isotope ratios for ethyne were not directly reported but were mentioned to be significantly enriched and mostly $>0\text{‰}$. These authors also measured stable carbon isotope ratios for NMHCs in ambient air near these source regions. Small but significant differences ($<4\text{‰}$) were observed during summer between the ambient and source signatures for the alkene and aromatic compounds. This difference was also observed for C_3 – C_5 alkanes but was smaller ($2.7 \pm 0.7\text{‰}$). Such effects were attributed to fractionation due to oxidation by OH radicals.

Formic acid in the exhaust of two different automobile models was also examined.⁷ A $\delta^{13}\text{C}$ value of -28‰ was found for emissions from a 1974 pre-catalytic converter Volvo combusting leaded gasoline, while emissions from a 1983 Toyota with a catalytic converter and unleaded gasoline had a signature of -48.6‰ . The authors attribute the large difference to a preferential destruction of ^{13}C in the converter.

4.1.3. Industrial Production

Usage, storage, and transport of solvents and other chemicals currently accounts for about 45% of the anthropogenic VOCs released in the United States.⁸² Kinetic and equilibrium fractionation effects that occur during the industrial processing of these compounds, such as purification or repackaging, could also have an impact on the isotopic signatures of these sources when process yields are $<100\%$.

Commercially available pure benzene and toluene had $\delta^{13}\text{C}$ values ranging from -23.9 to -29.4‰ and from -25.8 to -29‰ , respectively, when measured with off-line combustion followed by dual-inlet mass spectrometry.⁸⁴ Thompson and coauthors measured the stable carbon isotope ratio of commercial CFC113 (Sigma-Aldrich) to be $-31.3 \pm 0.5\text{‰}$.⁵ Hall et al.⁴⁸ measured $\delta^{13}\text{C}$ values of a commercial standard mix (Micromass UK Ltd.) of various $\geq \text{C}_{10}$ NMHCs including decane ($-28.5 \pm 0.1\text{‰}$).

Tanaka and Rye measured chlorine isotope ratios in several commercially manufactured solvents and a CFC to determine their usefulness in quantifying inorganic chlorine fluxes to the stratosphere.⁶⁹ The chlorine was extracted from the samples by heating with lithium, converted to CH_3Cl , and then analyzed by GC–MS. All compounds had $\delta^{37}\text{Cl} < 3\text{‰}$, signifying complete conversion of reaction products, except for CH_3Cl . This compound had significantly different vapor ($-6.82 \pm 0.15\text{‰}$) and liquid ($-6.00 \pm 0.14\text{‰}$) chlorine isotope signatures, which suggests a fractionation due to evaporation or condensation. Tanaka and Rye also suggested that the measurement of isotope ratios in ambient CH_3Cl would require thermal ionization or IRMS techniques due to low atmospheric mixing ratios. Holt et al.⁵⁶ measured a drastically different $\delta^{37}\text{Cl}$ for CH_3Cl (unspecified source) at -0.26‰ . The corresponding $\delta^{13}\text{C}$ value for this unspecified CH_3Cl source was -58.4‰ , which is between values reported for two different lots from Sigma-Aldrich analyzed by Harper et al.⁸⁵ (-46.9 and -61.9‰). Holt et al. also tested chloroform, which was found to have a $\delta^{13}\text{C}$ of -43.2‰ and a $\delta^{37}\text{Cl}$ of -1.5‰ .

Various types of fumigation activity, including field, product, and structural fumigation, are responsible for over a third of the known global CH_3Br emissions. McCauley and coauthors sampled CH_3Br manufactured by three companies that account for 82% of the world's production of CH_3Br used for fumigation. The $\delta^{13}\text{C}$ values ranged from -66.4 to -43.5‰ , with a production-weighted mean of -54.4‰ .⁴ In situ fumigation of agricultural soils with CH_3Br was tested by Bill and coauthors to investigate potential carbon isotope fractionations that might affect this source signature.⁸⁶ They found $\delta^{13}\text{C}$ values ranging from -52.8 to -42‰ , depending on how much of the applied CH_3Br was actually emitted. They calculated a KIE of 12‰ due to various loss processes in the soils. These authors also used their measurements to estimate lower and upper $\delta^{13}\text{C}$ limits for the global field fumigation emissions of CH_3Br . These values ranged from -53.2 to -47.5‰ , depending on fumigation conditions, climate conditions, and soil degradation rates.

Sakagawa and Kaplan⁸ measured the $\delta^{13}\text{C}$ of industrially produced formic and acetic acids during investigations of the carbon isotopic signatures of these organic acids in the atmosphere. They dissolved commercially available sodium formate and sodium acetate in water to create artificial rain samples and measured values of $-29.9 \pm 0.1\text{‰}$ and $-29.6 \pm 0.1\text{‰}$, respectively.

4.2. Biomass Burning

The most commonly recognized biomass burning sources include forest fires and clearing for agricultural purposes, but weed/plant control, biofuel cooking and heating, and waste removal also contribute. The variety of substrates and burning methodologies, as well as the process of combustion itself, results in the emission to the atmosphere of a wide range of volatile compounds. These can include the more abundant atmospheric gases such as CO and CO_2 , but numerous hydrocarbons, halogenated and oxygenated organics, nitrogen-containing and sulfur-containing compounds are also released.²⁶

The first $\delta^{13}\text{C}$ measurements of VOCs from burning biomass were made by Rudolph and coauthors on a C_3 Manuka plant.¹ Values ranged from -31.4 to -23.7‰ , with uncertainties ranging from 0.2 to 3.6‰. These are similar to the carbon isotope ratios of the wood itself (-28‰), with the exception of large fractionations for 1-butene ($-6.9 \pm 0.7\text{‰}$) and ethyne ($-13.0 \pm 1.6\text{‰}$). The stable carbon isotopic ratios of 19 NMHCs were also determined during the burning of Eucalyptus and Musasa woods, and none were found to be more than 5‰ different from the burnt wood $\delta^{13}\text{C}$ values.⁸⁷ This supports the original results of Rudolph and coauthors.¹ However, O'Malley et al.⁵¹ sampled aliphatic hydrocarbons $\geq \text{C}_{11}$ during the burning of various hardwoods, softwoods, and grasses. Burning emissions from C_3 plants were depleted by 7.5–11.5‰, and those from C_4 plants by 3.9–5.5‰, as compared to the bulk plant tissues. Values of $\delta^{13}\text{C}$ generally became more depleted with increasing carbon number, with those from C_3 plants ranging from -32.9 to -29.2‰ , and those from C_4 plants ranging from -25.3 to -20.6‰ .

The stage of the burn can also affect the isotopic signature of the released VOCs. The NMHC $\delta^{13}\text{C}$ values measured by Czapiewski et al. taken in the flaming phase were typically $2.2 \pm 1\text{‰}$ higher than those in the smoldering phase for any given compound.⁸⁷ Increasing fractionation was observed with increasing temperature for most NMHCs. This was consistent with a reservoir effect due to a NMHC loss process in the flame; however, an additional fractionation associated with the formation process could not be ruled out. Ethyne was an exception to these observations, with a $\delta^{13}\text{C}$ value enriched by $25 \pm 5\text{‰}$ relative to the burnt wood. This large enrichment in ethyne was also observed for transportation-related combustion processes.¹ Much of the variability in this measurement could be explained by temperature dependence, with smaller fractionations at higher temperatures. Czapiewski et al. suggest that these differences may be due to the different formation mechanism in fires for ethyne (recombination) as compared to other NMHCs (pyrolysis).⁸⁷

Methyl halides can also be released during biomass burning as Br^- , Cl^- , or I^- in the plant is methylated during combustion.⁸⁸ Burning of Manuka wood resulted in a $\delta^{13}\text{C}$ value for CH_3Cl of $-45.1 \pm 0.6\text{‰}$, which is depleted as compared to the burnt fuel ($\Delta = -17\text{‰}$).¹ Burning of Eucalyptus and Musasa wood released CH_3Cl with a carbon signature of -51.7‰ ,⁸⁷ which was also significantly depleted as compared to the burnt fuel ($\Delta = -24.8\text{‰}$). While there was a 20–25‰ difference between the CH_3Cl emitted by Eucalyptus and Musasa, there was no significant difference in fractionation between the flaming and smoldering stages of the burn for a given wood. This large interspecies variation in isotope ratio indicates a need to investigate numerous individual plant species when determining the average isotopic composition of VOCs emitted during biomass burning.

4.3. Biogenic Emissions

4.3.1. Terrestrial

The largest global source of isoprene to the atmosphere is release by trees and other higher order photosynthetic plants. Sharkey et al. measured the $\delta^{13}\text{C}$ of isoprene emitted by red oak, which was found to depend on the $\delta^{13}\text{C}$ value of source CO_2 used in the experiments.⁸⁹ Isoprene was depleted by $2.8 \pm 0.4\text{‰}$ relative to recently fixed carbon (-34.4‰ and -10.1‰). Affek and Yakir used ambient air as a CO_2 source and also found that $\delta^{13}\text{C}$ isoprene values ($-29.2 \pm 0.6\text{‰}$) were depleted ($\Delta = 7.7 \pm 0.7\text{‰}$) as compared to recently fixed carbon ($-21.7 \pm 0.3\text{‰}$).⁹⁰ However, they also found that the $\delta^{13}\text{C}$ value and $\Delta(\text{fixed carbon} - \text{isoprene})$ were *both* functions of the $\delta^{13}\text{C}$ of the CO_2 source. This was due to a significant portion of the isoprene being derived from a separate carbon source pool, with a different isotopic signature, than recently fixed CO_2 . Thus, it is not necessarily reliable to determine the stable carbon isotope ratio of emitted isoprene by use of a measured Δ . However, these authors used $\delta^{13}\text{C}$ of the bulk leaf biomass as a proxy for an average long-term value of $\delta^{13}\text{C}$ of fixed carbon, and determined that emitted

isoprene $\delta^{13}\text{C}$ values were depleted on average by 4–11‰ in comparison.

Average $\delta^{13}\text{C}$ values of $-27.7 \pm 2.0\text{‰}$ for isoprene emitted from velvet bean were measured by Rudolph et al.¹⁴ This was $2.6 \pm 0.9\text{‰}$ lighter than bulk leaf carbon, which is quite similar to the original measurements by Sharkey et al. However, insufficient information was reported to assess the results in light of the results of Affek and Yakir.⁹⁰ Slight dependences of the isoprene $\delta^{13}\text{C}$ values on light ($0.0026 \pm 0.0012\text{‰}/(\mu\text{mol photon m}^{-2} \text{ s}^{-1})$) and temperature ($0.16 \pm 0.09\text{‰/K}$) were also observed by Rudolph et al.,¹⁴ but it should be noted that a very limited number of these data points were taken.

Recent research indicates that alternative carbon sources to CO_2 can occur during biogenic isoprene production.⁹¹ These pathways may be particularly invoked during physiological stress. Significantly different fractionation between these pathways may result in emitted isoprene with wide-ranging $\delta^{13}\text{C}$ values.⁹⁰ Rudolph and coauthors¹⁴ suggest that $\delta^{13}\text{C}$ values may be useful in distinguishing various sources of isoprene. As by far the largest isoprene sources are from photosynthetic plants, this would require significant differences in fractionation *between* species during isoprene synthesis that are distinguishable from the natural variability of isoprene $\delta^{13}\text{C}$ values *within* a given species, as discussed above.

Ethane and propane have been observed by Orem-land et al. to be biogenically produced in various anoxic aquatic sediments.⁹² These authors measured $\delta^{13}\text{C}$ values of ethane ranging from -55 to -35‰ , which were depleted by $\sim 5\text{‰}$ as compared to the carbon substrates. Ethane was enriched in ^{13}C as compared to methane emissions from the same site. Microbial degradation of trichloroethane in contaminated groundwaters also resulted in production of ethane, for which the $\delta^{13}\text{C}$ values were measured.⁹³

Salt marsh plants produce between 5 and 15% of the global total sources of CH_3Br and CH_3Cl .⁹⁴ Bill et al.⁹⁵ measured $\delta^{13}\text{C}$ values of both methyl halides produced in the field by *Batis maritima* plants over a diurnal cycle. The isotopic signatures ranged from maximum values of -12 to -2‰ at night to minimum values of -65 to -59‰ at midday for CH_3Br . CH_3Cl signatures ranged from maximum values of -50 to -45‰ at night to minimum values of -71 to -69‰ at midday. The most depleted $\delta^{13}\text{C}$ values were found to be at the times of highest emission fluxes for both gases. Weighted average isotope ratios for CH_3Br and CH_3Cl emitted from the salt marsh were $-43 \pm 2\text{‰}$ and $-63 \pm 3\text{‰}$, respectively.

Kalin et al. measured $\delta^{13}\text{C}$ values of methyl halides emitted from various types of biological cultures.⁹⁶ Fungal cultures of *Phellinus pomaceus/tuberculosis* produced methyl chloride (-37 to -27‰) that was depleted in $\delta^{13}\text{C}$ compared to the carbon substrate (-11.7‰) and bulk biomass (-14.2‰) values. However, Harper et al.⁸⁵ reported significantly different values for CH_3Cl produced by that same fungal species ($\sim -42\text{‰}$). The CH_3Cl in this study was also depleted in ^{13}C as compared to both the wood substrate ($-25.4 \pm 0.8\text{‰}$) and bulk biomass ($-20.6 \pm 0.5\text{‰}$). Additionally, both *Solanum tuberosum* (potato) and

Batis maritima (halophyte) produced CH_3Cl that was depleted as compared to bulk tissue ($-62.2 \pm 4.6\text{‰}$ vs $-27.7 \pm 0.3\text{‰}$ for *S. tuberosum*; -65.7‰ vs $-28.9 \pm 0.2\text{‰}$ for *B. maritima*).⁸⁵

Formic acid is an oxygenated organic that is secreted from the glands of formicine ants for defense purposes.⁹⁷ Samples of formic acid in air collected from over *Formica fusca* and *Formica obscuripes* mounds, as well as extracted from the ant bodies themselves, were found to have an average stable carbon isotope ratio of -19‰ .⁷

4.3.2. Oceanic

Despite the recent debate on the importance of the oceans as either a net source or sink of various VOCs, there are no published data available on the isotopic signatures for any of the VOCs emitted from the oceans, nor KIEs and equilibrium isotope effects associated with oceanic uptake.

5. Kinetic Isotope Effects

The isotopic composition of atmospheric VOCs can be significantly enriched by the kinetic isotope effects of loss processes, or significantly depleted during photochemical production. The loss process of most importance globally for most VOCs is chemical oxidation. The major oxidants during daylight hours are OH and O_3 . Nitrate (NO_3) becomes an important sink at night when OH and O_3 are less abundant, and Cl may have a significant role in marine regions and in polar regions during springtime. Direct photolysis in the troposphere can only be an important sink for aldehydes and ketones, as these compounds can absorb the low-frequency solar radiation present there. Dry and wet deposition are expected to be minor sinks for most VOCs, except for compounds that have low Henry's law constants and are chemically long-lived (e.g., methanol, formic acid). Similarly, biological uptake is likely a minor sink for most VOCs. However, if very large KIEs are found to occur during these processes, they may still have a significant effect on ambient VOCs' isotopic signatures. KIEs or equilibrium fractionation effects may also exist for physical processes that transform VOCs into or out of the atmospheric gas phase, such as evaporation, deposition, or diffusion. These processes must be considered for direct use in modeling or interpreting the isotopic signatures of ambient VOCs. The KIEs for atmospherically relevant processes are summarized in Table 1 and Figure 4.

5.1. Chemical and Photochemical Processes

5.1.1. Production

Photochemically produced OVOCs, such as aldehydes and ketones, should generally reflect the isotopic composition of their parent materials, but they also likely have distinct isotopic signatures due to fractionation effects during their production. However, we are not aware of any published measurements or theoretical estimates of the isotope effects associated with photochemical production of OVOCs.

Changes in carbon isotope ratios have been measured during abiotic transhalogenation of CH_3Br to

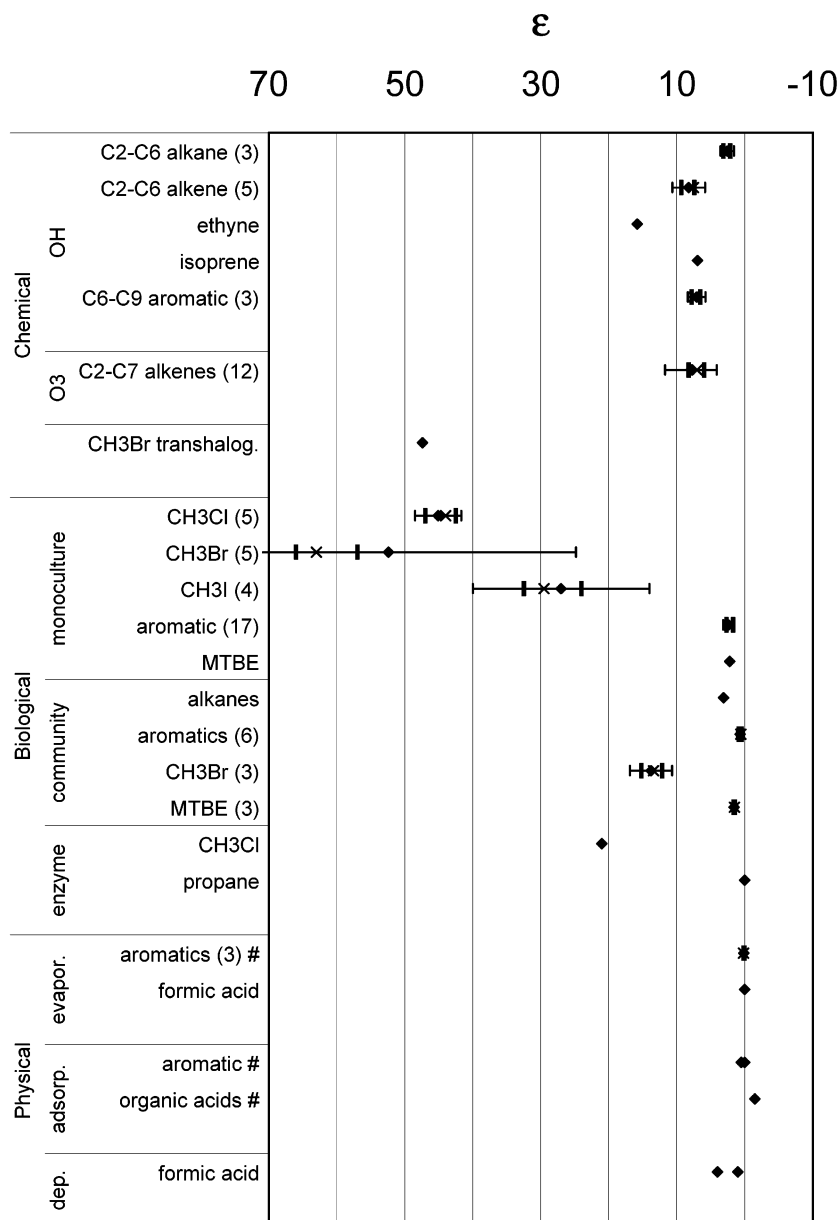


Figure 4. VOCs' kinetic isotope effects. Per mil units of ϵ , calculated as defined in section 1.3 if not already reported as such. Symbols and calculations as in Figure 2. Number of samples is reported in parentheses. The number sign indicates that these were reported as differences between signatures (Δ units), not as KIE (ϵ). References used, in same order as listed in figure: OH (refs 57; 10,57; 57; 57; 57,99), O_3 (103), transhalogen (96), monoculture (refs 114; 114; 114; 109,112; 63), community (refs 107; 107,109,111; 86,114; 63), enzyme (refs 114; 106), evaporation (refs 84,115; 7), adsorption (refs 52,109; 52), deposition (7).

CH_3Cl and have been found to be extremely large ($\sim -43\%$).⁹⁶ Complete halogen exchange was detected after sufficient time by a shift in $\delta^{13}C$ values from CH_3Br to CH_3Cl . Microbially mediated transhalogenation of the stable chlorine isotopes may also be possible.⁹⁸ These processes could occur in the ocean and/or soils but have never been measured under field conditions or at ambient atmospheric concentrations.

Measurements by Bill et al.⁹⁵ on CH_3Br and CH_3Cl emissions from a salt marsh showed major diurnal changes in isotopic composition which may have indicated a competition between uptake and release by the system which resulted in a net emission. The production term must be considered as a net term for natural systems or understood in more detail as

the integral of all production and consumption processes in the ecosystem.

5.1.2. Losses

Conny and Currie¹⁹ predicted that the largest KIE in the entire multistep oxidation pathway of alkanes would be in the initial OH reaction step, as it is for methane oxidation, due to the similar H abstraction oxidation pathway of this class of hydrocarbons. However, they suggested that these predictions may not hold for isoprene, because of the mechanistic difference in initial OH attack for alkanes and alkenes where OH is added to the double bond. Conny and Currie¹⁹ also suggested the non-methane alkane products of this oxidation in ambient air

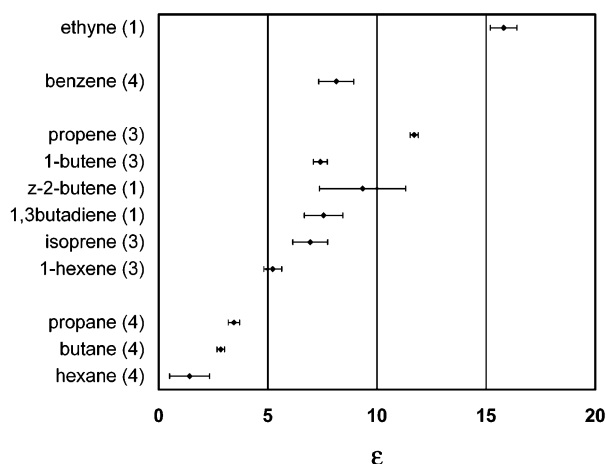


Figure 5. Subset of kinetic isotope effects for C_2 – C_6 VOCs oxidation by OH. Per mil units of ϵ . Symbols and calculations as in Figure 2. Averages and standard errors of the mean for replicates from Rudolph et al.⁵⁷ Number of samples is reported in parentheses.

would likely be enriched in $\delta^{13}C$ relative to their sources.

An estimate of the stable carbon isotope KIE for the ethane–OH reaction was first made by Tsunogai et al.¹¹ on the basis of comparison between atmospheric concentration and $\delta^{13}C$ measurements downwind of Japan. They assumed that a Rayleigh fractionation would explain the observations, and they calculated a KIE value of $3 \pm 1\%$. Rudolph et al.^{57,99} were the first to measure the KIE of the oxidation by OH for 11 different light n -alkanes, alkenes, dienes, benzene, and ethyne in a 30-L Teflon reaction chamber. Samples were automatically collected from the chamber, cryogenically concentrated, and separated by 2D-GC before a subsample was sent to an ion trap mass spectrometer for peak identification, and the remainder was combusted and sent to the IRMS. All KIE values were confirmed to be positive and to range from 1–4‰ for n -alkanes, 5–12‰ for alkenes, and 15.8‰ for ethyne. The KIE for isoprene was $6.9 \pm 0.8\%$. The measurement uncertainties were less than observed variations, typically at <12% of the KIE value. KIEs for the reaction of NMHCs and OH cover approximately the same range as for the reaction of methane and OH (e.g., 3.6‰,¹⁰⁰ 5.4‰,¹⁰¹ 3.9‰¹⁰²). This is in contrast to Conny and Currie, who predicted NMHC–OH KIEs to be generally smaller than that for methane–OH.

KIEs were generally higher for the unsaturated gases than the saturated gases (see Figure 5). The authors suggest that this may result from a large positive fractionation due to different activation energies of the transition state of the OH–alkene adduct. Within these groups NMHC–OH KIE values generally decreased with increasing carbon number (see Figure 5). Rudolph et al.⁵⁷ suggest that this is due to the decreasing probability that the single ^{13}C atom in the molecule is attacked by OH as the number of carbon atoms in the molecule increases. Using ambient concentrations, they estimated that most NMHC KIEs are sufficiently large to have an observable effect on ambient isotope ratios of those

gases, potentially in less than 1 h for the more reactive compounds.

Iannone et al.¹⁰³ measured the KIE for a series of alkene– O_3 reactions, which showed an inverse dependence on carbon number similar to that of NMHC–OH reactions. Values ranged from $18.9 \pm 2.8\%$ for ethene, the smallest alkene tested, to $4.3 \pm 0.7\%$ for 1-heptene, the largest alkene tested. On the basis of their measured KIE, the authors estimated that the effect of oxidation by ozone on ambient isoprene carbon isotope signatures would be small compared to that of oxidation by OH under typical daytime conditions. They also estimated that contributions of the fractionation due to loss by O_3 to that for total oxidative loss could reach 30–50% under polluted urban conditions for several C_2 – C_6 alkenes. KIEs associated with loss of VOCs to other oxidants, including NO_3 , and Cl may also significantly impact the isotopic value of atmospheric VOCs under certain conditions. However, we are not aware of any published KIEs for reaction of VOCs with NO_3 or Cl.

The hydrogen KIE for methane oxidation by OH has been measured to be 294‰,¹⁰² which is significantly larger than the carbon KIE for the same reaction (3–5‰).¹⁰² Thus, we might expect that the hydrogen KIE for NMHC oxidation by OH could be substantially larger than the carbon KIE for the same reaction. Currently there are no published hydrogen KIE measurements for any NMHC with natural abundance levels of deuterium; however, the KIE for OH reactions with some deuterium-labeled NMHCs have been measured by Droge, Tully, and coauthors.^{64–68} The amount of labeling varied, ranging from full and half substitution^{65–67} to more complex combinations.^{64,68} KIEs for ethane ranged from 900 to 3600‰, propane from 500 to 1650‰, isobutane from 230 to 910‰, butane from 910 to 1520‰, cyclopentane from 970 to 1740‰, and cyclohexane from 860 to 1590‰ for reactions at temperatures ranging from 1000 to 290 K, respectively. Theoretical entropies and enthalpies from electronic-structure calculations for the reactants and transition structures were consistent with the experimental results. The strong inverse temperature dependence of the KIE was consistent with an Arrhenius-type equation. Published measurements of carbon KIE associated with OH oxidation of NMHCs have all been performed near 290 K.^{10,57,99,103} If the temperature dependence is similar to that for hydrogen isotopes, these KIE values may change significantly over the range of atmospheric temperatures. Droge, Tully, and coauthors also observed that hydrogen isotope effects were largest when the hydrogen or deuterium atom was abstracted from a primary C (e.g., ethane), smaller for a secondary C (e.g., propane, butane, cyclopentane, and cyclohexane), and smallest for a tertiary C (e.g., isobutane). The extreme magnitude of these KIE measurements is relevant only to the deuterium-substituted compounds studied and is not directly atmospherically relevant due to the low natural abundance of deuterium. However, while these KIE results are larger than expected in the atmosphere, they suggest that the KIE should be significant even at natural abundance.

5.2. Biological Consumption

Lebedew et al.¹⁰⁴ observed enrichment in propane ^{13}C values during aerobic bacterial degradation in laboratory cultures. Bacteria require a monooxygenase enzyme to catalyze the initial hydrocarbon oxidation step.¹⁰⁵ In contrast to the culture work of Lebedew, carbon isotope measurements of propane degraded by an *in vitro* monooxygenase exhibited no KIE.¹⁰⁶ Similarly, Stahl¹⁰⁷ determined very small carbon KIEs of -1 to 1‰ for the degradation of bulk alkane, aromatic, and asphaltene fractions of North Sea petroleum.

Carbon and hydrogen stable isotope ratios have been measured simultaneously during microbial degradation of various organics. While this work was originally performed to trace transformations in polluted groundwaters, such sinks could be important to the atmospheric budgets of halogenated and oxygenated VOCs, and also could affect their global signatures if the associated sink KIEs are sufficiently large. Degradation of toluene by various aerobic, denitrifying, methanogenic, iron-reducing, sulfate-reducing bacteria and mixed bacterial consortia was shown to result in very small carbon KIEs of $2.0 \pm 0.5\text{‰}$.^{108–110} Carbon KIEs for benzene degradation in soil were also of this magnitude.¹¹¹ These values are likely not large enough to be detectable in the isotopic composition of ambient hydrocarbons since the soil sink is minor compared to oxidation of these compounds in the atmosphere. However, hydrogen KIEs for the same cultures as tested by Ahad et al. were much larger, reaching $>60\text{‰}$.⁶² Similar differences between carbon and hydrogen KIEs were observed for biodegradation of methyl *tert*-butyl ether, toluene, and large *n*-alkanes.^{63,112,113}

The largest fractionations of stable carbon isotopes observed in natural biological systems are for archaeal methane production ($\sim 70\text{‰}$). Miller et al.¹¹⁴ discovered fractionations occurring during methyl halide oxidation by aerobic methylotrophic bacteria that can also reach those values. Miller et al.¹¹⁴ tested whole cells of several α -proteobacteria strains isolated from coastal seawater, forest litter, and previously fumigated agricultural soils. Resulting fractionation factors in CH_3Cl , CH_3Br , and CH_3I were found to range from $4 \pm 2\text{‰}$ to $72 \pm 3\text{‰}$ for the various strains. The methyltransferase required for this oxidation was extracted from one strain and had a fractionation factor of $21 \pm 1\text{‰}$ for CH_3Cl . The discrepancy between whole cell and enzyme measurements was hypothesized to be due to an *in vitro* effect or to additional fractionations associated with subsequent steps in the degradation pathway. Interestingly, *in situ* fumigation of agricultural soil with CH_3Br resulted in a KIE of $\sim 12\text{‰}$,⁸⁶ which is on the low end of laboratory culture measurements.¹¹⁴ However, the *in situ* measurement includes all CH_3Br loss processes that occur, including chemical degradation by hydrolysis or transhalogenation, advection, and diffusion. KIEs for these processes have not been specifically reported in the literature.

A comparison of the KIEs for microbial biodegradation of various VOCs may indicate a rough trend of a smaller KIE for larger carbon number VOCs (see

Figure 4). This would not be unreasonable for intracellular fractionations (as opposed to those associated with transport to the cells and uptake across membranes) and is analogous to the statistical explanation of similar trends of KIEs due to OH oxidation with carbon number, as reported by Rudolph and co-workers.⁵⁷ In short, the probability that the oxidized atom is a carbon-13 rather than carbon-12 is inversely proportional to the number of carbon atoms in the molecule.

5.3. Physical Transformations in Soil and Water

5.3.1. Evaporation

Interest in using stable isotope analyses to characterize groundwater contaminant plumes has spurred research into potential physical fractionation effects. Slater et al.¹¹⁵ demonstrated that laboratory evaporation of benzene and toluene had no kinetic or equilibrium carbon isotope effects more significant than the $\pm 0.5\text{‰}$ reproducibility of the measurement. Harrington et al.⁸⁴ found that vaporization fractionation effects were positive but quite small ($\sim 0.2\text{‰}$) for benzene, toluene, and other aromatic hydrocarbons. It is unusual that this evaporative effect results in ^{13}C enrichment in the vapor phase, and not the liquid phase. This may be due to an equilibrium isotopic process.^{116,117} Similar effects were observed by Wang and Huang¹¹⁷ for hydrogen isotopes. They analyzed heptane, octane, and nonane for fractionation during progressive vaporization by GC–thermal conductivity (TC)–IRMS. Values of δD in the residues were decreased, resulting in fractionation factors of $44 \pm 2\text{‰}$, $43 \pm 1\text{‰}$, and $40 \pm 2\text{‰}$, respectively. These effects are significantly larger than those observed for carbon isotopes during vaporization, presumably due to the much larger relative difference in mass between the two hydrogen isotopes as compared to the carbon isotopes. Similarly, Ward et al.⁶² found δD depletion during toluene volatilization of approximately 6‰ . These large KIEs may imply a use for δD in atmospheric studies where carbon KIEs for various processes are not unique, as previously discussed.

5.3.2. Deposition

Adsorption to various soil matrices does not appear to cause significant carbon isotopic fractionation of aromatic hydrocarbons. Meckenstock et al.¹⁰⁹ found no carbon fractionations of toluene in abiotic soil columns, implying no significant liquid–solid phase interactions. Harrington et al.⁸⁴ found similar results for the carbon isotopes of benzene, toluene, and other aromatics. However, hydrogen isotope fractionations have been observed for these compounds during partitioning between aqueous and solid organic phases. Poulson et al.¹¹⁸ found that deuterium-containing benzene and toluene were preferentially retained in the aqueous phase as compared to the organic carbon phase (i.e., soil). This preference was not observed for non-deuterated compounds and implies that the heavier hydrogen isotope experiences a stronger interaction with water than the lighter isotope. No isotope fractionation factors were given,

as the study investigated partition coefficients and not KIEs.

Johnson and Dawson⁷ estimated the fractionation factor for carbon that might be expected during dry deposition of formic acid to the ground or vegetation. They assumed that the lighter isotope diffuses more rapidly through the stagnant boundary layer at the surface than the heavier isotope, and they calculated a 4‰ fractionation on the basis of a molecular weight technique. Johnson and Dawson⁷ also measured the carbon fractionation in formic acid between equilibrated gaseous and aqueous phases and found it to be negligible. This information, combined with a statistical thermodynamics estimation of ionization fractionation, allowed them to conclude that only a very small fractionation exists for wet deposition of this compound, if at all. These results should be confirmed experimentally; however, if they hold, the implication is that atmospheric isotopic signatures of oxygenated organics may not be affected by wet deposition.

5.3.3. Diffusion

The process of gaseous diffusion prescribes a more rapid movement of lighter molecules than heavier ones and allows for potential associated isotopic fractionations. However, fractionations would only be observed in a closed system if the process was sampled while incomplete or if a loss mechanism existed. For example, gases such as ethane and propane in deep gas formations may experience fractionation at the migrating front. However, hydrocarbon exploration studies almost always assume a negligible fractionation associated with migration because gas reservoirs are typically closed systems that have experienced extremely long storage time scales.²⁰

Bill et al.⁸⁶ sampled the CH₃Br emitted for several days after the fumigation of an agricultural field. In contrast to a natural gas reservoir, the ambient CH₃Br concentrations at the field site were still changing rapidly during the period of isotopic sampling. The result was an approximate 5‰ difference in $\delta^{13}\text{C}$ values between samples taken under or through a tarp, which was assumed to be diffusion-induced.

6. Theoretical Advances and Applications

The application of carbon isotope measurements of VOCs has focused on providing quantitative estimates of either contributions from a variety of sources to the atmosphere or the extent of photochemical degradation. In this section we review recent theoretical advances in using stable isotopes to determine the photochemical age of an air mass and the use of isotopes in studying VOC atmospheric budgets.

6.1. Photochemical Age

The isotopic composition of VOCs in the atmosphere is altered by photochemical loss processes that preferentially react with lighter isotopes, thus isotopically enriching the material remaining in the

atmosphere.^{1,2,11} Tsunogai et al.¹¹ observed that, as ethane concentrations decreased in air going from urban to marine environments off the coast of Japan, the $\delta^{13}\text{C}$ of ethane became enriched. They assumed a Rayleigh dependence between isotopic composition and mixing ratio, estimated the KIE for atmospheric ethane oxidation to be $3 \pm 1\%$, and suggested that observations of isotopic changes as a result of photochemical oxidation may provide a method to distinguish between different oxidation pathways if the KIEs associated with each pathway were known. Rudolph et al.⁵⁷ published the first laboratory measurements of the KIE for a series of non-methane hydrocarbons reacting with OH and suggested that the dependence observed by Tsunogai et al. was due to dilution and mixing processes, and not necessarily indicative of a KIE.

Rudolph and Czuba² introduced the “isotopic hydrocarbon clock” for estimating the photochemical age of an air mass from $\delta^{13}\text{C}$ measurements and knowledge of the KIEs. This method is independent of concentration measurements. The isotopic hydrocarbon clock is a variant on the “hydrocarbon clock” method, as discussed by McKeen et al.,¹¹⁹ that determines OH radical concentrations from reactive hydrocarbon concentration measurements. The hydrocarbon clock method uses the change in the ratio of two hydrocarbons with different OH rate constants relative to a reference composition (or compound) to estimate the average “photochemical age” of an air mass ($[\text{OH}]t_{\text{ave}}$). This method is of limited use when air masses of different photochemical ages mix, which is typically the case in the atmosphere.¹²⁰ However, Rudolph and Czuba² show that the photochemical age calculated from changes in isotopic composition is equivalent to considering two compounds with different lifetimes, yet due to the small KIEs for the oxidation of hydrocarbons, the calculated photochemical lifetime provides a linearly averaged age which is independent of the mixing of air parcels with different lifetimes. The photochemical age can be estimated from (see Rudolph and Czuba² for derivation)

$$[\text{OH}]t_{\text{ave}} = \frac{\delta_z - \delta_{z0}}{\epsilon^{\text{OH}} k_z}$$

where the isotopic composition of compound z in the air mass is δ_z , δ_{z0} is the emission source isotopic composition (or time zero isotopic composition), ϵ is the KIE fractionation factor defined in section 1, and $^{\text{OH}}k_z$ is the OH reaction rate constant. The uncertainty of the photochemical age depends on the variability of the isotopic composition of the sources, the KIE of the oxidation process, and the accuracy of the isotopic composition measurements. The atmospheric lifetime of a compound determines the temporal and spatial scale over which the estimate of photochemical age is relevant. Thus, studying a series of compounds with different lifetimes could provide significantly more information than studying a single compound.

Measurements of the KIEs associated with other photochemical loss processes, including reactions

with O_3 , NO_3 , and Cl , are needed to properly interpret the photochemical age of air masses using the isotopic hydrocarbon clock approach unless OH is the only significant loss process. Despite the lack of KIE information for other oxidants, this approach has been applied to calculate the OH concentration or photochemical age in a few environments, assuming that OH is the dominant loss process impacting the isotopic composition of the measured compounds. Rudolph et al.⁵⁷ and Rudolph and Czuba² applied the method to a limited data set from Toronto, Canada, and showed that the approach gave reasonable estimates of the summer daytime OH radical concentrations. Saito et al.³ applied this method to isotopic measurements of ethane and *n*-butane and compared the inferred air mass ages to results of backward trajectory analysis. Their analysis assumed that the measured hydrocarbons were coming from known source regions and not from the ocean, and OH concentrations were also assumed. The estimated ages for each compound increased with increasing compound lifetime, consistent with the idea that the atmospheric concentration of shorter-lived compounds would be influenced more by recent emissions. It is not clear from this study, or the studies by Rudolph et al. in Toronto, whether the analysis of isotopic composition for these anthropogenically emitted hydrocarbons provided different or additional information on photochemical age that could not have been derived from hydrocarbon concentration measurements alone. A study directly comparing results from the "isotopic hydrocarbon clock" method with the more traditional "hydrocarbon clock" method should provide a useful test of the new methodology.

Rudolph et al.¹⁴ showed that isotopic measurements of biogenically emitted isoprene can also be used as an indicator of photochemistry in areas downwind of emission sources, and could be used to provide quantitative information on the origin and extent of recent formation of photochemical oxidation products of isoprene. This is an excellent example of a situation where the conventional hydrocarbon clock could not be used because there are no other hydrocarbons emitted together with isoprene in a well-defined ratio, but the isotopic hydrocarbon clock can be uniquely applied assuming the isoprene source signature is relatively constant. In order for uncertainties in applying this method to be reduced, more work is needed to characterize the natural variability of the isotopic composition of isoprene emitted from plants and to quantify the KIEs of reactions between isoprene and all the major oxidants which may remove it from the atmosphere.

6.2. Atmospheric Budgets

To understand the atmospheric budgets of VOCs, it is critical to develop methods for determining the relative contributions of different sources to the atmospheric burden. Radiocarbon measurements provide an enticing opportunity to separate the sources into two specific categories: (1) biogenically derived VOCs from direct plant emissions, combustion of fresh plant material, or secondary photochemical production from primary emissions that contain ^{14}C

concentrations comparable to atmospheric CO_2 , and (2) fossil-fuel-derived primary and secondary VOCs that contain no measurable ^{14}C . This differentiation is typically assumed to separate biogenic from anthropogenic sources, but it could be misleading when anthropogenic emissions are derived from recently photosynthesized carbon such as burning biomass for heat or cooking, or use of biogenic feedstock for production of gasoline additives such as ethanol.^{17,18} Additionally, these radiocarbon measurements are difficult due to analytical considerations ranging from the sensitivity of accelerator mass spectrometry (requiring microgram samples) to the ability to collect and completely separate the compound or compounds of interest and convert them to a measurable form without contamination or fractionation.

Klouda et al. developed a method to quantify the biogenic contribution to total atmospheric VOCs using ^{14}C measurements and applied it in Atlanta, Georgia,¹⁷ and in the South Coast Air Basin of California, 46 km downwind of the Los Angeles urban center.¹⁸ The upper limit of the percentage of VOCs from biomass sources (percent modern carbon, pMC) was reported for two measurements in Atlanta in summer 1992, indicating 9% and 17% pMC in the morning and evening hours, respectively. However, the level of the process blank and the uncertainty for these two measurements suggested that the percentage could be as low as zero and indicated the importance of carefully evaluating all steps of the analytical procedure for potential errors.¹⁷ A study with more samples and more detailed quality control was done in 1997 in Los Angeles. On the basis of careful evaluation of each step of the analytical procedure, substantial corrections to the measured pMC were made for process blanks and for residual CO_2 that was not removed from the atmospheric VOCs samples (mean correction = 28 pMC). Percent modern carbon was also measured on whole gasoline samples, vegetation samples, and atmospheric CO_2 samples in order to compare with and correct the atmospheric VOCs measurements. The median fraction of biogenic VOCs observed varied over the course of a day from 7% (range of -9 to 24%, $n = 5$) from 0600 to 0900 hours (LT), to 27% (range of 11 to 39%, $n = 4$) from 1300 to 1600 hours, to $34 \pm 7\%$ for a single sample from 1700 to 2000 hours.¹⁸ These measurements suggest a substantial contribution of biogenic VOCs to the total VOCs observed in the afternoon in an area with extremely high air pollution levels.

Radiocarbon measurements have also been used to determine the relative contribution of biogenic and anthropogenic sources to atmospheric VOCs whose dominant sources are secondary photochemical production, such as formic and acetic acids and formaldehyde or a sum of aldehydes. Radiocarbon measurements of these gases should provide information on the origin of their precursor VOCs. Glasius et al.¹² measured samples from a rural and a semiremote area of Denmark collected over 5–6-day periods in winter and spring (method described in section 2.3). They found that 80–100% of the formic acid was from biogenic sources, even during winter when biogenic

emissions were quite low. Glasius et al.¹³ published a broader study with measurements at sites across Europe. The biogenic fraction of formic acid ranged from 56 to 99%, while the fraction for acetic acid ranged from 64 to 100%. The minimum biogenic contributions were observed in samples from the urban areas of Oslo and Milan. In areas designated as rural, semirural, or remote, the biogenic fraction was typically 90–100%. In most cases there was a slightly higher fraction of acetic acid, attributable to biogenic sources, compared to formic acid. These studies indicate that photochemical oxidation of biogenic VOCs is the major source of both formic and acetic acids in Europe, with the biogenic contribution being greater than 50%, even in cities during winter. Tanner et al.⁹ measured the radiocarbon content of formaldehyde in August 1993 at the southern tip of Nova Scotia during periods of predominantly local influence, periods of substantial pollutant influences from continental air masses crossing eastern Canada and the northeastern United States, and periods when cleaner air masses were transported from predominantly marine trajectories. For all of these air mass trajectories, the pMC of formaldehyde ranged from 74 to 96%, with a mean value of approximately 80%. This study indicates that formaldehyde sources are dominated by biogenic emissions, or secondary formation from biogenic compounds, in summer at this site downwind of eastern North America. Larsen et al.¹⁶ collected the sum of carbonyls (mainly formaldehyde, acetaldehyde, acetone, propanal, and butanal) on DNPH cartridges during late summer in a semirural site in Ispra, Italy. They found that this sum of carbonyl compounds was 41–57% biogenic and 43–59% anthropogenic.

A comprehensive approach is emerging for using stable carbon isotopes to study the atmospheric budgets of methyl chloride⁵ and methyl bromide.⁴ Thompson et al.⁵ published the first paper to analyze the atmospheric budget of CH₃Cl using $\delta^{13}\text{C}$ measurements. They measured $\delta^{13}\text{C}$ of CH₃Cl at 2- to 3-week intervals for slightly more than one full year at Alert, Canada, for most of a year at Fraserdale, Canada, for most of a year at Baring Head, New Zealand, and from a few samples collected at other locations. As CH₃Cl can be assumed well-mixed due to its 1.5-year lifetime, they were able to determine a global average $\delta^{13}\text{C}$ of $-36.2 \pm 0.3\text{‰}$ (error of mean) on the basis of 78 measurements. They observed an insignificant seasonal variation at Alert ($0.69 \pm 0.78\text{‰}$ (error of difference)) and a larger seasonal variation at Fraserdale ($3.47 \pm 1.61\text{‰}$), and found that interhemispheric differences were insignificant when samples that were likely impacted by local emissions were excluded. These measurements all lie within the larger range of values measured by Tsunogai et al.¹¹ in the remote maritime atmosphere over the western North Pacific (-44 to -30‰), some of which were assumed to be impacted by industrial emissions, and the two ambient air measurements reported by Rudolph et al.¹ A limited number of measurements have been made to characterize $\delta^{13}\text{C}$ of CH₃Cl from several of the major source types, including biomass burning (weighted mean -47‰ ;⁵

range -38 to -68‰ ^{1,87}), salt marshes (-62‰ ⁹⁵), fungi (-43‰ ⁸⁵), and industrial production (-41.9 and -60‰ ^{1,11}). However, the isotopic compositions of emissions from the ocean (major source), higher plants (source strength highly uncertain), coal combustion (minor source), and incineration (minor source) have yet to be measured, and the variability of the measured source signatures is still poorly constrained. The KIE of the dominant loss process, reaction with OH in the troposphere, has not been measured. The KIE of photolysis in the stratosphere (minor loss) has also not been measured. The KIE of uptake by soils (minor loss) has not been measured directly, but the KIE associated with consumption by three strains of methylotrophic bacteria¹¹⁴ suggests that the biological component of the soil sink could have a KIE between 20 and 50‰. Although there are several important unknown source and sink signatures remaining in the carbon isotope budget of atmospheric CH₃Cl, Thompson et al.⁵ used the existing measurements, and an estimate of the OH loss KIE of $5 \pm 5\text{‰}$, to constrain the average isotopic composition of all sources whose isotopic composition is unknown to be $-41.6 \pm 7.8\text{‰}$. This constraint will be much stronger when isotopic effects associated with major contributions to the budgets are quantified.

Even less data is currently available to analyze the global budget of CH₃Br using $\delta^{13}\text{C}$ measurements. The only atmospheric measurements for $\delta^{13}\text{C}$ of CH₃Br to date were collected in Berkeley, California by Bill et al.¹²¹ These measurements demonstrate the feasibility of the analytical approach and provide a first look at atmospheric values, but do not provide information on their temporal or spatial distribution. On the basis of seven measurements, an average $\delta^{13}\text{C}$ of $-43.1 \pm 1.5\text{‰}$ (standard deviation) was determined. This isotopic value is enriched compared to the directly emitted anthropogenic source signature (-54.4‰ ⁴) and the majority of emissions from agricultural field fumigations (-52.8 to -42‰ depending on the fraction of applied CH₃Br that escapes to the atmosphere⁸⁶), but it is indistinguishable from mean salt marshes emissions (-43‰ ⁹⁵), the only natural source whose isotopic signature has been measured. The isotopic compositions of emissions from the ocean (major source), non-salt marsh plants (source strength highly uncertain), and biomass burning (major source) have yet to be measured. The KIE of the photochemical loss processes in the atmosphere (reaction with OH in the troposphere is dominant) and uptake by the ocean have also not been measured. The KIE of soil uptake for CH₃Br in fumigated fields has been measured at 12‰,⁸⁶ although this may not represent the KIE which occurs during soil consumption at background atmospheric concentrations, and this sink is minor compared to oxidation by OH. Although there are several important unknown source and sink signatures remaining in the carbon isotope budget of atmospheric CH₃Br, Bill et al.¹²¹ used the existing measurements, and the assumption that anthropogenic sources are currently 25–50% of the total source, to predict that the effective KIE of all loss processes combined should be in the range 2–4‰,

that the expected change in $\delta^{13}\text{C}$ of atmospheric CH_3Br should be 0.07‰ per % change in anthropogenic contribution to the total source (so a total phaseout should result in a 2–4‰ increase in $\delta^{13}\text{C}$ of atmospheric CH_3Br), and that this change would be difficult to detect, given the 1–2‰ precision of the current analytical method. These predictions could be incorrect if the atmospheric measurements are not broadly representative, or if the current knowledge of source signatures is not representative of the mean anthropogenic or natural values.

7. Conclusions and New Directions

Advances in analysis techniques for compound-specific measurements of C isotopes in small samples have opened a new method of inquiry for scientists interested in atmospheric chemistry and biogeochemistry. Information on source signatures for a wide variety of fossil-fuel-derived VOCs has been available for decades, but its application to the study of atmospheric photochemical processes has just begun. Since 1997, characterization of the isotopic signatures for a much wider variety of VOCs sources has occurred, new measurements of the isotopic composition of atmospheric VOCs have been made, and new theoretical approaches have been developed to utilize this information. In evaluating the potential utility of stable isotopes for studying VOCs in the atmosphere, it is important to identify areas of research where isotope measurements can teach us more than concentration measurements alone. For example, studies on photochemical processing would be a more useful application than source apportionment for compounds for which the source signatures are similar but loss KIEs are large (i.e., biogenic and anthropogenic NMHCs). However, source apportionment studies would be appropriate for compounds whose source signatures vary more widely (due to larger variety of source types), such as the methyl halides and possibly oxygenated VOCs.

The rapid development of the use of carbon isotopes to study atmospheric VOCs has highlighted the power of isotopic information to constrain atmospheric budgets and provide information on atmospheric processing. However, we are currently quite limited by the minimal amount of data available. For most compounds, insufficient data exist to provide a solid statistical representation of the natural variability in time and space of their atmospheric isotopic composition, or of the isotopic signatures of their sources and sinks. Furthermore, studies of the dependencies of these source and sink signatures on controlling factors, such as temperature, are extremely sparse. These gaps in our current knowledge base represent important areas of research opportunities.

Advancement of isotopic hydrocarbon clock and atmospheric budget studies will require further measurements or estimates of KIEs associated with atmospheric loss processes. A few comprehensive laboratory studies have been performed to determine the KIEs for reaction of series of NMHCs with OH and O_3 , but KIE measurements for reactions such as oxygenated VOCs and methyl halides with OH are

still needed. Measurements of the KIE for reaction between VOCs and other oxidants are needed to determine whether the signature from OH oxidation is unique. No KIE measurements of VOCs with NO_3 or Cl have been published, but some will undoubtedly be available soon.¹²² Theoretical ab initio calculations of KIEs for the relevant reactions of VOCs with OH, O_3 , NO_3 , and Cl, and their comparison with measurements, might be an interesting approach for improving our general understanding of isotope effects in the oxidation of VOCs, but we know of no work being done in this area. However, it should be noted that previous ab initio calculations for reaction of methane with both OH and Cl resulted in KIE values that were up to a factor of 2 different than measured values,¹²³ indicating that the accuracy of this method might be insufficient for interpretation of atmospheric stable isotope ratio measurements.

Source apportionment of trace gases with a combination of primary and secondary sources to the atmosphere, such as aldehydes and ketones, which cannot be separated by concentration alone, provides a particularly interesting and challenging opportunity for the use of isotopes. It is currently impossible to separate direct emissions and formation by oxidation in the atmosphere using stable isotopes because no information is available on the fractionations associated with photochemical production of these compounds, nor with their loss by photolysis. More research is needed on these signatures. Particularly interesting compounds to start with might include relatively abundant species whose atmospheric budget is poorly constrained, such as acetone, acetaldehyde, methanol, and ethanol.

In addition to their use in studying trace gas budgets and local to regional photochemical processes, it is likely that atmospheric stable isotope measurements and kinetic isotope effects can be used to study larger scale photochemistry. Seasonal cycles of the isotopic composition of VOCs in rural to remote areas of the atmosphere as a function of latitude could serve as indicators of OH concentrations, integrated over the spatial domain relevant to the lifetime of each compound. Seasonal cycles in mixing ratio of C_2 – C_6 VOCs have been used to infer latitudinally resolved seasonal changes in OH concentrations,¹²⁴ and it is likely that isotopic information would be of use to improve those estimates.

All of the published measurements for isotopic composition of atmospheric VOCs have focused on the C isotopes. Given the capabilities of commercially available instrumentation for also measuring H, N, or O in continuous-flow mode following chromatographic separation, there is an opportunity for significant further development in the measurement of isotopes for other elements in VOCs. Combinations of isotopes, such as C, H, O, N, Cl, or Br, would likely provide additional constraints on source or sink apportionment. Application of this multi-element isotope approach has thus far been restricted to less reactive trace gases. Schoell¹²⁵ demonstrated that D/H ratios can be used to verify suspected bacterial sources of methane in natural gas reservoirs determined from $^{13}\text{C}/^{12}\text{C}$ ratios. In the atmosphere, both

D/H and $^{13}\text{C}/^{12}\text{C}$ ratios have been successfully used as independent tracers of the methane budget.^{126–128} Thus, the carbon and hydrogen data can provide useful complementary information when investigated simultaneously.

The most likely non-carbon candidate element for immediate further isotopic study in atmospheric VOCs is hydrogen. Much larger differences between various source signatures or loss KIEs would be expected in hydrogen isotopic signatures as compared to those of larger atomic weight elements (i.e., N or Cl), as discussed in section 1.3. It should be noted that current measurement precision limitations on hydrogen isotopes are at best 1–2‰,^{50,113} and larger samples may be required compared to those used for studies on carbon. Assuming that differences between source signatures or sink KIEs are large compared to this precision, combining carbon and hydrogen isotope information should result in useful data for distinguishing between the various VOC cycling processes.

Similarly, intramolecular isotope distributions may provide another layer of information for elucidating VOCs cycling processes. This technique has been applied to the study of atmospheric N_2O ,^{129,130} but no published work has addressed intramolecular isotope distributions in atmospheric VOCs.

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9. Appendix

Data shown in Figures 2–5 were obtained from the identified references using information in tables when available, or directly from figures when necessary. The definition of a treatment, or grouping of data, was taken from the original authors where possible, and thus the representation of data from all references could not be treated consistently. For example, in biomass burning experiments, data shown may represent different burning stages, such as flaming and smoldering, and a range of biomass types burned. However, all atmospheric measurements were taken as individual treatments due to the potential for high temporal and spatial variability. Similarly, all field sample replicates in VOC biodegradation studies were taken individually, and laboratory cultures of different species were taken as separate treatments, but replicate laboratory cultures of a given species were averaged. The average values reported for each treatment were represented in our figures, while errors or precision measurements, such as standard deviations, were not included. The number of resulting data points is presented on the figures, along with the averages,

medians, standard deviations, and 25th and 75th percentiles of the treatments. If information was reported in the references not as original data, but as a mean and standard deviation of multiple treatments, we also report the data as such.

These figures were created with the goal of providing a concise but representative summary of the available isotopic data for atmospheric VOC and to highlight areas in need of further research. As expected, summarizing the data produces results with tight deviations around the average values and evenly distributed percentiles with a median near the average when numerous similar treatments were reported. However, there are other cases where our methodology of bulking data minimizes the presentation of information contained in the original data. Thus, we recommend that the reader should always return to the original references for detailed descriptions and analysis of measurements before using this dataset.

10. References

- (1) Rudolph, J.; Lowe, D. C.; Martin, R. J.; Clarkson, T. S. *Geophys. Res. Lett.* **1997**, *24*, 659.
- (2) Rudolph, J.; Czuba, E. *Geophys. Res. Lett.* **2000**, *27*, 3865.
- (3) Saito, T.; Tsunogai, U.; Kawamura, K.; Nakatsuka, T.; Yoshida, N. *J. Geophys. Res., [Atmos.]* **2002**, *107*, 10.1029/2000JD000127.
- (4) McCauley, S. E.; Goldstein, A. H.; DePaolo, D. J. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 10006.
- (5) Thompson, A. E.; Anderson, R. S.; Rudolph, J.; Huang, L. *Biogeochemistry* **2002**, *60*, 191.
- (6) Johnson, B. J.; Dawson, G. A. *Environ. Sci. Technol.* **1990**, *24*, 898.
- (7) Johnson, B. J.; Dawson, G. A. *J. Atmos. Chem.* **1993**, *17*, 123.
- (8) Sakagawa, H.; Kaplan, I. R. *Geophys. Res. Lett.* **1995**, *22*, 1509.
- (9) Tanner, R. L.; Zielinska, B.; Ubrerna, E.; Harshfield, G.; McNichol, A. P. *J. Geophys. Res., [Atmos.]* **1996**, *101*, 28961.
- (10) Czuba, E. Masters thesis, York University, 1999.
- (11) Tsunogai, U.; Yoshida, N.; Gamo, T. *J. Geophys. Res., [Atmos.]* **1999**, *104*, 16033.
- (12) Glasius, M.; Wessel, S.; Christensen, C. S.; Jacobsen, J. K.; Jorgensen, H. E.; Klitgaard, K. C.; Petersen, L.; Rasmussen, J. K.; Stroyer Hansen, T.; Lohse, C.; Boaretto, E.; Heinemeier, J. *Atmos. Environ., Part A* **2000**, *34*, 2471.
- (13) Glasius, M.; Boel, C.; Bruun, N.; Easa, L. M.; Hornung, P.; Klausen, H. S.; Klitgaard, K. C.; Lindeskov, C.; Moller, C. K.; Nissen, H.; Petersen, A. P. F.; Kleefeld, S.; Boaretto, E.; Hansen, T. S.; Heinemeier, J.; Lohse, C. *J. Geophys. Res., [Atmos.]* **2001**, *106*, 7415.
- (14) Rudolph, J.; Anderson, R. S.; Czapiewski, K. V.; Czuba, E.; Ernst, D.; Gillespie, T.; Huang, L.; Rigby, C.; Thompson, A. E. *J. Atmos. Chem.* **2003**, *44*, 39.
- (15) Currie, L. A.; Klouda, G. A.; Cooper, J. A. *Radiocarbon* **1980**, *22*, 349.
- (16) Larsen, B. R.; Brussol, C.; Kotzias, D.; Veltkamp, T.; Zwaagstra, O.; Slanina, J. *Atmos. Environ., Part A* **1998**, *32*, 1485.
- (17) Klouda, G. A.; Lewis, C. A.; Rasmussen, R. A.; Rhoderick, G. C.; Sams, R. L.; Stevens, R. K.; Currie, L. A.; Donahue, D., J.; Jull, A. J. T.; Seila, R. L. *Environ. Sci. Technol.* **1996**, *30*, 1098.
- (18) Klouda, G. A.; Lewis, C. A.; Stiles, D. C.; Marolf, J. L.; Ellenson, W. D.; Lonneman, W. A. *J. Geophys. Res., [Atmos.]* **2002**, *107*, 10.1029/2001JD000758.
- (19) Conny, J. M.; Currie, L. A. *Atmos. Environ., Part A* **1996**, *30*, 621.
- (20) Fuex, A. N. *J. Geochem. Explor.* **1977**, *7*, 155.
- (21) Brand, W. A. *J. Mass Spectrom.* **1996**, *31*, 225.
- (22) Lichtfouse, E. *Rapid Commun. Mass Spectrom.* **2000**, *14*, 1337.
- (23) Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; Pierce, T.; Scholes, B.; Steinbrecher, R.; Tallamraju, R.; Taylor, J.; Zimmerman, P. B. *J. Geophys. Res., [Atmos.]* **1995**, *100*.
- (24) Fuentes, J. D.; Lerdau, M.; Atkinson, R.; Baldocchi, D.; Bottenheim, J. W.; Ciccioli, P.; Lamb, B.; Geron, C.; Gu, L.; Guenther, A.; Sharkey, T. D.; Stockwell, W. *Bull. Am. Meteor. Soc.* **2000**, *81*, 1537.
- (25) Fehsenfeld, F.; Calvert, J. G.; Fall, R.; Goldan, P.; Guenther, A.; Hewitt, C. N.; Lamb, B.; Liu, S. C.; Trainer, M.; Westberg, H.; Zimmerman, P. B. *Global Biogeochem. Cycles* **1992**, *6*, 389.

- (26) Finlayson-Pitts, B. J.; Pitts, J.; James N. *Chemistry of the Upper and Lower Atmosphere, Theory, Experiments, and Applications*; Academic Press: San Diego, 2000.
- (27) *Reactive Hydrocarbons in the Atmosphere*; Hewitt, C. N., Ed.; Academic Press: San Diego, 1999.
- (28) Singh, H. B.; et al. *J. Geophys. Res.*, [Atmos.] **2000**, *105*, 3795.
- (29) Singh, H. B.; Chen, Y.; Staudt, A.; Jacob, D.; Blake, D.; Heikes, B.; Snow, J. *Nature (London)* **2001**, *410*, 1078.
- (30) Heikes, B. G.; Chang, W.; Pilson, M. E. Q.; Swift, E.; Singh, H. B.; Guenther, A.; Jacob, D. J.; Field, B. D.; Fall, R.; Riemer, D.; Brand, L. *Global Biogeochem. Cycles* **2002**, *16*, 10.1029/2002GB001895.
- (31) Jacob, D.; Field, B. D.; Jin, E.; Bey, I.; Li, Q.; Logan, J. A.; Yantosca, R. M. *J. Geophys. Res.*, [Atmos.] **2002**, *107*, 10.1029/2001JD000694.
- (32) Prinn, R. G.; Weiss, R. F.; Miller, B. R.; Huang, J.; Alyea, F. N.; Cunnold, D. M.; Fraser, P. J.; Hartley, D. E.; Simmons, P. G. *Science (Washington, D.C.)* **1995**, *269*, 187.
- (33) Spivakovskiy, C. M.; Logan, J. A.; Montzka, S. A.; Balkanski, Y. J.; Foreman-Fowler, M.; Jones, D. B. A.; Horowitz, L. W.; Fusco, A. C.; Brenninkmeijer, C. A. M.; Prather, M. J.; Wofsy, S. C.; McElroy, M. B. *J. Geophys. Res.*, [Atmos.] **2000**, *105*, 8931.
- (34) Kurylo, M. J.; Rodriguez, J. M. *Scientific Assessment of Ozone Depletion: 1998*; World Meteorological Organization: Geneva, 1998.
- (35) Craig, H. *Geochim. Cosmochim. Acta* **1957**, *12*, 133.
- (36) Fuchs, G.; Thauer, R.; Ziegler, H.; Stichler, W. *Arch. Microbiol.* **1979**, *120*, 135.
- (37) Games, L. M.; Hayes, J. H.; Gunsalus, R. P. *Geochim. Cosmochim. Acta* **1978**, *42*, 1295.
- (38) Summons, R. E.; Franzmann, P. D.; Nichols, P. D. *Org. Geochem.* **1998**, *28*, 465.
- (39) Craig, H. *Science (Washington, D.C.)* **1961**, *133*, 1833.
- (40) Mariotti, A. *Nature (London)* **1984**, *311*, 251.
- (41) Long, A.; Eastoe, C. H.; Kaufmann, R. S.; Martin, J. G.; Wirt, L.; Finley, J. B. *Geochim. Cosmochim. Acta* **1993**, *57*, 2907.
- (42) Matthews, D. E.; Hayes, J. H. *Anal. Chem.* **1978**, *50*, 1465.
- (43) McKinney, D. R.; McCrea, J. M.; Epstein, S.; Allen, H. A.; Urey, H. C. *Rev. Sci. Instrum.* **1950**, *21*, 724.
- (44) Dumke, I.; Faber, E.; Poggenburg, J. *Anal. Chem.* **1989**, *61*, 1.
- (45) Sano, M.; Yotsui, Y.; Abe, H.; Sasaki, S. *Biomed. Mass Spectrom.* **1976**, *3*, 1.
- (46) Barrie, A.; Bricout, J.; Koziol, J. *Biomed. Mass Spectrom.* **1984**, *11*, 583.
- (47) Ricci, M. P.; Merritt, D. A.; Freeman, K. H.; Hayes, J. H. *Org. Geochem.* **1994**, *21*, 561.
- (48) Hall, J. A.; Barth, J. A. C.; Kalin, R. M. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 1231.
- (49) Greenberg, J. P.; Zimmerman, P. B. *J. Geophys. Res.*, [Atmos.] **1984**, *89*, 4767.
- (50) Hilkert, A. W.; Douthitt, C. B.; Schluter, H. J.; Brand, W. A. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 1226.
- (51) O'Malley, V. P.; Burke, R. A.; Schlotzhauer, W. S. *Org. Geochem.* **1997**, *27*, 567.
- (52) Dias, R. F.; Freeman, K. H. *Anal. Chem.* **1997**, *69*, 944.
- (53) Bishop, R. W.; Valis, R. J. *J. Chromatogr. Sci.* **1990**, *28*, 589.
- (54) de Andrade, J. B.; Tanner, R. L. *Atmos. Environ., Part A* **1992**, *26A*, 819.
- (55) van Warmerdam, E. M.; Frape, S. K.; Aravena, R.; Drimmie, R. J.; Flatt, H.; Cherry, J. A. *Appl. Geochem.* **1995**, *10*, 547.
- (56) Holt, B. D.; Sturchio, N. C.; Abrajano, J.; Teofilio; Heraty, L. J. *Anal. Chem.* **1997**, *69*, 2727.
- (57) Rudolph, J.; Czuba, E.; Huang, L. *J. Geophys. Res.*, [Atmos.] **2000**, *105*, 29329.
- (58) Thompson, A. E.; Rudolph, J.; Rohrer, F.; Stein, O. *J. Geophys. Res.*, [Atmos.] **2003**, *108*, 10.1029/2002JD002883.
- (59) Quay, P. D.; King, S. L.; Stutsman, J.; Wilbur, D. O.; Steele, L. P.; Fung, I.; Gammon, R. H.; Brown, T. A.; Farwell, G. W.; Grootes, P. M.; Schmidt, F. H. *Global Biogeochem. Cycles* **1991**, *5*, 25.
- (60) Chebbi, A.; Carlier, P. *Atmos. Environ.* **1996**, *30*, 4233.
- (61) Yeh, H.-W.; Epstein, S. *Geochim. Cosmochim. Acta* **1981**, *45*, 753.
- (62) Ward, J. A. M.; Ahad, J. M. E.; Lacrampe-Couloume, G.; Slater, G. F.; Edwards, E. A.; Sherwood Lollar, B. *Environ. Sci. Technol.* **2000**, *34*, 4577.
- (63) Gray, J. R.; Lacrampe-Couloume, G.; Gandhi, D.; Scow, K. M.; Wilson, R. D.; Mackay, D. M.; Sherwood Lollar, B. *Environ. Sci. Technol.* **2002**, *36*, 1931.
- (64) Droge, A. T.; Tully, F. P. *J. Phys. Chem.* **1986**, *90*, 1949.
- (65) Droge, A. T.; Tully, F. P. *J. Phys. Chem.* **1986**, *90*, 5937.
- (66) Droge, A. T.; Tully, F. P. *J. Phys. Chem.* **1987**, *91*, 1222.
- (67) Tully, F. P.; Droge, A. T.; Koszykowski, M. L.; Melius, C. F. *J. Phys. Chem.* **1986**, *90*, 691.
- (68) Tully, F. P.; Goldsmith, J. E. M.; Droge, A. T. *J. Phys. Chem.* **1986**, *90*, 5932.
- (69) Tanaka, N.; Rye, D. M. *Nature (London)* **1991**, *353*, 707.
- (70) Singh, H. B.; Zimmerman, P. B. In *Gaseous Pollutants: Characterization and Cycling*; Nriagu, J. O., Ed.; John Wiley & Sons: New York, 1992.
- (71) Des Marais, D. J.; Donchin, J. H.; Nehring, N. L.; Truesdell, A. H. *Nature (London)* **1981**, *292*, 826.
- (72) Yuen, G.; Blair, N.; Des Marais, D. J.; Chang, S. *Nature (London)* **1984**, *307*, 252.
- (73) Berner, U.; Faber, E. *Org. Geochem.* **1988**, *13*, 67.
- (74) Baylis, S. A.; Hall, K.; Jumeau, E. J. *Org. Geochem.* **1994**, *21*, 777.
- (75) Xu, S.; Nakai, S. i.; Wakita, H.; Xu, Y.; Wang, X. *J. Asian Earth Sci.* **1997**, *15*, 89.
- (76) Rowe, D.; Muehlenbachs, K. *Org. Geochem.* **1999**, *30*, 861.
- (77) Harris, S. A.; Whiticar, M. J.; Eek, M. K. *Org. Geochem.* **1999**, *30*, 721.
- (78) Sackett, W. M. *Geochim. Cosmochim. Acta* **1978**, *42*, 571.
- (79) Jenden, P. D.; Kaplan, I. R. *Appl. Geochem.* **1986**, *1*, 631.
- (80) Deines, P. In *Handbook of Environmental Isotope Geochemistry*; Fritz, P., Fontes, J. Ch., Eds.; Elsevier: Amsterdam, 1980; Vol. 1.
- (81) Oremland, R. S.; Des Marais, D. J. *Geochim. Cosmochim. Acta* **1983**, *47*, 2107.
- (82) U.S. EPA Air Quality Trends and Analysis Group. *National Air Quality and Emission Trends Report, 1999*; EPA: Research Triangle Park, NC, 2000.
- (83) Rudolph, J.; Czuba, E.; Norman, A. L.; Huang, L.; Ernst, D. *Atmos. Environ., Part A* **2002**, *36*, 1173.
- (84) Harrington, R. R.; Poulson, S. R.; Drever, J. I.; Colberg, P. J. S.; Kelly, E. F. *Org. Geochem.* **1999**, *30*, 765.
- (85) Harper, D. B.; Kalin, R. M.; Hamilton, J. T. G.; Lamb, C. *Environ. Sci. Technol.* **2001**, *35*, 3616.
- (86) Bill, M.; Miller, L. G.; Goldstein, A. H. *Biogeochemistry* **2002**, *60*, 181.
- (87) Czapiewski, K. V.; Czuba, E.; Huang, L.; Ernst, D.; Norman, A. L.; Koppman, R.; Rudolph, J. *J. Atmos. Chem.* **2002**, *43*, 45.
- (88) Andreae, M. O.; Atlas, E.; Harris, G. W.; Helas, G.; de Kock, A.; Koppman, R.; Maenhaut, W.; Mano, S.; Pollock, W. H.; Rudolph, J. *J. Geophys. Res.*, [Atmos.] **1996**, *101*, 23603.
- (89) Sharkey, T. D.; Loreto, F.; Delwiche, C. F.; Treichel, I. W. *Plant Physiol.* **1991**, *97*, 463.
- (90) Affek, H. P.; Yakir, D. *Plant Physiol.* **2003**, *131*, 1727.
- (91) Kreuzwieser, J.; Graus, M.; Wisthaler, A.; Hansel, A.; Rennenberg, H.; Schnitzler, J. P. *New Phytol.* **2002**, *156*, 171.
- (92) Oremland, R. S.; Whiticar, M. J.; Strohmaier, F. E.; Kiene, R. P. *Geochim. Cosmochim. Acta* **1988**, *52*, 1895.
- (93) Bill, M.; Schuth, C.; Barth, J. A. C.; Kalin, R. M. *Chemosphere* **2001**, *44*, 1281.
- (94) Rhew, R. C.; Miller, B. R.; Weiss, R. F. *Nature (London)* **2000**, *403*, 292.
- (95) Bill, M.; Rhew, R. C.; Weiss, R. F.; Goldstein, A. H. *Geophys. Res. Lett.* **2002**, *29*, 4.
- (96) Kalin, R. M.; Hamilton, J. T. G.; Harper, D. B.; Miller, L. G.; Lamb, C.; Kennedy, J. T.; Downey, A.; McCauley, S. E.; Goldstein, A. H. *Rapid Commun. Mass Spectrom.* **2001**, *15*, 357.
- (97) Lofqvist, J. *Insect Physiol.* **1976**, *22*, 1331.
- (98) Harper, D. B.; Kalin, R. M.; Larkin, M. J.; Hamilton, J. T. G.; Coulter, C. *Environ. Sci. Technol.* **2000**, *34*, 2525.
- (99) Anderson, R. S.; Czuba, E.; Ernst, D.; Huang, L.; Thompson, A. E.; Rudolph, J. *J. Phys. Chem. A* **2003**, *107*, 6191.
- (100) Rust, F.; Stevens, C. M. *Int. J. Chem. Kinet.* **1980**, *12*, 371.
- (101) Cantrell, C. A.; Shetter, R. E.; McDaniel, A. H.; Calvert, J. G.; Davidson, J. A.; Lowe, D. C.; Tyler, S. C.; Cicerone, R. J.; Greenberg, J. P. *J. Geophys. Res.* **1990**, *95*, 22455.
- (102) Saueressig, G.; Crowley, J. N.; Bergamaschi, P.; Bruhl, C.; Brenninkmeijer, C. A. M.; Fischer, H. *J. Geophys. Res.*, [Atmos.] **2001**, *106*, 23127.
- (103) Iannone, R.; Anderson, R. S.; Rudolph, J.; Huang, L.; Ernst, D. *Geophys. Res. Lett.* **2003**, *30*, 10.1029/2003GL017221.
- (104) Lebedew, W. C.; Owsjannikow, G. A.; Mogilevskij, G. A.; Bodganow, W. M. *Angew. Geol.* **1969**, *15*, 621.
- (105) *Brock Biology of Microorganisms*, 9th ed.; Madigan, M. T., Martinko, J. M., Parker, J., Eds.; Prentice-Hall: Upper Saddle River, NJ, 2000.
- (106) Huang, D.-S.; Wu, S.-H.; Wang, Y.-S.; Yu, S. S.-F.; Chan, S. I. *ChemBioChem* **2002**, *3*, 760.
- (107) Stahl, W. *J. Geochim. Cosmochim. Acta* **1980**, *44*, 1903.
- (108) Ahad, J. M. E.; Sherwood Lollar, B.; Edwards, E. A.; Slater, G. F.; Sleep, B. E. *Environ. Sci. Technol.* **2000**, *34*, 4577.
- (109) Meckenstock, R. U.; Morasch, B.; Warthmann, R.; Schink, B.; Annweiler, E.; Michaelis, W.; Richnow, H. H. *Environ. Microbiol.* **1999**, *1*, 409.
- (110) Sherwood Lollar, B.; Slater, G. F.; Ahad, J.; Sleep, B. E.; Spivack, J.; Brennan, M.; MacKenzie, P. *Org. Geochem.* **1999**, *30*, 813.
- (111) Stehmeier, L. G.; Francis, M. M.; Jack, T. R.; Diegor, E.; Winsor, L.; Abrajano, J., T. *Org. Geochem.* **1999**, *30*, 821.
- (112) Morasch, B.; Richnow, H. H.; Schink, B.; Meckenstock, R. U. *Appl. Environ. Microbiol.* **2001**, *67*, 4842.
- (113) Pond, K.; Huang, Y.; Wang, Y.; Kulpa, C. *Environ. Sci. Technol.* **2002**, *36*, 724.
- (114) Miller, L. G.; Kalin, R. M.; McCauley, S. E.; Hamilton, J. T. G.; Harper, D. B.; Millet, D. B.; Oremland, R. S.; Goldstein, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 5833.

- (115) Slater, G. F.; Dempster, H. S.; Sherwood Lollar, B.; Ahad, J. *Environ. Sci. Technol.* **1999**, *33*, 190.
- (116) Huang, L.; Sturchio, N. C.; Abrajano, J., T.; Heraty, L. J.; Holt, B. D. *Org. Geochem.* **1999**, *30*, 777.
- (117) Wang, Y.; Huang, Y. *Org. Geochem.* **2001**, *32*, 991.
- (118) Poulson, S. R.; Drever, J. I.; Colberg, P. J. S. *Chemosphere* **1997**, *35*, 2215.
- (119) McKeen, S. A.; M., T.; Hsie, E.-Y.; Tallamraju, R. K.; Liu, S. C. *J. Geophys. Res., [Atmos.]* **1990**, *95*, 7493.
- (120) McKeen, S. A.; Liu, S. C.; Hsie, E.-Y.; Lin, X.; Bradshaw, J. D.; Smyth, S.; Gregory, G. L.; Blake, D. *J. Geophys. Res., [Atmos.]* **1996**, *101*, 2087.
- (121) Bill, M.; Conrad, M. E.; Goldstein, A. H. *Geophys. Res. Lett.*, in press.
- (122) Anderson, R. S.; Iannone, R.; Rudolph, J.; Thompson, A. E.; Huang, L.; Ernst, D. Presented at the Joint International Symposium on Atmospheric Chemistry within the Earth System, Heraklion, Crete, 2002.
- (123) Gupta, M. L.; McGrath, M. P.; Cicerone, R. J.; Rowland, F. S.; Wolfsberg, M. *Geophys. Res. Lett.* **1997**, *24*, 2761.
- (124) Goldstein, A. H.; Spivakovsky, C. M.; Wofsy, S. C. *J. Geophys. Res., [Atmos.]* **1995**, *100*, 21023.
- (125) Schoell, M. *Geochim. Cosmochim. Acta* **1980**, *44*, 649.
- (126) Quay, P. D.; Stutsman, J.; Wilbur, D. O.; Snover, A.; Dlugokencky, E.; Brown, T. A. *Global Biogeochem. Cycles* **1999**, *13*, 445.
- (127) Bergamaschi, P.; Braunlich, M.; Marik, T.; Brenninkmeijer, C. A. M. *J. Geophys. Res., [Atmos.]* **2000**, *105*, 14531.
- (128) Snover, A.; Quay, P. D.; Hao, W. M. *Global Biogeochem. Cycles* **2000**, *14*, 11.
- (129) Brenninkmeijer, C. A. M.; Rockmann, T. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 2028.
- (130) Yoshida, N.; Toyoda, S. *Nature (London)* **2000**, *405*, 330.

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