Isotopic Composition of Non-Methane Hydrocarbons in Emissions from Biomass Burning

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Abstract. The stable carbon isotope ratios of nonmethane hydrocarbons (NMHC) and methyl chloride emitted from biomass burning were determined by analyzing seven whole air samples collected during different phases of the burning process as part of a laboratory study of wood burning. The average of the stable carbon isotope ratios of emitted alkanes, alkenes and aromatic compounds is identical to that of the burnt fuel; more than 50% of the values are within a range of ±1.5‰ of the composition of the burnt fuel wood. Thus for the majority of NMHC emitted from biomass burning stable carbon isotope ratio of the burnt fuel a good first order approximation for the isotopic composition of the emissions.

Of the more than twenty compounds we studied, only methyl chloride and ethyne differed in stable carbon isotope ratios by more than a few per mil from the composition of the fuel. Ethyne is enriched in ^{13}C by approximately 20–30‰, and most of the variability can be explained by a dependence on flame temperature. The δ^{13}C values decrease by 0.019 ‰/K (±0.0053‰/K) with increasing temperature.

Methyl chloride is highly depleted in ^{13}C, on average by 25‰. However the results cover a wide range of nearly 30‰. Specifically, in two measurements with wood from Eucalyptus (Eucalyptus delegatensis) as fuel we observed the emission of extremely light methyl chloride (–68.5‰ and –65.5‰). This coincides with higher than average emission ratios for methyl chloride (15.5×10^{-5} and 18×10^{-5} mol CH_3Cl/mol CO_2). These high emission ratios are consistent with the high chlorine content of the burnt fuel, although, due to the limited number of measurements, it would be premature to generalize these findings. The limited number of observations also prevents any conclusion on a systematic dependence between chlorine content of the fuel, emission ratios and stable carbon isotope ratio of methyl chloride emissions. However, our results show that a detailed understanding of the emissions of methyl chloride from chloride rich fuels is important for understanding its global budget. It is also evident that the usefulness of stable carbon isotope ratios to constrain the global budget of methyl chloride will be complicated by the very large variability of the stable carbon isotope ratio of biomass burning emissions. Nevertheless, ultimately the large fractionation may provide additional constraints for the contribution of biomass burning emissions to the atmospheric budget of methyl chloride.

Key words: stable carbon isotope ratios, biomass burning, atmospheric emissions, nonmethane hydrocarbons, methyl chloride.

1. Introduction

Isotopic composition measurements have been successfully used to improve our insight into the budgets and the processes determining the distributions of CO, CO_2, CH_4 and other trace gases in the atmosphere (Keeling *et al.*, 1979; Mook *et al.*, 1983; Lowe *et al.*, 1994; Francey *et al.*, 1995; Ciais *et al.*, 1995; Fung *et al.*, 1997) and it can be expected that isotope ratio measurements will be equally useful to study atmospheric volatile organic compounds (VOC). Indeed, in the last few years a number of papers have been published, which study various aspects of the stable carbon isotope composition of atmospheric VOC (Rudolph *et al.*, 1997; Tsunogai *et al.*, 1999; Rudolph and Czuba, 2000; Rudolph *et al.*, 2000; McCauley *et al.*, 1999). Nevertheless, our understanding of the spatial and temporal distribution of the stable carbon isotope ratios of atmospheric VOC, the isotopic composition of VOC emissions and the fractionation associated with atmospheric reactions of VOC is still extremely limited.

On a global scale, biomass burning is one of the most important sources of atmospheric VOC (cf. Andreae, 1991; Lobert *et al.*, 1991; Koppmann *et al.*, 1997). However, there is only one study of the stable carbon isotope ratio of a few selected VOC emitted from biomass burning (Rudolph *et al.*, 1997). To our knowledge no other study of this type has been published. Obviously, this is an extremely unsatisfactory basis for the interpretation or modeling of the stable carbon isotope ratios of VOC in the atmosphere. In this paper we present results from studies of the stable carbon isotope ratios of a number of NMHC emitted from wood burning under controlled conditions in a laboratory.

2. Experiment

Three experiments with two different types of wood were conducted under defined conditions in a laboratory set-up at the Max-Planck-Institute for Chemistry in Mainz, Germany. Details of the experimental set-up are described by Lobert *et al.* (1991). In total 7 samples of the exhaust gas were collected cryogenically in aluminum cylinders of 10-L volume. Samples were integrated over periods from 10 to 45 minutes depending on the duration of the studied stage of the burning processes. The composition of the two types of fuel wood used in the experiments is given in Table I and the main characteristics of the studied fires and the burning conditions during sampling are summarized in Table II.

The samples were analyzed in the laboratory at the Forschungszentrum Jülich, Germany, and at York University, Toronto, Canada, for the concentrations of various VOC as well as for CO, CO_2 and CH_4. The elemental composition (C, H, O, Cl) of the fuel wood was determined at the Forschungszentrum Jülich (Germany) with a commercial elemental analyzer.

The isotopic composition of the VOC was determined by an online GC-IRMS (Finnigan, MAT 252) system at the Meteorological Service of Canada, Environment Canada, Toronto (Ontario). The measurement method is very similar to that

Table I. Elemental and isotopic composition of wood types used for emission studies

Fuel wood	Carbon	Hydrogen	Nitrogen	Chlorine	$\delta^{13}C$
Eucalyptus (Eucalyptus delegatensis)	485 g/kg	62 g/kg	4 g/kg	540 mg/kg	–26.7‰
Musasa (Brachystegia spiciformis)	480 g/kg	61 g/kg	12 g/kg	29 mg/kg	–23.6‰

Table II. Overview of experimental conditions and collected samples for biomass burning experiments

Fire #	Wood	Fuel mass,[a] g	Burning stage[d] (sample identification)	Burnt mass, g[c]	Average temp.,[e] °C	CO/CO_2 %
A	Eucalyptus	1926	Flaming (AF)	1368	379	4.2
			Smoldering (AS)	370	290	12.0
B	**Musasa**	**1268**	**Complete fire (BC)**		489	9.2
			Flaming (BF)		746	7.0
			Smoldering (BS)		494	15.7
C	Musasa	1320[b]	Flaming (CF)	580	708	13.9
			Smoldering (CS)	198	602	6.0

[a] Generally the fuel wood was cut into pieces of about 20 cm length and 2 cm diameter.
[b] Nearly half the total amount of fuel consisted of one single piece.
[c] During experiment B the balance failed, thus no burnt mass data are available.
[d] Based on visual observations during sampling.
[e] Temperature about 10 cm above the surface of the burning material averaged over the sampling period.

described by Rudolph *et al.* (1997) for measurements in ambient air. However, due to the relatively high VOC concentrations and the complex composition of the samples, some modifications were made for the biomass burning samples. Specifically, the sample volume used for analysis is reduced to approximately 100 cm^3 (STP), whereas the procedure described by Rudolph *et al.* (1997) is suitable for sample sizes of several dm^3 (STP).

Prior to enrichment of the VOC from the samples, carbon dioxide is removed by passing the samples at 335 K through a small trap packed with potassium carbonate. Water is trapped at 253 K on the surface of an electro-polished stainless steel tube. The VOC in the samples are enriched cryogenically on a Varian Sample Preconcentrator Trap® (SPT) at 110 K. The trapped VOC are mobilized by rapidly heating (40K/s) the sample loop to 473 K. Subsequently the VOC are separated on a combination of a DB-1 capillary column (60 m, 0.32 mm i.D., 1 μm film thickness) and a GS-GasPro® porous layer open tubular column (60 m, 0.32 mm i.D.). Carrier gas flow rate was 3.9 ml/min (He). Flow rate was kept constant by varying the column head pressure as a function of column temperature using a commercial electronic pressure control unit.

About 0.3 ml/min of the column effluent are 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 interface that converts hydrocarbons to carbon dioxide and water. The design of the interface is very similar to that described by Matthews and Hayes (1978). After removal of water by a Nafion® permeation dryer, about 0.5 ml/min of the carrier gas is transferred via an open split and a fused silica restriction capillary to the ion source of the isotope ratio mass spectrometer (Finnigan MAT 252). For calibration of the isotope ratio measurements a reference gas containing carbon dioxide with a known $^{13}C/^{12}C$ ratio is added via an open split for 20 s at the beginning and end of each analysis. Masses 44 ($^{12}C^{16}O_2$), 45 ($^{13}C^{16}O_2$ and $^{12}C^{17}O^{16}O$) and 46 ($^{12}C^{18}O^{16}O$, $^{13}C^{17}O^{16}O$, $^{12}C^{17}O^{17}O$) are monitored and stored in digitized form for subsequent evaluation of the chromatograms.

The areas of the chromatographic peaks for masses 44, 45 and 46 are integrated using a commercial software package (ISODAT). Peak boundaries and baselines are defined manually. The $^{13}C/^{12}C$ ratio is calculated from the mass 45/44 ratio after applying a small correction for the ^{17}O contribution to mass 45 following the procedure suggested by Santrock *et al.* (1985). Several of the samples were analyzed twice. The reproducibility derived from these repeat measurements is in the range of 0.5‰ to 0.9‰.

All stable carbon isotope ratios are presented as $\delta^{13}C$ in per mil (‰) relative to the Vienna Peedee belemnite reference point (VPDB). The accuracy of the absolute calibration has been tested for several alkanes, alkenes and aromatic compounds by analyzing artificial mixtures of VOC with known stable carbon isotope ratios in air. Based on these tests we estimate that the accuracy of the calibration procedure is better than 0.5‰. However it should be noted that no such tests were made for ethyne or other alkynes. Furthermore, in most samples our stable carbon isotope ratio measurements of ethyne have a larger uncertainty than those of the other compounds due to chromatographic interference from the tailing of a major peak. However, due to the very high ethyne concentrations in the range of 300 nmol/mol to 700 nmol/mol this, most likely, only has a minor impact on the results of our measurements of biomass burning emissions.

The samples were also analyzed for NMHC mixing ratios by established GC-FID methods, closely following the procedure described by McLaren and Singleton, (1996) and Rudolph (1999). The reproducibility of these measurements is in the range of 5%, the estimated accuracy 10% or better.

The isotopic composition of the burnt fuel was determined offline using an established standard technique. Finely ground samples of wood and cleaned CuO and Cu_2O are placed in a quartz tube, evacuated then sealed. At 500 °C the wood carbon is completely converted to CO_2. The isotope ratios of the formed CO_2 are determined by dual-inlet IRMS analysis.

3. Results and Discussion

3.1. ALKANES, ALKENES AND AROMATIC HYDROCARBONS

Stable carbon isotope ratios were determined for approximately 20 VOC. The reason for this limited number of compounds is the need for a complete or nearly-complete separation of the individual components from neighboring peaks. Although the mass spectrometric information from the ion trap allows identifying overlapping peaks, it does not allow retrieving unambiguous isotope ratios from merged peaks. For alkanes, alkenes and aromatics the stable carbon isotope ratios are generally close to that of the burnt wood; the stable carbon isotope ratio of none of these compounds differs by more than 5‰ from that of the fuel. Less than 15% of the measured stable carbon isotope ratios differ by more than 3‰ from that of the fuel, 50% of the measurements are within a range of ±1.5‰. The average of the stable carbon isotope ratios of all alkenes, alkanes and aromatic compounds studied differs by only 0.1‰ ± 0.2‰ from the composition of the fuel. Thus the composition of the parent fuel is a good first order approximation for the stable carbon isotope ratio of many NMHC emitted from wood burning.

On an absolute scale the stable carbon isotope ratio of NMHC emitted from the fires is –26.6‰, very close to the composition of the fuel (–26.7‰). The stable carbon isotope ratios of the alkanes, alkenes and aromatic compounds range from –30.8‰ to –22.4‰, the 10 and 90 percentiles are –29.3‰ and –23.5‰, respectively. Part of the variability is systematic. An example is the difference in stable carbon isotope ratios of NMHC emissions during the flaming and smoldering phase of the fires (Figure 1). Also shown in Figure 1 are the emission ratios of the NMHC relative to carbon dioxide and the stable carbon isotope ratio of the burnt fuel.

The $\delta^{13}C$ values observed during the flaming phase of the Eucalyptus fire are generally higher than those found during the smoldering phase. On average the difference is 2.3‰ with a standard deviation of 0.8‰. There are also significant differences in the stable carbon isotope ratios between different compounds, e.g., ethene and 1,3-butadiene are about 3–5‰ heavier than propane and n-butane.

Very similar differences between flaming and smoldering phase are found for all studied fires. In Figure 2 we compare the average fractionation occurring during flaming and smoldering combustion. Also included are the results from one sample averaged over a complete fire. However, it should be noted that due to the substantially higher emission ratios of NMHC during smoldering combustion (cf. Figure 1), the composition of this sample is heavily biased towards the smoldering stage. Thus it is not surprising that the stable carbon isotope ratios for this sample are in many aspects similar, although not completely identical, to those found in smoldering combustion samples.

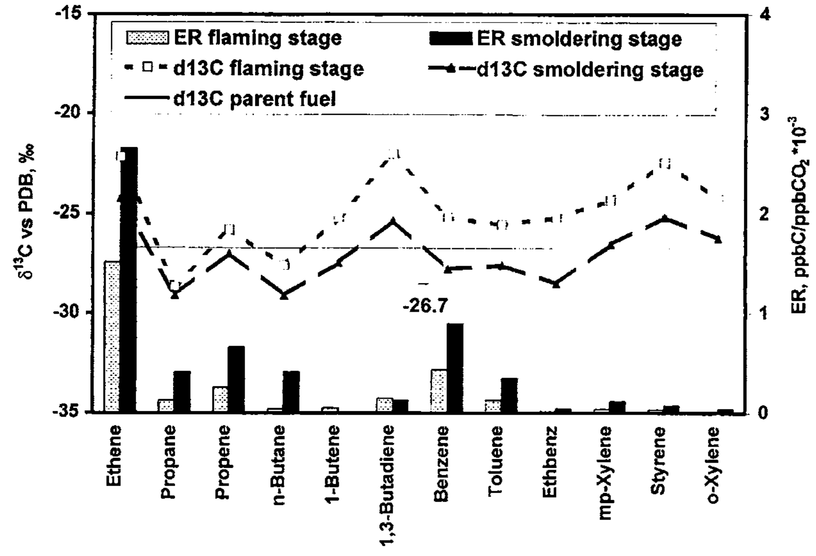

Figure 1. Emission ratios, and isotopic composition of several VOC for Eucalyptus. The horizontal line represents the ^{13}C value of the fuel. The columns represent the emission ratios (ER) relative to CO_2. The diamonds and triangles show $\delta^{13}C$ (‰) for the flaming and smoldering stage, respectively.

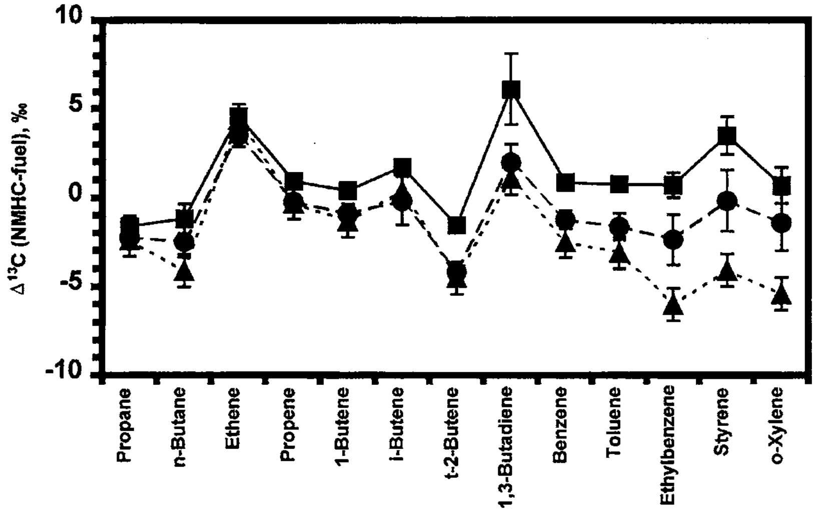

Figure 2. Comparison of average stable carbon isotope fractionation of NMHC emitted during the flaming (squares) and smoldering (circles) stage of three wood fires. Also shown are the results for a sample averaged over a complete fire (triangles).

On average the difference of the stable carbon isotope ratios between smoldering and flaming combustion is 2.2 ± 1‰. However, this difference is compound dependent. For propane and n-butane the difference is only 0.6 ± 0.7‰ and 1.3 ± 1.2‰, respectively, which is lower than the average for all NMHC and not significantly different from zero. Similarly, the differences for ethene, propene and 1-butene are only small, in the range of 1.1–1.3‰.

Isotope fractionation in VOC emitted by biomass burning may be due to two different types of processes; fractionation during the formation of the VOC and isotope dependent removal rates in the flame. Fractionation relative to the bulk composition of the fuel during formation may be caused by two mechanisms. The formation mechanism may be associated with an isotope fractionation process, or the formation of a specific compound may preferentially occur from a precursor substance that differs in $\delta^{13}C$ from the bulk of the material. E.g., lipids in plants are slightly depleted in ^{13}C relative to the average of photosynthetically fixed carbon and therefore we would expect that compounds preferentially formed from pyrolisis or partial oxidation of lipids will be slightly depleted in ^{13}C.

Obviously, this rather complex situation does not allow us to directly associate the stable carbon isotope fractionation for VOC emitted from wood burning with a specific process, especially since most of the observed isotope fractionations are only small (see above). However, to some extent the temperature dependence of the $\delta^{13}C$ in the VOC can provide additional evidence. In general isotope fractionation effects are temperature dependent (cf. Kaplan, 1975). Compounds containing ^{13}C possess lower zero point energies and thus activation energies and enthalpies for reactions involving ^{13}C are generally higher. With increasing temperature the impact of such a difference in activation enthalpy will decrease. Thus we expect that isotope fractionation would be lower at higher temperatures if the isotope fractionation during formation determines the temperature dependence of the stable carbon isotope ratios. However, if the fractionation is due to differences in isotopic composition of the precursor, we would expect no temperature dependence.

Removal of VOC in the flame is in general more efficient at higher temperatures. This is one of the reasons for the lower emission ratios of most VOC in the flaming stage compared to the smoldering phase (cf. Figure 1). For an isotope fractionation due to removal in the flame, the change in the residual NMHC will increase with increasing efficiency of the removal process. Since removal of VOC in flames is more efficient at higher temperature, this can result in a larger change in isotopic composition at higher temperatures. This type of isotope fractionation processes are generally called reservoir effects.

Qualitatively the difference in stable carbon isotope ratios between flaming and smoldering phase suggests a reservoir effect. Figure 3 shows examples of Arrhenius type plots of the observed stable carbon isotope fractionation versus nominal average flame temperature. It should be noted that due to the complex nature of a flame the average temperature at a given position is not identical to a representative spatial average flame temperature. Still, we expect that observations at the same

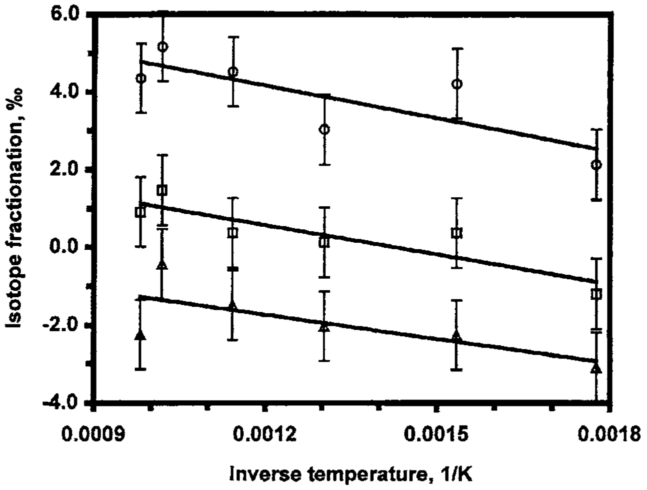

Figure 3. Stable carbon isotope fractionation (δ^{13}C of hydrocarbon minus δ^{13}C of fuel wood) for ethene (circles), propene (squares) and propane (triangles) emitted from wood burning as function of temperature. The solid lines are linear least square fits to the data, the regression parameters are shown in Figure 4.

location will be a reasonable approximation for differences in the average flame temperature between individual fires or burning phases of the same fire.

For most of the NMHC the changes of the stable carbon isotope fractionation during the burning process can, within the uncertainties of the δ^{13}C measurements, be explained by a systematic temperature dependence due to a reservoir effect. However, this dependence is statistically significant only for a limited number of compounds. Figure 4 gives an overview of the temperature dependence of the stable carbon isotope fractionation for the studied NMHC. Also shown are the linear regression coefficients. For the alkanes, alkenes, and aromatic compounds the temperature dependencies are small, with one exception below 10^{-2}‰ K^{-1}. The temperature dependence is nearly always positive, i.e., a significant decrease of δ^{13}C with increasing temperature is not found for any of the alkenes, alkanes or aromatic compounds.

Very little is known about the carbon isotope fractionation associated with reactions of NMHC in flames, but we expect that such removal reactions will be dominated by normal, mass dependent isotope effects and result in an enrichment of ^{13}C containing compounds in the remaining unreacted reservoir. This is supported by results of a very recent study of the kinetic isotope effects (KIE) for reaction of a number of NMHC with OH-radicals (Rudolph *et al.*, 2000). Although these studies were conducted at ambient temperatures all measured KIE showed a preferential reaction for ^{12}C. These findings are consistent with a normal isotope effect for the removal of NMHC by radical chemistry in flames. Thus the observed

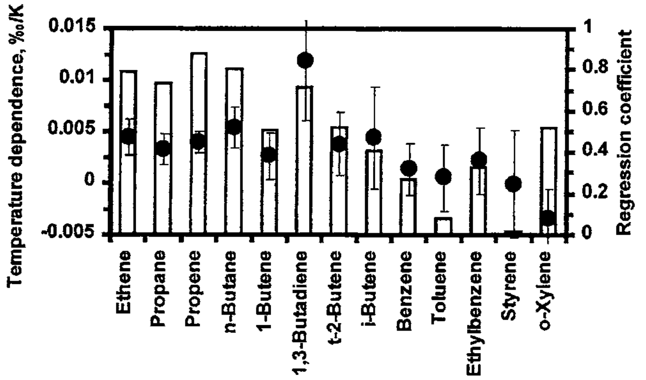

Figure 4. Temperature dependence of stable carbon isotope fractionation of NMHC emitted from wood fires (circles). The error bars represent the 1σ uncertainty. The vertical columns give the linear regression coefficients.

temperature dependence of the stable carbon isotope ratios of alkanes, alkenes, and aromatic compounds emitted from wood burning are consistent with a reservoir effect.

However, not all of the observed stable carbon isotope fractionations can be completely explained by a normal, temperature dependent isotope fractionation during the removal process. At low flame temperature, i.e., in the smoldering stage, propane, n-butane, and t-2-butene are depleted in ^{13}C relative to the fuel wood (Figures 1 and 2). Although these effects are small, the differences are larger than the measurement uncertainties. Similarly, the difference in fractionation between flaming and smoldering combustion for the aromatic hydrocarbons is on average 2.7‰ with a range from 2.1‰ to 3.7‰. Less than 0.8‰ of this variation can be explained by systematic temperature dependence. This points towards the existence of stable carbon isotope fractionation associated with the formation process of the NMHC (see above).

The only other data for stable carbon isotope ratios of NMHC emitted by biomass burning are those published by Rudolph *et al.* (1997). They studied emissions from Manuka, a native New Zealand C3 plant. Their δ^{13}C values for alkanes and alkenes are on average –27‰ ± 2.2‰. The stable carbon isotope ratio in C3 plants is generally in the range of –27‰, thus these values are fully compatible with our findings of only very small fractionation between fuel and emitted alkanes and alkenes. Only for 1-butene did Rudolph *et al.* report a δ^{13}C value that is significantly higher than our results, –6.9‰ ± 0.7‰.

3.2. ETHYNE AND METHYL CHLORIDE

In contrast to alkanes, alkenes and aromatic compounds, the stable carbon isotope fractionation for ethyne and methyl chloride in biomass burning emissions is very

Table III. Emission ratios, isotopic composition and isotopic fractionation for methyl chloride and ethyne. Given are the average values and their standard deviation. Due to experimental problems no isotopic composition could be determined for methyl chloride in sample CF

Samples	CH_3Cl/CO_2 $* 10^5$	$\delta^{13}C_{CH_3Cl}$, ‰	$\Delta^{13}C_{CH_3Cl}$, ‰	Ethyne/CO_2 $* 10^4$	$\delta^{13}C_{C_2H_2}$, ‰	$\Delta^{13}C_{C_2H_2}$, ‰
AF	18.0	-68.5	-41.8	4.7	3.3	30.0
AS	15.9	-65.5	-38.8	5.4	1.6	28.3
BC	0.52	-51.8	-14.7	4.2	7.7	31.3
BF	0.52	-43.9	-20.4	11.9	-3.6	20.0
BS	0.52	-38.3	-14.7	4.9	-2.4	21.2
CF	0.57			9.1	-3.5	20.1
CS	0.37	-42.0	-18.4	6.6	-0.2	23.3
Average	6.0	-51.7	-24.8	10.4	-0.4	24.8
Stdev	8.5	12.7	12.2	10.2	4.1	4.8

substantial (Table III). Relative to the burnt fuel ethyne is on average enriched by about 25‰ (± 5‰) in ^{13}C, methyl chloride on average depleted by 25‰ (±12‰). Furthermore the variability of the fractionation is by far more pronounced than for the other studied VOC. The stable carbon isotope ratios of ethyne emitted from the wood fires vary by 11‰, for methyl chloride the data cover a range of 26‰.

A considerable part of the variation of the stable carbon isotope fractionation of ethyne can be explained by systematic temperature dependence (Figure 5). There are significant differences between ethyne and other NMHC. With -1.9×10^{-2} ‰/K ($\pm 5.3 \times 10^{-3}$ ‰/K) the magnitude of the temperature dependence of the stable carbon isotope fractionation is about a factor of four more pronounced for ethyne than for the other NMHC. Furthermore, in contrast to the other NMHC, the enrichment of ^{13}C in ethyne decreases with increasing temperature. The emission ratios for ethyne relative to carbon dioxide for the flaming phase are higher or similar to those for the smoldering phase (Table IV), the opposite of what is observed for most other NMHC (cf. Figure 1).

These differences between ethyne and other NMHC are compatible with the known formation mechanism for ethyne in flames; the recombination of two CH fragments, whereas the source of most other light NMHC is pyrolysis of larger molecules. The very substantial fractionation effect is compatible with the formation of the strong C–C triple bond during recombination of the CH radicals. We expect a substantial difference in the zero point energies between a ^{12}C–^{12}C and a ^{13}C–^{12}C triple bond. This lower zero point energy of ^{13}C substituted ethyne will result in a higher stability of the additiona-reaction product. This is qualitatively compatible with a stable carbon isotope fractionation resulting in a

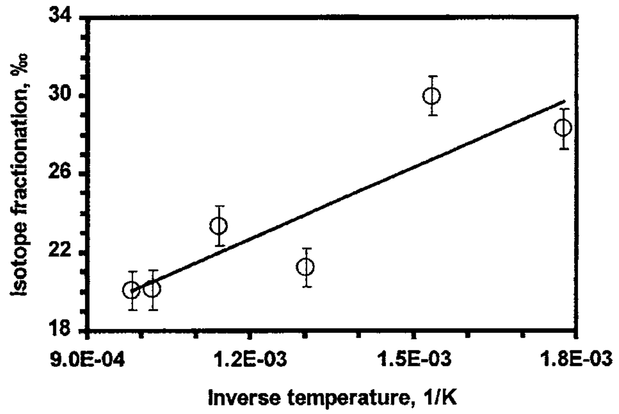

Figure 5. Stable carbon isotope fractionation (δ^{13}C of hydrocarbon minus δ^{13}C of fuel wood) of ethyne emitted from wood burning as function of inverse temperature. The solid line shows a linear least square fit to the data ($R = 0.8751$).

preferential formation of isotopically heavier ethyne. We would also expect that isotope fractionation will be lower at higher temperature, compatible with our findings (Figure 5). Similarly, the stability of ^{13}C–H will be higher than that of ^{12}C–H and consequently may contribute to the isotope fractionation of ethyne formed in burning processes.

Rudolph *et al.* (1997) report a δ^{13}C value of –13‰ ± 1.6‰ for ethyne emitted from biomass burning. The burnt fuel was Manuka, a native New Zealand C3 plant. This value indicates a somewhat lower isotope fractionation for the formation of ethyne in an outdoor fire. A potential explanation may be a higher average flame temperature. Unfortunately no details of the burning process are available for this study. Nevertheless, the results of Rudolph *et al.* (1997) are fully compatible with our findings that ^{13}C in ethyne emitted from biomass burning is significantly enriched compared to the composition of other NMHC emitted by the burning process.

In all our measurements, methyl chloride is significantly depleted relative to the burnt fuel. Moreover, there is no obvious dependence on burning conditions. For individual fires the results suggest that methyl chloride emitted during the smoldering stage of the burn is a few per mil heavier than emissions during flaming combustion. However, there is no statistically significant temperature dependence and the differences in the stable carbon isotope fractionation between different types of fuel wood by far exceed the differences between smoldering and flaming combustion. Methyl chloride emitted from burning of Eucalyptus wood is 20–25‰ lighter than methyl chloride formed by the combustion of Musasa wood.

For Eucalyptus wood as fuel, the emission ratios of methyl chloride relative to carbon dioxide are at the upper end of the data reported in literature (cf. Lobert *et al.*, 1999). They are a factor of approximately 35 higher than for Musasa wood fueled fires (Table II). The chlorine contents of the fuel wood show a similar difference (Table I), which suggests that the chlorine content of the burnt wood has a significant impact on the emission ratios of methyl chloride. Lobert *et al.* (1999) hypothesize that, similar to emissions of nitrogen containing trace gases from biomass burning, the emission ratios for chlorine containing trace gases will depend on the chlorine content of the fuel. However, they present no experimental evidence and we are not aware of any systematic study of the dependence between chlorine content of bio-fuels and methyl chloride emissions. Our observation is experimental evidence supporting this hypothesis, although due the limited number of different types of fuel wood in our study we cannot completely rule out that this observed dependence is a fortuitous coincidence.

In any case, a dependence of methyl chloride emission ratios on chlorine content of the fuel does not directly explain the very high depletion of ^{13}C in methyl chloride emitted from Eucalyptus wood fueled fires. Our results indicate that either the fuel itself or some details of the burning process may have a substantial impact on the stable carbon isotope ratios of methyl chloride emitted. Presently we have no convincing explanation for the substantial fractionation of methyl chloride or for the large variability of the stable carbon isotope fractionation of methyl chloride. Rudolph *et al.* (1997) report a δ^{13}C value of –45.1‰ ± 0.6‰ for methyl chloride emitted from biomass burning. This value is fully compatible with our observations for the burning of Musasa wood. This suggests that the very large depletion of ^{13}C in methyl chloride emitted from Eucalyptus wood fueled fires indeed is unusual. However, due to the extremely limited number of available data we presently cannot decide whether this is systematically related to the high chlorine contents of the fuel or a mere coincidence.

4. Conclusions

Most VOC studied in our experiments have stable carbon isotope ratios very close to that of the burnt fuel wood. This suggests that the stable carbon isotope ratio of fuel wood will be a very useful first order approximation for the composition of NMHC emitted by biomass burning. For many NMHC there are indications for a systematic dependence of their stable carbon isotope composition on flame temperature. However, with very few exceptions, this dependence is only small, very seldom exceeding 0.005 ‰/K. Our results indicate that both the cracking processes responsible for formation of VOC during combustion and the efficiency of the oxidation process in the flame can cause small isotope fractionations.

The observation that the stable carbon isotope ratios of NMHC emitted from wood burning are similar to the composition of the burnt fuel parallels the findings of Rudolph *et al.* (2001, submitted publication). They report that stable carbon isotope ratios of NMHC from petroleum usage related emissions are generally very similar to the average composition of crude oil. This parallel behaviour has significant consequences for the possibility to use stable carbon isotope ratio measurements for constraining the atmospheric budgets of NMHC. The most abundant plants in temperate and boreal regions have, on average, stable carbon isotope ratios in the range of –27‰ (C3-metabolism), and from our results we conclude that biomass burning emissions of NMHC at mid and high latitudes will predominantly have stable carbon isotope ratios in this range. Since on average petroleum has very similar stable carbon isotope ratios in the range of –27‰, we expect that VOC emitted from burning of C3-plant biomass and from petroleum usage will have very similar stable carbon isotope ratios. This may limit the possibility to use stable carbon isotope measurements for source apportionment studies. However, it will reduce uncertainties in the isotopic composition of VOC sources and thus increase the reliability of photochemical age estimates based on isotopic composition measurements (Rudolph and Czuba, 2000).

Nevertheless, the existence of representative average compositions does not imply that all emissions have identical isotopic compositions. Since many VOC have short atmospheric residence times, often less than one day, their isotopic composition will be determined by the composition of local or regional sources. We have very little information on the actual local or regional variability of the stable carbon isotope ratios of VOC emissions. Presently we therefore cannot decide how useful in general stable isotope ratio measurements will be for the identification of specific sources on a local or regional scale. However, in the case of biomass burning we can already identify one potentially very useful application. There is a significant variation in the stable carbon isotope ratio of plant material, depending on the metabolic pathways of carbon fixation. Savanna grasses contain a substantial amount of C4 plants, which on average are enriched by 14‰ in ^{13}C compared to C3-plants. Since savanna fires contribute substantially to biomass burning in some tropical and subtropical regions, we can expect a systematic regional dependence of the stable carbon isotope ratio of VOC emitted from biomass burning. Although this obviously adds complexity to the atmospheric budgets of stable carbon isotope ratios for atmospheric VOC with significant contributions from biomass burning, it also creates a possibility to differentiate between source categories, e.g., savanna burning and forest fires.

In our experiments only two compounds, ethyne and methyl chloride, showed substantial stable carbon isotope fractionation relative to the parent fuel. Ethyne emitted from wood burning is highly enriched in ^{13}C, compatible with the specific formation process of acetylene in flames. This observation is similar to the finding of substantial ^{13}C enrichment in ethyne emitted from transportation related sources (Rudolph *et al.*, 2001, submitted publication). Although internal combustion engines and biomass burning are very different types of burning processes, this qualitatively is compatible with the general idea of a substantial enrichment of ^{13}C in ethyne emitted from incomplete combustion processes.

The most complex behavior is found for methyl chloride. It is not only highly depleted in ^{13}C relative to the parent fuels, the observed δ^{13}C values also span a range of approximately 30‰, with the lowest values close to –70‰ and the highest values around –40‰. The factors determining the stable carbon isotope fractionation of methyl chloride emitted from biomass burning seem to be complex and the limited data presently available do not allow a representative average estimate of the stable carbon isotope ratio of biomass burning derived methyl chloride to be determined. Nevertheless, our findings of a strong depletion of ^{13}C in methyl chloride from biomass burning and its high variability is compatible with the measurements of the stable carbon isotope ratios in the range of –30‰ to –45‰ for atmospheric methyl chloride published by Rudolph *et al.* (1997) and Tsunogai *et al.* (1999). However, these data sets are very limited and not necessarily representative for the whole troposphere.

Unfortunately, very little is known about the fractionation of methyl chloride associated with its atmospheric removal. Miller *et al.* (2001) report that one of the potential removal processes for atmospheric methyl chloride, oxidation by methyltrophic bacteria, is associated with large carbon isotope fractionations. However, by far the most dominant removal mechanism for atmospheric methyl chloride is reaction with OH-radicals, for which, to our knowledge, the KIE has not yet been measured. Still, all measured KIE for reaction of VOC with OH-radicals are positive (Rudolph *et al.*, 2000). It is therefore very unlikely that atmospheric removal of methyl chloride will result in significant depletion of ^{13}C. Consequently it seems plausible that at least one of the major sources of atmospheric methyl chloride has $\delta^{13}C$ values in the range of –40‰ or less. This is consistent with our results for $\delta^{13}C$ of methyl chloride emitted from biomass burning and the substantial contribution of biomass burning to the atmospheric methyl chloride budget (Crutzen *et al.*, 1979; Rudolph *et al.*, 1995). Still, the overall picture is quite complex and the use of stable carbon isotope ratios to constrain the atmospheric budget of methyl chloride will require detailed knowledge of the isotopic composition of methyl chloride emissions and the fractionation associated with its atmospheric loss processes. Based on the substantial fractionation that is found for methyl chloride emitted from biomass burning it is evident that biomass burning will have a strong impact not only on the tropospheric concentration of methyl chloride, but also on its stable carbon isotope ratio. This opens the possibility to use stable carbon isotope ratios of methyl chloride to constrain the contribution of biomass burning to the budget of atmospheric methyl chloride.

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