The Stable Carbon Isotope Ratio of Biogenic Emissions of Isoprene and the Potential Use of Stable Isotope Ratio Measurements to Study Photochemical Processing of Isoprene in the Atmosphere

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Abstract. A technique was developed that allows the determination of the stable carbon isotope ratio of isoprene in air. The method was used for a limited number of ambient measurements as well as laboratory studies of isoprene emitted from Velvet Bean (*Mucana pruriens L.* var. *utilis*), including the light and temperature dependence.

The mean stable carbon isotope ratio ($\delta^{13}C$) of isoprene emitted from Velvet Bean (*Mucana pruriens L.* var. *utilis*) for all our measurements is –27.7‰ ± 2.0‰ (standard deviation for 23 data points). Our results indicate a small dependence of the stable carbon isotope ratios on leaf temperature and photosynthetic photon flux density (PPFD). The light dependence is 0.0026 ± 0.0012‰/(μmol of photons m^{-2} s^{-1}) for the studied range from 400 to 1700 μmol of photons m^{-2} s^{-1}. The temperature dependence is 0.16 ± 0.09‰/K. On average, the emitted isoprene is 2.6 ± 0.9‰ lighter than the leaf carbon.

An uncertainty analysis of the possibility to use stable carbon isotope ratio measurements of isoprene for estimates of its mean photochemical age suggests that meaningful results can be obtained. This is supported by the results of a small number of measurements of the stable carbon isotope composition of ambient isoprene at different locations. The results range from approximately –29‰ to –16‰. They are consistent with vegetation emissions of isoprene that is slightly depleted in ^{13}C relative to the plant material and enrichment of ^{13}C in the atmosphere due to isotope fractionation associated with the reaction with OH-radicals. The stable carbon isotope ratio of ambient isoprene at locations directly influenced by isoprene emissions is very close to the values we found in our emission studies, whereas at sites located remote from isoprene emitting vegetation we find substantial enrichment of ^{13}C. This suggests that stable carbon isotope ratio measurements will be a valuable, quantitative method to determine the extent of photochemical processing of isoprene in ambient air.

Key words: isoprene, stable carbon isotope ratios, biogenic emissions, ambient measurements, photochemical processing

1. Introduction

Isoprene is one of the most important trace gases in the troposphere. It is the organic trace gas with the highest emission rate into the atmosphere (Pierotti *et al.*, 1990) and its estimated annual emission of 1150 TgC/yr is nearly half of the total global emission rate of all volatile organic compounds (Guenther *et al.*, 1995). Isoprene is an important precursor for ozone and other photo-oxidants and a major player in the odd oxygen (OH, HO_2, RO_2) chemistry of the lower troposphere and thus has a major impact on the self-cleansing capability or oxidation capacity of the atmosphere.

The atmospheric mixing ratio of isoprene exhibits an extremely high spatial and temporal variability, which is the consequence of its short atmospheric residence time and the interaction between varying emission rates, fast atmospheric removal, and the complex transport processes in the lowermost troposphere. It is therefore not surprising that our ability to quantitatively describe and predict atmospheric isoprene mixing ratios is still unsatisfactory. One of the difficulties is the lack of experimental tools that allow differentiating, on the basis of observations, between these processes. During the past years, a number of studies used ratios of concentrations of different hydrocarbons (Parrish *et al.*, 1992; Roberts *et al.*, 1984; McKeen *et al.*, 1990, 1996; McKenna *et al.*, 1995, 1997; Rudolph and Johnen, 1990) or the variance of hydrocarbon concentrations (Jobson *et al.*, 1998, 1999; Ehhalt *et al.*, 1998; Williams *et al.*, 2000) to differentiate between the impact of transport or dilution and of chemical removal reactions. This requires that the emissions of the different hydrocarbons be, at least on average, well correlated. Since isoprene emissions generally are not correlated with emissions of any other volatile organic compounds (VOC) such procedures are not suitable for isoprene. Measurements of typical products formed by photo-oxidation of isoprene, e.g., methyl vinyl ketone, methacrolein, or MPAN allow insight into the impact of photochemical oxidation of isoprene for specific conditions (Montzka *et al.*, 1993, 1995; Williams *et al.*, 1997). Such studies have contributed considerably to a more detailed insight into the atmospheric chemistry of isoprene. Still, due to the different atmospheric lifetimes of the individual compounds and the complex interactions between transport and chemistry, the interpretation of such measurements is complex and not always straightforward.

Isotopic composition measurements have been extremely useful for better understanding the sources, sinks, and distribution of several atmospheric trace gases, e.g., CH_4, CO, and CO_2, (Lowe *et al.*, 1994; Brenninkmeijer *et al.*, 1995). Rudolph *et al.* (1997) describe a technique for compound specific measurements of stable carbon isotope ratios in atmospheric VOC. Very recently it has been shown that carbon isotope ratio measurements allow the calculation of the extent of photochemical processing for individual non-methane hydrocarbons (NMHC) (Rudolph and Czuba, 2000). Studies of man made NMHC in an urban atmosphere (Rudolph *et al.*, 2000) demonstrate that stable carbon isotope ratio measurements allow quantitative estimates of the impact of OH-processing. In this paper we look at the possibility of using stable carbon isotope ratios to study the atmospheric chemistry of isoprene.

2. Experiment

Measurements of rates and stable carbon isotope ratios of emissions of isoprene from Velvet Bean (*Mucana pruriens L.* var. *utilis*) were conducted in flow-through plant and leaf enclosures of 40 dm^3 and 2.5 dm^3 volume in the laboratory. The studied plants were grown in a climate chamber under artificial light at 293/299 K day/night temperatures. The growth chamber is continuously flushed with air from outside the laboratory building. Several series of experiments were conducted at different temperatures and intensities of photosynthetic photon flux density (PPFD). Temperature varied between 293 K and 306 K, PPFD between 440 μmol m^{-2} s^{-1} and 1700 μmol of photons m^{-2} s^{-1}. After each series of experiments the area of the enclosed leaves is measured, for several of the experiments the stable carbon isotope ratio of the leaf material is also determined. The enclosures are continuously flushed with ambient air. Prior to entering the enclosures NMHC are removed from the ambient air by passing it through a heated (670 K) cartridge packed with an oxidation catalyst (Carulite, Carus Chemical Company, Illinois, U.S.A.). Isoprene concentrations in this scrubbed ambient air are below our detection limit of 1 ppt. Carbon dioxide concentration and humidity are monitored at the inlet and outlet of the enclosures. The flow rates are adjusted for each experiment so that the change in carbon dioxide concentration between inlet and outlet of the enclosures is approximately 15 ppm. Flow rates through the leaf enclosure ranged from 4.5 to 8.5 L/min, and for the larger plant enclosure from 30 to 50 L/min. Passing the in-flowing air through a trap at sub-ambient temperature allows control of the humidity in the enclosure. At the outlet of the enclosure pressurized air samples are collected in electropolished stainless steel canisters of 3 dm^3 volume. Sampling flow rate is always kept well below the flow rate of air through the enclosure in order to avoid contamination with laboratory air. Sampling is started after the monitored parameters (air- and leaf temperature, humidity, and carbon dioxide concentrations at in- and outlet) have been stable for at least five minutes. The air samples are analyzed for isoprene concentrations by conventional gas chromatography and for stable carbon isotope ratios by GC-IRMS. Emission rates are calculated from the flow rates through the enclosures, the measured mixing ratios at the outlet of the enclosures, and the area of the enclosed leaves.

In addition to the emission studies, 13 air samples from urban, suburban and rural areas of Canada were analyzed for the concentration and stable carbon isotope ratio of isoprene. These air samples were collected in stainless steel canisters of 3 dm^3 volume at a pressure of approximately 300 kPa. Sampling locations and times are presented in Table I.

Table I. Stable carbon isotope ratio and mixing ratios of isoprene at different locations

Location and season	Mixing ratio,[a] ppb		δ^{13}C,[a] ‰		Mean photochemical age, 10^{10} OH-radicals s cm^{-3}	
Downtown Vancouver[b]	0.03	0.04	–16.8 ± 4.0	–18.5 ± 3.5	1.9 ± 0.8	1.6 ± 0.7
Sub-urban Vancouver[c]	0.36	0.29	–23.3 ± 0.7	–16.2 ± 0.8	0.9 ± 0.4	2.0 ± 0.6
Simcoe[d]	0.30		–24.7 ± 0.2		0.7 ± 0.4	
Rural Victoria Island[e]	2.53		–25.2 ± 0.5		0.6 ± 0.5	
Fraserdale[f]	0.56		–28.8 ± 1.5		1.1 ± 0.5	

[a] If only one or two measurements are available, the results of the individual measurements and their errors are given; otherwise the average and standard deviation are presented.

[b] The samples were collected at 8 p.m. and 8 a.m. Pacific Daylight Saving Time in June 2000.

[c] The samples were collected at 8 p.m. and 3 p.m. Pacific Daylight Saving Time in June 2000.

[d] Average of three measurements made at the Ontario Ministry of the Environment monitoring site at a rural location about 20 km inland from Lake Erie. The samples were collected between 12 p.m. and 1 p.m. Eastern Daylight Saving Time in June 2000. The station is surrounded by farmland; patches of deciduous and coniferous trees cover some 10% of the area.

[e] The sample was collected in a forest clearing over a patch of flowering Scotch broom (*Cytisus scoparius L.*) between 2:15 and 2:30 p.m. Pacific Time on 31 May 2000.

[f] Five measurements at a Meteorological Services of Canada Baseline Air Chemistry Station in northern Ontario. The samples were collected between 10 a.m. and 7 p.m. Eastern Time between May and August, 2000. The station is situated in a mixed boreal forest. Vegetation in the immediate vicinity is white and black spruce, balsam fir, white birch, and aspen.

The method we employed for stable carbon isotope ratio measurements of isoprene in air is derived from the procedure described by Rudolph *et al.* (1997). The method is based on a two-step cryogenic preconcentration procedure followed by gas chromatographic separation, on-line oxidation of the VOC to carbon dioxide and continuous isotope ratio mass spectrometry. Tsunogai *et al.* (1999) used a very similar method for measurements over the Pacific and Japan. However, these papers do not report results for isoprene measurements in the atmosphere, or information on the applicability of the method to isoprene measurements. To our knowledge there are no published methods describing techniques suitable for isotope ratio measurements of isoprene in air samples.

We developed a two-column technique that is optimized for carbon isotope ratio measurements of isoprene in air. Since the method is very similar to that developed by Rudolph *et al.* (1997) we will only briefly describe the procedure and focus on the changes implemented to optimize the isoprene separation. We use a Varian 3600 gas chromatograph equipped with a HP-1 wall coated capillary column (60 m, 0.32 mm i.D., 5 μm film thickness) and a GS-GasPro porous layer open tubular column (60 m, 0.32 mm i.D.). This column combination was used for the emission studies, for the analysis of ambient samples a combination of a Poraplot Q and the HP-1 columns was used. The columns are connected via a zero dead-volume four-way valve (Valco) in a configuration that allows selective transfer from the HP-1 column to the GS-GasPro column. For isoprene measurements the fraction of the effluent from the HP-1 column that contains the isoprene peak is transferred to the GS-GasPro column for separation of isoprene from possible coeluting interferences. The duration of the transfer is 150 s, sufficient to ensure a complete transfer of isoprene even in the case of minor variations in retention time. Carrier gas flow rate for each column is 1.5–1.8 ml/min (He). Flow rate is kept constant by changing the column head pressure as a function of column temperature using a commercial electronic pressure control unit. A second 4-way valve allows transferring the column effluents to either detection system. About 0.3 ml/min of the effluent from the selected column is transferred via a deactivated fused silica capillary to an Ion Trap mass spectrometer for peak identification and verification of peak purity. The remainder of the carrier gas flow enters a commercial (Finnigan MAT) combustion furnace similar to that described by Matthews and Hayes (1978). Water vapour is removed from the sample by passing the effluent of the combustion furnace through a Nafion dryer and about 0.5 ml/min of the dried gas is transferred to the ion source of a Finnigan 252 Isotope Ratio Mass Spectrometer (IRMS). For calibration of the isotope ratio measurements of a reference gas containing carbon dioxide with a $^{13}C/^{12}C$ ratio traceable to Vienna Peedee belemnite (VPDB), the internationally accepted reference point, is added via an open split for 20 s at the beginning and end of each analysis. Results of $^{13}C/^{12}C$ ratio measurements are generally presented as delta values ($\delta^{13}C$), the relative difference between the sample and a reference:

$$\delta^{13}\mathrm{C}(‰) = (c_{13}/c_{12} - {}^{ref}c_{13}/{}^{ref}c_{12})/({}^{ref}c_{13}/{}^{ref}c_{12}) \times 1000\,. \qquad (1)$$

Here c_{13} and c_{12} denote the abundance of the different isotopes in the studied compound and ${}^{ref}c$ in the standard. All results presented in this paper are given relative to VPDB.

Reproducibility of the measurements is derived from repeat analysis of samples and artificial mixtures of isoprene in air. Accuracy of the instrument is determined by analyzing a synthetic air standard containing isoprene and several other hydrocarbons with known stable carbon isotope ratios. This mixture is prepared by a procedure identical to that described for ethane and methyl chloride by Rudolph *et al.* (1997).

The known δ^{13}C value of isoprene in the synthetic mixture is –21.43‰ ± 0.06‰. Eight repeat measurements of samples that contained between 2 ng and 4 ng of isoprene gave an average value of –21.1‰ ± 0.4‰. For samples that contain a few ng of carbon or more we estimate that our measurements have a reproducibility of 0.3 to 0.5‰. Thus the results of the stable carbon isotope ratio measurements of isoprene in the test mixture agree with the known δ^{13}C value within the precision of the method. Similar to the procedure described by Rudolph *et al.* (1997), our method allows enrichment of hydrocarbons from sample volumes of several dm^3. Based on excellent agreement between the result of our analysis and the known stable carbon isotope ratio of the synthetic mixture we estimate that for mixing ratios of approximately 0.1 ppb our stable carbon isotope ratio measurements have a better than ±1‰ accuracy; for isoprene mixing ratios exceeding 0.5 ppb the accuracy is 0.5‰ or better. For mixing ratios below 0.1 ppb the uncertainty of the measurements drastically increases due to a variety of difficulties associated with poor signal to noise ratios for the mass 45 signal of the IRMS.

For the ambient air samples the timing of the column switching is modified to allow analysis of a broader range of compounds. This decreases the selectivity of the separation and thus increases the risk of incomplete separation and overlapping peaks. However, the mass spectra from the ion trap showed no evidence for an overlap of the isoprene peak in the samples analyzed as part of this study.

Hydrocarbon concentrations were determined by established gas chromatographic techniques, McLaren and Singleton (1996) and Rudolph (1999) presented detailed descriptions and evaluations of this method. Detection limit of the concentration measurements is in the range of a few ppt, and the average relative reproducibility is 5% for mixing ratios exceeding 100 ppt.

3. Stable Carbon Isotope Ratios of Isoprene Emitted from Velvet Bean

Figure 1 shows the stable carbon isotope ratio of isoprene emitted from Velvet Bean (*Mucana pruriens L.* var. *utilis*) as function of leaf temperature for different levels of PPFD. The mean δ^{13}C of all 23 measurements is –27.7‰ with a standard deviation of 2.0‰. The results indicate a small, but systematic dependence on both leaf temperature and PPFD. The light dependence is 0.0026 ± 0.0012‰/(μmol of photons m^{-2} s^{-1}) for the studied range between 400 and 1700 μmol of photons

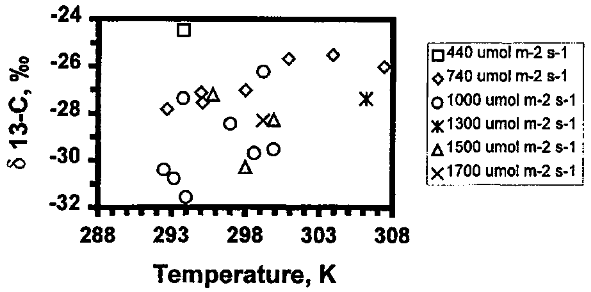

Figure 1. Stable carbon isotope ratio of isoprene emitted from Velvet Bean (*Mucana pruriens L.* var. *utilis*) as function of temperature for different levels of photosynthetic photon flux densities.

m^{-2} s^{-1}. The temperature dependence for the temperature range from 294 K to 307 K is 0.16 ± 0.09‰/K. These dependencies have substantial relative uncertainties. However since these dependencies are very weak, the resulting absolute uncertainties are only small, about 1 to 1.5‰ for the studied temperature and PPFD range. It should be noted that a considerable part of these uncertainties are due to uncertainties in the $\delta^{13}C$ measurements and the generally small variations of the $\delta^{13}C$ values.

For 8 of the 23 measurements the $\delta^{13}C$ value of the leaf carbon was determined. On average, isoprene emitted from the plants is 2.6 ± 0.9‰ lighter than the leaf carbon itself, indicating a small, but significant fractionation specific for the biosynthesis of isoprene. Sharkey *et al.* (1991) conducted laboratory studies of the fractionation of ^{13}C for isoprene emitted from oak leaves relative to the recently photo-synthetically fixed carbon. They found an average decrease in $\delta^{13}C$ of 2.8‰ ± 1.1 (standard deviation from 6 measurements), fully compatible with our findings. Such a small fractionation effect is also compatible with our findings of a very low light and temperature dependence of the stable carbon isotope ratio of isoprene emitted from Velvet Bean (*Mucana pruriens L.* var. *utilis*) (see above).

4. Photochemical Removal of Isoprene in the Atmosphere and Stable Carbon Isotope Ratios

In the atmosphere isoprene rapidly reacts with OH-radicals (k at 298 K is $9.7 * 10^{-11}$ cm^3 $molecules^{-1}$ s^{-1}, Atkinson, 1997). Isoprene also reacts with ozone, however during daytime the loss due to reaction with OH-radicals dominates. For average background conditions (average OH-radical concentration of some 10^6 molecules cm^{-3}, ozone mixing ratio of 30 ppb) approximately 95% of the removal occurs via OH-radical reaction (cf. Martin *et al.*, 1991). In our following discussion we therefore concentrate on OH-reaction as the dominant daytime loss mechanism for atmospheric isoprene.

Since chemical reactions generally are associated with a change in isotope ratios, the removal of atmospheric isoprene by OH-radicals results in a change of the stable carbon isotope ratio. The kinetic isotope effect (KIE) for the reaction of isoprene with OH-radicals is defined as:

$$^{\mathrm{OH}}\mathrm{KIE} = {}^{\mathrm{OH}}k_{12}/{}^{\mathrm{OH}}k_{13}\,. \tag{2}$$

Here $^{\mathrm{OH}}k_{12}$ is the rate constant for reaction of isoprene containing only ^{12}C-atoms with OH-radicals, $^{\mathrm{OH}}k_{13}$ the rate constant for isoprene that contains a ^{13}C-atom. Such fractionation effects are generally very close to 1, and therefore they are often expressed in per mil relative to the reaction rate constant ($^{\mathrm{OH}}\varepsilon_{\mathrm{KIE}}$), similar to stable carbon isotope ratios:

$$\begin{aligned} {}^{\mathrm{OH}}{}_{i}\varepsilon_{\mathrm{KIE}}(‰) &= ({}^{\mathrm{OH}}{}_{i}k_{12} - {}^{\mathrm{OH}}{}_{i}k_{13})/{}^{\mathrm{OH}}{}_{i}k_{13} * 1000 \\ &= ({}^{\mathrm{OH}}{}_{i}k_{12}/{}^{\mathrm{OH}}{}_{i}k_{13} - 1) * 1000\,. \end{aligned} \tag{3}$$

The dependence between removal by OH-radicals and the stable isotope ratio (${}_{i}\delta$) is described by the following equation (Rudolph and Czuba, 2000):

$${}_{i}\delta = ({}^{\mathrm{OH}}{}_{i}k_{12} * [\mathrm{OH}]_{av} * t_{av}) * {}^{\mathrm{OH}}{}_{i}\varepsilon_{\mathrm{KIE}} + {}_{i}\delta^{0} \tag{4}$$

${}_{i}\delta$: Observed stable carbon isotope ratio of isoprene in an air mass,
${}_{i}\delta^{0}$: Stable carbon isotope ratio of isoprene emitted into the atmosphere,
${}^{\mathrm{OH}}{}_{i}k_{12}$: Rate constant for reaction of isoprene with OH-radicals,
${}^{\mathrm{OH}}{}_{i}\varepsilon_{\mathrm{KIE}}$: Kinetic isotope effect or reaction of isoprene with OH-radicals,
$[\mathrm{OH}]_{av}$: Average OH-radical concentration,
t_{av}: Average of the time elapsed between emission and observation.

The extent of chemical processing in an air mass is often referred to as the photochemical age of the air mass (Parrish *et al.*, 1992). In analogy with this terminology we use 'mean photochemical age' for $[\mathrm{OH}]_{av} * t_{av}$. It is important to recognize that the mean photochemical age is a property of the studied compound, not necessarily representative for other NMHC in the studied air mass or the air mass in general (Rudolph and Czuba, 2000). Rearranging (4) gives a simple expression that allows calculating the mean photochemical age of isoprene in an air mass from stable carbon isotope ratio measurements:

$$t_{av} * [\mathrm{OH}]_{av} = (\delta_{i} - {}^{0}\delta_{1})/({}^{\mathrm{OH}}{}_{i}\varepsilon_{\mathrm{KIE}} * {}^{\mathrm{OH}}{}_{i}k_{12})\,. \tag{5}$$

For all realistic atmospheric conditions this value is a true linear average (Rudolph and Czuba, 2000). In other words, $[\mathrm{OH}]_{av} * t_{av}$ is an average property of the studied isoprene in the exact meaning of an average property of a studied population. Equations (4) or (5) are useful descriptions of the dependence between stable carbon isotope ratio and mean photochemical age under the assumption that for the studied air mass the stable carbon isotope ratio of isoprene emissions is known. Consequently variations in the isotopic composition of emitted isoprene will contribute to the uncertainty of the mean photochemical age derived from (5). Furthermore, measurement errors and uncertainties of the parameters needed for the calculations contribute to the overall uncertainty of mean photochemical ages calculated according to (5). Consequently the usefulness of (4) or (5) will critically depend on the variability of source composition relative to the magnitude of the KIE, the uncertainty of the KIE, and the accuracy of the measurements, but also the accuracy of the rate constant for the OH-radical reaction of isoprene is important.

The uncertainty of the photochemical age of isoprene derived from (5) can be determined using Gaussian error propagation:

$$\begin{aligned}\Delta(t_{av} * [\mathrm{OH}]_{av}) \;=\; & \{(\Delta^2\delta_i - \Delta^{20}\delta_i)/({}^{\mathrm{OH}}{}_i\varepsilon_{\mathrm{KIE}} * {}^{\mathrm{OH}}{}_i k_{12})^2 + \\ & + (\Delta^{2\,\mathrm{OH}}{}_i\varepsilon_{\mathrm{KIE}}/{}^{\mathrm{OH}}{}_i\varepsilon^2_{\mathrm{KIE}} + \Delta^{2\,\mathrm{OH}}{}_i k_{12}/{}^{\mathrm{OH}}{}_i k^2_{12}) * \\ & * (t_{av} * [\mathrm{OH}]_{av})^2\}^{1/2}, \end{aligned} \tag{6}$$

where Δ indicates the errors of the values.

The KIE for the reaction of isoprene with OH-radicals is 6.9 ± 0.8‰ (Rudolph *et al.*, 2000). The room temperature (298 K) rate constant for reaction of isoprene with OH-radicals is $9.7 * 10^{-11}$ cm^3 molecules^{-1} s^{-1}; the agreement between recent different determinations of this rate constant is better than 10% (Atkinson, 1997). Our knowledge of the source composition and its variability is still limited. Our results indicate that the variability is only small, but they are based only on a study of one plant species (*Mucana pruriens L.* var. *utilis*) and therefore not necessarily representative. However, as mentioned above, the fractionation between isoprene and recently fixed carbon for oak reported by Sharkey *et al.* (1991) is fully consistent with our observations for Velvet Bean, which suggests that the stable the stable carbon isotope fractionation of isoprene relative to recently fixed carbon is only small, although the sparseness of existing data does not allow firm conclusions. For our error analysis we use an uncertainty for of ±2‰, the standard deviation of all our emission measurements, independent of systematic dependencies on PPFD or temperature. This may underestimate the uncertainty of the source composition due possible variability of the stable carbon isotope composition of isoprene emitted from different plant species. Finally, we assume that ambient measurement can be made with an accuracy of 0.5‰, compatible with the reproducibility of our method.

In Figure 2 the uncertainties are shown as a function of the mean photochemical age of isoprene. Figure 2(a) shows the overall absolute uncertainty as well as the contributions of the individual errors. For mean photochemical ages below $2.5 * 10^{10}$ OH-radicals s cm^{-3} the largest error is due to the uncertainty of the source composition. At longer mean photochemical ages the uncertainties of the rate constant and of the KIE dominate and the uncertainty of the ambient measurements becomes less important. The crucial role of the uncertainty of the source composition is demonstrated in more detail in Figure 2(b), which shows the relative uncertainties of the mean photochemical age for different uncertainties of the source composition. It is evident that for a mean photochemical age of less than $1 * 10^{10}$ OH-radicals s cm^{-3} the uncertainty of the source composition determines

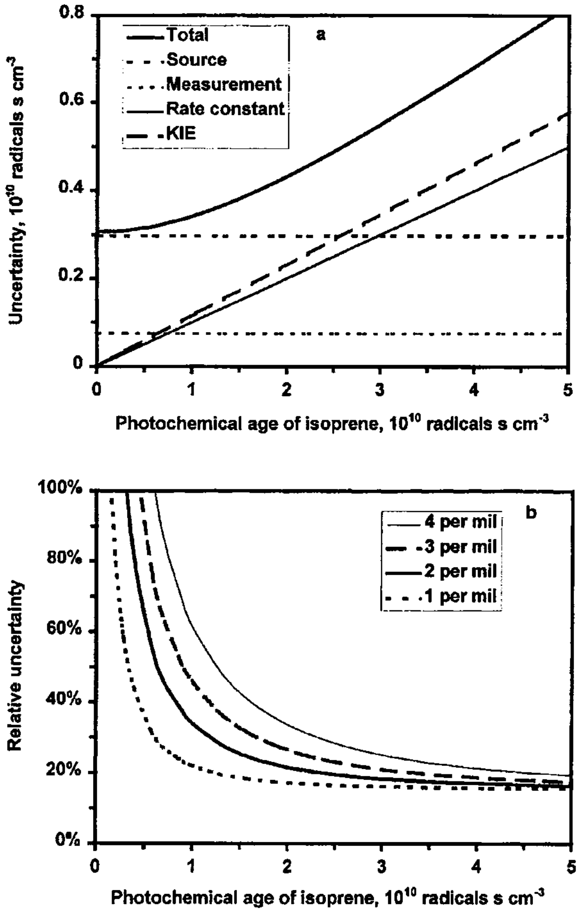

Figure 2. Error of the photochemical age of isoprene determined from stable carbon isotope ratio measurements. (a) Contribution of the different sources of uncertainty to the overall absolute error, details see text. (b) Relative error calculated for different uncertainties of the stable carbon isotope ratio of the isoprene emissions.

whether useful estimates of the mean photochemical age are feasible. E.g. in the case of a 1‰ uncertainty of the source composition an estimate of the mean photochemical age within a 30% error will be possible for a mean photochemical age of $0.5 * 10^{10}$ OH-radicals s cm^{-3}, for a 3‰ source uncertainty the relative error of the mean photochemical age approaches 100%. A mean photochemical age of $1 * 10^{10}$ OH-radicals s cm^{-3} corresponds to the average atmospheric lifetime of isoprene.

Obviously, the corresponding mean physical age can only be determined if the atmospheric OH-radical concentration is known. Based on daytime summer OH-radical concentrations in the range of 10^6 to 10^7 radicals cm^{-3}, the atmospheric lifetime of isoprene will be in the range from 10 minutes to a few hours. Based on the variability of the isotopic composition of isoprene emission in our experiments we estimate that stable carbon isotope ratio measurements may be used to study atmospheric processing of isoprene on timescales as short as 10–15 minutes. However, this is based only on studies of Velvet Bean (*Mucana pruriens L.* var. *utilis*) and it cannot be excluded that the dependence of the stable carbon isotope ratio on environmental conditions is different for other plant species or that variability between different plant species will add to the overall uncertainty.

5. Ambient Measurements

The results of the stable carbon isotope ratio measurements in ambient isoprene are summarized in Table I. Since there are in total only 13 measurements and the number of data points for several locations is too small to derive a representative averages, we will use our results primarily to demonstrate the type of information that can be derived from the stable carbon isotope ratio measurements. The observed stable carbon isotope ratios are consistent with the results of our laboratory emission studies and the concept that atmospheric removal results in enrichment of ^{13}C. All our ambient observations are either within the range observed in our laboratory studies or show enrichment in ^{13}C.

No studies of the stable carbon isotope ratios of isoprene emissions were conducted concurrent to the ambient measurements. Consequently the ambient observations can only be compared to first order estimates of emission compositions derived from laboratory studies. Our laboratory studies give an average of –27.7‰ ± 2‰. Sharkey *et al.* (1991) found an average carbon isotope fractionation of –2.8‰ for isoprene emitted from oak leaves relative to recently fixed carbon, very similar to the fractionation of –2.6‰ that we found for velvet bean (*Mucana pruriens L.* var. *utilis*) (see above). For the region of our studies only plants with a C3 metabolism are relevant as source of isoprene. Based on the average of approximately –27‰ for carbon assimilated by the C3-metabolism, and the variability observed in our laboratory studies, we estimate that the plausible range for isoprene emitted from vegetation is from –27‰ to –32‰.

Based on this estimated isotopic composition of the emissions we used (5) to calculate the mean photochemical age of ambient isoprene and (6) to determine its error. The results are included in Table I.

We can distinguish three groups of observations. The measurements at Fraserdale fully fall into the range of the emission estimates. In this case atmospheric reactions do not have a significant impact on the observed stable carbon isotope ratios. This demonstrates that the observed ambient isoprene levels are predominantly due to local emissions, compatible with the concept of the vegetation surrounding the station being the dominant source (for details of this site see Jobson *et al.*, 1994). Although the uncertainty of the δ^{13}C values of the emissions results in some uncertainty of the photochemical age of isoprene (see above), the observations show that for these observations the relevant transport and dilution processes occur on time scales well below the atmospheric lifetime of isoprene.

Other observations indicate some photochemical processing of the observed isoprene, in the range of $1 * 10^{10}$ OH-radicals s cm^{-3}, corresponding to the average atmospheric residence time of isoprene. Due to the short atmospheric lifetime of isoprene, the variability of the OH-radical concentration, and the complexity of atmospheric transport and mixing processes, we can expect that the extent of processing at a given location will show considerable variability. Indeed, the two measurements in sub-urban Vancouver indicate substantial differences in the mean photochemical age of isoprene, likely due to differences in OH-radical concentrations. This is consistent with the time of sample collection; the sample with the higher mean photochemical age was collected in the afternoon, the other in the evening. The afternoon measurement falls into the group of observations, which show a substantial extent of isoprene processing. Two other observations which indicate substantial processing are from downtown Vancouver. The low isoprene concentrations in these samples indicate only marginal impact from nearby sources, compatible with location and time of day of the measurements. The stable carbon isotope ratios indicate a significant mean photochemical age; compatible with the idea that advection of isoprene from sources at some distance will be the main source for the observed isoprene levels. However a contribution of traffic related emissions to the isoprene levels observed cannot be excluded since isoprene has been reported as a minor component in engine exhaust (McLaren *et al.*, 1996). No studies of the stable carbon isotope ratio of isoprene emissions from traffic, industrial or other civilization related sources are known to us. However, recent studies (Rudolph *et al.*, 2001, Czapiewski *et al.*, 2001) show that the stable carbon isotope ratio of non-methane hydrocarbons emitted from incomplete combustion processes, including traffic related emissions, are very similar to that of the burnt fuel, generally in the range of –25‰ to –30‰, similar to biogenic emissions. Therefore it seems unlikely that the observed stable carbon isotope ratio of isoprene in downtown Vancouver reflect that of isoprene from urban emissions.

Obviously, the extent of processing will depend on site selection and the specific synoptic conditions during sampling. The stable carbon isotope ratio measurements provide us with a possibility to estimate the minimum concentration of isoprene the air mass would have without processing, but undergoing the same transport and dilution processes. This value, ${}_ic_{em}$, can be calculated from the mean photochemical age and the measured isoprene concentration, ${}_ic_m$, assuming a uniform photochemical age for isoprene according to a simple equation.

$${}_ic_{em} = {}_ic_m * \exp(t_{av} * [\mathrm{OH}]_{av}/{}^{\mathrm{OH}}{}_ik_{12} = {}_ic_m * \exp[(\delta_i - {}^0\delta_i)^{\mathrm{OH}}{}_i\delta_{\mathrm{KIE}}] . \quad (7)$$

Since stable carbon isotope ratio measurements only allow calculation of a mean photochemical age, the assumption of a uniform photo-chemical age is not necessarily valid. However, this assumption gives the minimum concentration the air mass would have in the absence of photochemical removal of isoprene. Further-

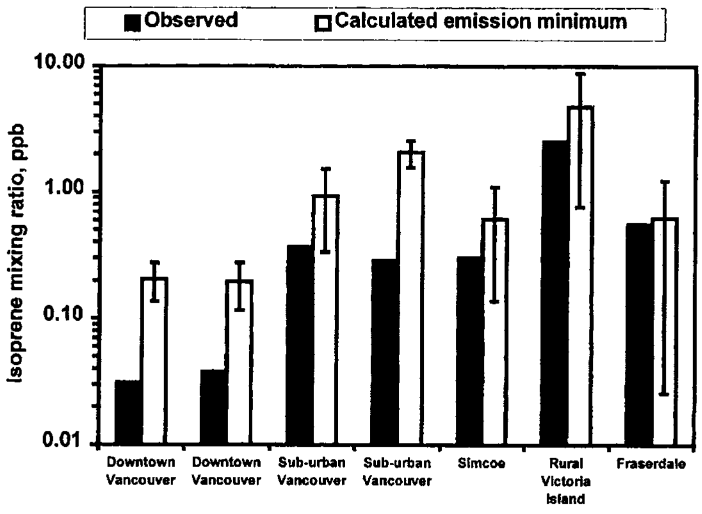

Figure 3. Comparison of measured isoprene concentrations with the minimum recent emission levels calculated according to Equation (7). The error bars indicate the uncertainties due to errors of the mean photochemical age of isoprene.

more, isoprene stable carbon isotope ratio measurements do not provide direct information on processes that occurred on time scales that are very long compared to the atmospheric lifetime of isoprene. Obviously, our calculation only can provide constraints on recent emissions that still have a visible impact on concentration and stable carbon isotope ratio of isoprene in the studied air mass. We therefore will refer to the values calculated according to (7) as recent minimum emission level. Figure 3 compares calculated minimum recent emission levels with measured isoprene concentrations.

For those measurements with low mean photochemical age the minimum recent emission level is similar to the measured concentrations; the measured isoprene concentrations will allow a realistic estimate of the importance of recent isoprene emissions for the chemistry of the studied air mass. In the case of significant photochemical processing, it is obvious that recent isoprene emissions into the studied air mass are larger than one would expect from the concentrations alone. For the downtown Vancouver measurements the minimum recent emissions level is still small, especially if compared to the high mixing ratios of hydrocarbons in the center of major cities. For one of the measurements in a suburban area of the greater Vancouver our result demonstrates the existence of an isoprene source that is sufficiently strong to maintain isoprene levels of several hundred ppt in a substantially aged air mass. To understand the importance for the chemistry of the studied air mass we have to consider the short atmospheric lifetime of isoprene. Due to the high reactivity of isoprene, the products of the photochemical oxidation of isoprene will still have a significant impact on atmospheric chemistry even if a substantial part of the isoprene originally emitted into the air mass already is oxidized, provided the amount of oxidized isoprene is significant. In other words, the mean photochemical age of isoprene derived from the stable carbon isotope ratio can be used as an indicator for the levels of isoprene oxidation products in the studied air mass. E.g. the difference between the two measurements in suburban Vancouver suggests a significantly higher influence of isoprene oxidation products in one of the air masses, although the measured isoprene concentrations are nearly identical. However, it has to be remembered that photochemical age information derived from stable carbon isotope ratios represent an average value. Although the knowledge of such an average can be used to estimate the minimum impact of recent isoprene emissions for the studied air mass (see above), it is not sufficient to reconstruct details of the recent temporal development of the photo oxidation products of isoprene without additional information.

6. Conclusions

Our laboratory studies indicate that the stable carbon isotope ratio of isoprene emitted from Velvet Bean (*Mucana pruriens L.* var. *utilis*) is very close to that of recently fixed carbon. This is fully compatible with stable carbon isotope fractionation observed for oak leaves (Sharkey *et al.*, 1991) but since no such studies for other plant species are known to us extrapolations to other types of vegetation remain uncertain. Nevertheless, the observed ambient stable carbon isotope ratios agree with the assumption that the stable carbon isotope ratio of isoprene emitted from vegetation is close to that of the recently fixed carbon and our understanding of the impact of local isoprene sources on isoprene mixing ratios for the different observation sites. At locations directly impacted by substantial isoprene emissions the ambient stable carbon isotope ratios are close to the composition of the emissions. At sites where local impact is low and observed isoprene is predominantly advected from sources in some distance, isoprene is, relative to the emissions, enriched in ^{13}C. This can be explained by the isotope fractionation associated with the removal of isoprene by reaction with OH-radicals during transport to the observation site. The change in stable carbon isotope ratio of isoprene can be used to determine the extent of photochemical processing of isoprene in the studied air mass.

The information deduced from the change in stable carbon isotope ratio between emission and observation is otherwise not readily available from observations. The stable carbon isotope ratio will predominantly provide insight into atmospheric processing. This additional information is useful for characterizing air masses, testing and improving numerical models and deriving quantitative information on the origin and extent of recent formation of products of the photochemical oxidation of isoprene.

The mean photochemical age derived from ambient isoprene measurements in our study has significant uncertainties. The main source of error is the limited number of studied plant species and the absence of field studies of the stable carbon isotope ratio of isoprene emitted from vegetation. There is some evidence that the stable carbon isotope ratio of isoprene changes for emissions from plants under heavy stress (Sharkey *et al.*, 1991). Furthermore, our study indicates that ambient parameters such as light intensity and leaf temperature to some extent influence the isotopic composition of isoprene emissions. It can be expected that further studies will provide a more detailed understanding of the factors determining the stable carbon ratio of isoprene emissions and thus increase the accuracy of mean photochemical ages calculated from stable carbon isotope ratios.

Finally it should be considered that reaction with the OH-radical is the dominant, but not the only relevant loss reaction for atmospheric isoprene. To some extent also reaction with ozone contributes to the atmospheric removal of isoprene. Since the stable carbon isotope fractionation of this reaction is unknown, this adds additional uncertainty to the stable carbon isotope ratio based estimates of the mean photochemical age of isoprene.

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