Stable carbon isotope composition of nonmethane hydrocarbons in emissions from transportation related sources and atmospheric observations in an urban atmosphere

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Abstract

The stable carbon isotope ratios of nonmethane hydrocarbons (NMHC) emitted by traffic related sources are presented. Six sets of samples were collected in the greater Toronto area at locations heavily impacted by engine exhaust, fuel losses and fuel evaporation. Furthermore, two series of measurements were made in a suburban area. The stable isotope ratios of alkanes and arenes in the emission studies are on average −27.7 ± 1.7‰ (relative to Vienna Peedee belemnite, VPDB), fully compatible with the average composition of crude oils. On average alkenes are enriched by 2‰ in ^{13}C relative to alkanes and arenes. The differences between measurements at locations impacted predominantly by specific source types, e.g. tailpipe emissions, fuel evaporation, and losses, seldom are statistically significant and only occasionally exceed 2‰. Ethyne emitted from engine exhaust is enriched in ^{13}C by several tens of per mil relative to other NMHC studied.

The ambient measurements at a suburban location in the greater Toronto area showed that the ambient stable carbon isotope ratios are close to the source composition, but not completely identical. On average ambient NMHC are enriched in ^{13}C relative to the average of the sources by a few per mil. Furthermore, for most NMHC the ambient measurements exhibit a higher overall variability than the source compositions. The small, but nevertheless often significant differences between source composition and ambient observations can be explained by the isotope fractionation associated with the reaction of NMHC with OH-radicals; the most important atmospheric loss process for NMHC. Overall the results demonstrate that for the metropolitan region the variability of the stable carbon isotope ratios of NMHC emitted from traffic related sources is small.

Keywords: Stable carbon isotope ratios; Nonmethane hydrocarbons; Urban emissions; Automotive sources; Ambient measurements

1. Introduction

Isotopic composition measurements have successfully been used to improve our insight into the budgets and the processes determining the distributions of CO, CO_2 and CH_4 and other trace gases in the atmosphere (Mook et al., 1983; Lowe et al., 1994). Very recently, Rudolph et al. (1997) described a method to determine the stable carbon isotope ratios of nonmethane hydrocarbons (NMHC) in the atmosphere, providing the possibility to use isotopic composition measurements to study atmospheric NMHC. Since then a few papers on this subject have been published (Tsunogai et al., 1999; Rudolph and Czuba, 2000; Rudolph et al., 2000; Norman et al., 2000; McCauley et al., 1999) demonstrating that isotopic composition measurements potentially can be extremely valuable to study various important aspects of the atmospheric chemistry of volatile organic compounds (VOC). However, the necessary information needed to interpret atmospheric observations of stable carbon isotope ratios of atmospheric VOC is still extremely limited. Isotope specific information needed for interpretation of atmospheric measurements of stable isotope ratios of VOC is the isotopic signature of the sources, and the fractionation effects associated with removal processes.

Specifically, Rudolph and Czuba (2000) suggest that atmospheric measurements of NMHC stable carbon isotope ratios can be used for the determination of the extent of photochemical processing of individual NMHC. This requires, in addition to atmospheric measurements, knowledge of the kinetic isotope effect (KIE) for reactions of NMHC in the atmosphere and of the average isotopic composition of the relevant sources. Moreover, they demonstrated that the uncertainty of the results of this approach depends on the variability and uncertainty of the isotopic composition of the sources. In a recent study Rudolph et al. (2000) present measurements of the KIE associated with the reaction of OH-radicals with several NMHC. This is the most important atmospheric loss mechanism for these compounds. Although this single study does not provide a complete understanding of kinetic isotope fractionation occurring during removal of NMHC from the atmosphere, an understanding of the magnitude of the KIE and its dependence on chemical structure is slowly emerging. However, our knowledge of the stable carbon isotope ratio of NMHC emissions is extremely limited. Rudolph et al. (2000) present a few average values, but otherwise we know of no published experimental studies of the stable carbon isotope ratios of NMHC emissions.

In this paper we present measurements of the stable carbon isotope ratios of a number of NMHC emitted from transportation related sources, which is, on a global scale, the most important source of NMHC. We will also present results of ambient measurements in a suburban region of Toronto for comparison with the emission studies.

2. Experiment

Six sets of samples were collected at different sites heavily impacted by local sources in the greater Toronto area. The air samples were pressurized to about 3 bar above ambient pressure into stainless steel canisters of 3 l volume, using battery powered Teflon membrane pumps and then transferred to the laboratory for analysis. Each set consisted of 2–5 samples. Two sets (January 1998 and August 1999) were collected in a downtown Toronto tunnel, one near a fuel station (January 1998), two in an underground garage (January 1998 and May 1999), and one very close to a refinery outside the greater Toronto area. Most of these sites are heavily influenced by emissions from internal combustion engines, but at some locations evaporative sources also contribute to the ambient VOC levels.

Furthermore, 25 measurements of stable carbon isotope ratios and concentrations of atmospheric NMHC were made at York University in December 1997 and June 1999. York University is located about 20 km northwest of downtown Toronto in a suburban, mixed industrial/residential area. Details about the sampling location and its characterization are given by McLaren and Singleton (1996). Sample collection was done by the procedure that was used for the source studies.

The isotopic composition of the VOC was determined by an online GC-IRMS (Finnigan, MAT 252) instrument at the Meteorological Service of Canada, Toronto, Canada. The method is very similar to that 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. Therefore a brief description of the method is presented.

Prior to enrichment of the VOC from the air 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. For small sample volumes (several 100 cm^3 or less) the NMHC in the samples are enriched from the air samples in a Varian Sample Preconcentrator Trap® (SPT) at 110 K. For large sample volumes (up to several 1000 cm^3) a two-step enrichment procedure similar to that described by Rudolph et al. (1997) is used. The trapped VOC are mobilized by rapidly heating (40 K/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 ID, 1 μm film thickness) and a GS-GasPro® porous layer open tubular column (60 m, 0.32 mm ID). The carrier gas flow rate is 3.9 ml/min (He). The flow rate is kept constant during the temperature–programmed separation 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 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 passes through 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 ($^{12}C^{18}O^{16}O$) 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 ratios 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 in order to determine the reproducibility of the measurements for realistic sample compositions.

All stable carbon isotope ratios are presented as $\delta^{13}C$ in per mil (‰) relative to the Vienna Peedee belemnite (VPDB) reference point. 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 some samples our stable carbon isotope ratio measurements of ethyne have a larger than usual uncertainty due to chromatographic interference from the tailing of a major peak. The reproducibility of the measurements was derived from the repeat analysis of more than 15 samples. With the exception of ethyne, the reproducibility for all compounds presented here is in the range of 0.5–0.9‰ for source samples, for the ambient samples collected in 1999 between 0.3‰ and 1‰; for the 1997 samples the uncertainties are higher, generally between 0.7‰ and 2‰. Except for ethyne, we could not identify any substance or compound group specific uncertainties. It has been shown that the uncertainty of stable carbon isotope ratio measurements depends to some extent on the available amount of sample (Rudolph et al., 1997), a consequence of the decrease of the signal to noise ratio of the measurements with decreasing signal size. For the source studies this is of minor importance since, due to the high NMHC concentrations in these samples, the reproducibility of the measurements is not noise limited. For some of the ambient measurements the limited amount of sample available for individual compounds resulted in increased uncertainties, but for all measurements presented here the signal to noise ratio is sufficient for a determination of the stable carbon isotope ratio with a better than 2‰ reproducibility.

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). Detection limit of these concentration measurements is in the range of a few ppt, and the average relative reproducibility approximately 5% for mixing ratios exceeding 100 ppt. We estimate that the relative accuracy of the calibration for most of the NMHC is in the range of 10%.

3. Results and discussion

3.1. *Source studies*

The results of our studies in the greater Toronto area are summarized in Table 1. The different sampling sites can be characterized by differences in impact from various source types. The tunnel samples are dominated by tailpipe emissions from cars and trucks at moderate speed, the gas station samples by evaporative and fuel loss emissions, but also by tailpipe emissions. Underground parking samples will be mainly determined by evaporative and cold start losses of gasoline and tailpipe emissions from passenger cars at low velocity. The refinery samples reflect primarily the composition of losses occurring during fossil fuel processing and of the feedstock itself.

The results show that although different source types dominate the sampling locations, the stable carbon isotope ratios exhibit only a small spread. Furthermore, at −27.1‰, the average of the stable carbon isotope ratio of the NMHC is well defined and fully compatible with the isotopic composition expected for crude oil derived compounds. The standard deviation for all emissions is 2.1‰, the error of the mean only 0.2‰. The median value is −27.3‰ with the 90 and 10 percentiles being −24.8‰ and −29.3‰. There are some differences between individual compounds or compound groups, but they are seldom significant. The 90% confidence intervals for most of the values in Table 2 are between 0.8‰ and 1.3‰. This uncertainty is mainly due to measurement errors and the relatively small number of samples in each category.

The only group of compounds that does not completely fit into this pattern is the alkenes. On average they are slightly enriched in ^{13}C. The average of the stable carbon isotope ratios for alkanes and aromatic compounds is −27.7‰ (S.D. 1.7‰, error of mean 0.2‰), slightly lower than the average alkene $\delta^{13}C$ value of −25.3 (S.D. 1.9‰, error of mean 0.4‰). The difference of 2.4‰ is, although relatively small, statistically significant.

Fig. 1 shows the frequency distribution of the stable carbon isotope ratios for alkanes and aromatic compounds. The observed distribution can, within their uncertainties, be described by a Gauss function with a σ of 1.7‰ and a center of −27‰. Also shown in Fig. 1 is

Table 1
Overview of stable carbon isotope ratios (in ‰ relative to VPDB) for NMHC at locations influenced by different types of transport related emissions[a]

Compound	Tunnel Average±S.D.	Gas station Average±S.D.	Underground garage Average±S.D.	Refinery Average±S.D.
Propane	−27.7±0.3		−28.7±1.2	−33.2±2.2
n-Butane	−30.6±1.2		−30.9±0.6	−29.3±0.9
n-Pentane	−28.5±1.2	−28.4±1.0	−29.3±0.7	−27.3±1.0
n-Hexane	−26.3±1.3	−26.6±0.4	−27.3±0.8	−26.5±0.9
n-Heptane	−25.8±0.9	−25.4±1.2	−27.9±1.3	−26.3±0.9
n-Octane	−25.8±2.6	−27.7±1.5	−27.6±0.5	
Cyclopentane	−24.2±1.1	−27.4±0.4	−26.6±0.0	−24.6±0.4
Cyclohexane	−26.7±2.5	−30.8±3.0	−31.8±3.2	−27.1±1.3
i-Butane			−32.0±0.9	−30.5±1.3
i-Pentane	−29.3±0.9	−29.2±1.2	−29.8±0.5	−28.3±1.0
2,2-Dimethylbutane				−28.0±1.8
2,3-Dimethylbutane	−28.5±0.5	−29.9±2.1	−28.5±0.8	−28.4±3.1
2-Methylpentane	−28.4±1.0	−26.8±0.8	−28.2±0.6	−26.9±1.2
3-Methylpentane	−27.6±1.4	−28.2±0.2	−28.4±1.1	−26.9±0.8
2,4-Dimethylpentane	−27.9±1.9	−26.9±2.2	−28.3±0.4	
3-Methylhexane	−26.9±1.0	−25.5±1.3	−27.1±1.0	−26.0±1.4
2,3,4-Trimethylpentane	−27.3±2.0	−22.6±4.1	−25.4±1.0	
Ethene	−22.2±0.7		−25.0±0.9	
Propene	−25.2±0.9		−25.1±1.6	
1-Butene	−26.8±3.1		−23.8±1.0	
t-2-Butene	−26.4±1.7			
1-Pentene	−27.1±1.2	−27.5±1.1	−24.8±0.2	
2-Methyl-1-butene	−26.4±0.7	−28.8±3.6	−26.8±1.1	
t-2-Pentene	−25.3±0.4	−29.2±6.4	−26.1±0.3	
c-2-Pentene	−20.8±1.7	−25.6±4.9	−23.5±0.3	
2-Methyl-2-butene	−23.9±2.4	−26.1±0.3	−25.2±0.7	
Cyclopentene	−23.5±2.6	−24.9±0.8	−25.9±0.7	
1,3-Butadiene	−22.2±1.5			
Benzene	−26.5±1.0	−29.1±0.3	−27.7±0.7	−28.6±0.1
Toluene	−27.5±1.0	−27.4±0.6	−27.1±0.7	−28.4±2.9
Ethylbenzene	−27.4±0.9	−28.2±0.4	−27.5±1.1	
m+*p*-Xylene	−26.9±2.0	−27.7±0.5	−27.7±1.0	
o-Xylene	−27.3±0.4	−27.1±0.6	−27.2±1.1	
n-Propylbenzene	−26.3±1.6	−27.6±0.9	−27.8±0.3	
2-Ethyltoluene	−27.9±0.4	−25.5±0.2	−28.2±0.1	
t-Butylbenzene[b]	−26.9±1.2	−26.7±0.3	−27.4±0.9	
Total average	−26.4±2.1	−27.3±1.7	−27.4±2.0	−27.9±2.0
n-Alkanes	−27.4±1.9	−27.0±1.3	−28.6±1.4	−28.5±2.9
Cyclo and *i*-Alkanes	−27.4±1.5	−27.5±2.5	−28.6±2.1	−27.4±1.7
Alkanes	−27.4±1.9	−27.3±2.1	−28.6±1.8	−27.8±2.1
Alkenes	−24.5±2.2	−27.0±1.8	−25.1±1.0	
Aromatic compounds	−27.1±0.5	−27.4±1.1	−27.6±0.4	

[a] The standard deviations are derived from 3 to 7 measurements.

[b] Tentative identification.

the probability distribution for the δ^{13}C values of alkenes. The maximum of this distribution is slightly shifted towards heavier values. Possible explanations are isotope fractionation during incomplete combustion or a preferred removal of isotopically light alkenes by catalytic converters.

The NMHC content of all our samples is highly elevated compared to ambient levels, e.g. the ethene mixing ratios in the samples range from some 10 nmol/mol to nearly 100 nmol/mol. Nevertheless, it cannot be completely ruled out that ambient air to some extent influences the stable carbon isotope ratios found in the

Table 2
Average and median of the stable carbon isotope ratios from two studies of diurnal cycles of ambient NMHC at York University (Toronto, Canada)[a]

Compound	Summer 99				Winter 97			
	Average ± S.D. (90% confidence interval)	Percentiles			Average ± S.D. (90% confidence interval)	Percentiles		
		Median	90	10		Median	90	10
Propane	−27.1 ± 1.5 (0.6)	−26.5	−25.6	−29.1				
n-Butane	−28.5 ± 1.7 (0.7)	−28.3	−27.1	−30.7				
n-Pentane	−26.9 ± 1.4 (0.6)	−26.8	−25.2	−28.8	−27.5 ± 2.0 (1.0)	−27.3	−25.9	−28.0
n-Hexane	−27.0 ± 2.5 (1.2)	−26.7	−24.7	−30.5	−25.9 ± 2.7 (1.5)	−26.4	−22.5	−28.3
n-Decane	−24.8 ± 3.2 (1.3)	−27.5	−26.4	−28.2	−25.2 ± 2.9 (1.8)	−24.6	−22.7	−28.6
i-Butane	−29.9 ± 2.2 (0.9)	−29.4	−27.6	−32.7				
i-Pentane	−27.7 ± 1.3 (0.9)	−27.2	−26.3	−29.6	−28.0 ± 2.2 (1.0)	−28.4	−27.1	−30.1
2-Methylpentane					−26.0 ± 2.0 (1.0)	−25.7	−24.3	−28.1
3-Methyl hexane					−25.2 ± 4.7 (2.6)	−27.1	−20.5	−29.6
2-Methylheptane[b]	−25.5 ± 2.9 (1.2)	−25.7	−22.7	−28.2				
Ethene	−23.2 ± 3.9 (2.4)	−22.3	−18.9	−27.1				
Propene	−21.6 ± 4.0 (1.6)	−21.9	−17.1	−25.3				
1-Butene	−26.4 ± 1.9 (0.8)	−26.6	−24.1	−28.9				
t-2-Butene[b]	−24.5 ± 6.5 (5.3)	−26.7	−18.3	−29.0				
i-Butene[b]	−23.9 ± 2.3 (1.9)	−24.0	−21.8	−26.0				
Benzene	−24.6 ± 2.3 (0.3)	−24.8	−22.4	−27.3	−23.8 ± 2.5 (1.2)	−23.6	−20.1	−27.0
Toluene	−25.0 ± 1.1 (0.9)	−25.0	−23.7	−26.6	−26.9 ± 0.9 (0.4)	−26.6	−26.0	−27.5
Ethylbenzene	−25.3 ± 2.7 (0.5)	−24.4	−22.9	−29.1	−26.5 ± 3.0 (1.4)	−27.3	−23.9	−29.1
m + *p*-Xylene	−25.6 ± 1.0 (1.1)	−25.6	−24.5	−26.8	−27.4 ± 1.7 (0.8)	−27.2	−25.7	−29.4
o-Xylene	−24.9 ± 1.5 (0.4)	−24.6	−23.9	−26.7	−26.3 ± 3.3 (1.6)	−26.3	−22.4	−29.5
n-Propylbenzene	−23.7 ± 1.9 (0.6)	−23.5	−21.6	−25.6				
Total average	−25.8 ± 3.3 (0.3)	−25.9	−22.3	−29.2	−26.3 ± 2.8 (0.4)	−26.8	−22.3	−29.4
Alkanes	−27.2 ± 2.6 (0.4)	−27.1	−24.6	−30.1	−26.5 ± 2.9 (0.6)	−27.1	−22.3	−29.6
Alkenes	−23.8 ± 4.0 (1.0)	−24.6	−18.9	−28.0				
Aromatic compounds	−24.8 ± 2.7 (0.5)	−24.8	−22.6	−27.1	−26.2 ± 2.7 (0.6)	−26.5	−23.1	−29.3

[a] The stable carbon isotope data are given in per mil relative to VPDB. The data in parentheses following the values for average and median are the standard deviation and the 90% confidence intervals and the 90 and 10 percentiles.

[b] Tentative identification.

source samples. However, as shown by the data presented below, the difference in stable carbon isotope ratios between our source studies and urban ambient samples is only small, generally a few per mil or less. Furthermore, there is no systematic dependence between stable carbon isotope ratios and concentration in our source samples. Thus a significant bias of our observations due to an impact of ambient air seems extremely unlikely.

To our knowledge, there is only one very limited data set that can directly be compared with our measurements of traffic related emissions. Rudolph et al. (1997) present stable carbon isotope ratio measurements of 4 light alkanes and 3 light alkenes in one sample collected in a tunnel in Wellington (New Zealand). Their findings of $\delta^{13}C$ values of −27.3‰ (S.D. 3‰) for alkanes and −23.7‰ (S.D. 1.9‰) for alkenes are fully compatible with our results.

In contrast to alkanes, alkenes and aromatic compounds, there is substantial isotope fractionation for ethyne. Although the data set for $\delta^{13}C$ of ethyne emitted from traffic related sources is very limited it is fully compatible with a substantial enrichment of ^{13}C during formation of ethyne. Measurement of ethyne stable carbon isotope ratios was possible for only 6 of the samples (3 from tunnel, 3 from underground garage). All six measurements show significant enrichment in ^{13}C; most of the values are above zero. There is no statistically significant difference between the two sets of samples.

3.2. Comparison of stable carbon isotope ratios in VOC in urban air with source signatures

Observations made in urban areas in the vicinity of major sources generally are heavily influenced by these

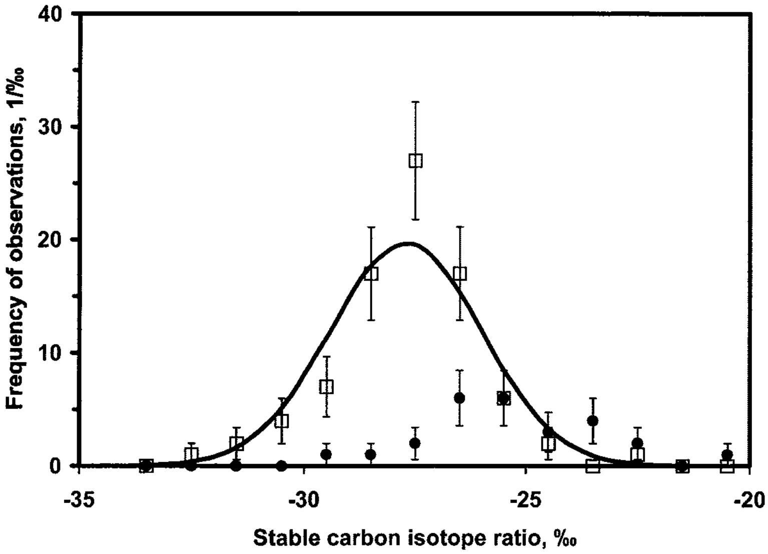

Fig. 1. Frequency distribution for $\delta^{13}C$ of alkanes and aromatic compounds (squares) and alkenes (circles) in samples characteristic for fossil fuel derived emissions. Width of the intervals is 1‰. The error bars are calculated from counting statistics for the given interval. For comparison a Gaussian distribution defined by the mean and standard deviation for all values measured for alkanes and aromatic hydrocarbons is also shown (solid line).

local emissions. We therefore can expect that stable carbon isotope ratio measurements made in such areas will be very similar to those of the emissions. Indeed, at a first glance the results from our ambient measurements at York University (Table 2) are compatible with fossil fuel derived emissions and similar to the results of our source studies (Table 1).

Nevertheless, a closer look shows some variations that require an explanation. On average the stable carbon isotope ratios from our ambient measurements are −25.8‰ with a 90% confidence interval of 0.3‰ and −26.3‰ with a 90% confidence interval of 0.4‰ for 1999 and 1997, respectively. This is at the upper end of the source signatures, which range from −26.4‰ to −27.9‰. The largest fractionations are observed for the alkenes and aromatic compounds in the summer 99 ambient data. With −23.8‰ and −24.8‰, respectively, these values indicate that there is a small, but nevertheless significant difference between sources composition and ambient measurements. Furthermore, the average stable carbon isotope ratios for aromatic compounds differ on average by 1.4‰ between the summer 99 and the winter 97 ambient measurements. This difference is significant on more than a 90% level. In contrast to this the stable carbon isotope ratios for alkanes on average only show a small difference between source composition and ambient values and the difference of 0.7‰ between the two ambient data sets is statistically not significant.

Unfortunately, the number of compounds with data from source studies and both ambient measurement series is limited. Only for the aromatic compounds we have sufficiently complete data for a detailed comparison. For this compound group the differences between average source composition and the mean of the ambient measurements is shown in Fig. 2. On average the ambient measurements of all aromatic compounds are enriched in ^{13}C relative to the sources. For the observations from summer 99 the differences are generally significant, the enrichment in ^{13}C is between 2‰ and 4‰ and uncertainties range around 1‰. For benzene the fractionation determined from the ambient measurements in winter 97 is, within the statistical uncertainties, identical to the findings in summer 99. The alkyl benzenes in the ambient samples from winter 97 are, on average, considerably less enriched in ^{13}C. The enrichments of 0.5–2‰ are statistically not significantly different from zero. Nevertheless, it is very unlikely that the enrichment in ^{13}C for all alkyl benzenes is only a coincidence. Although it cannot be completely ruled out that this is due to a difference in sources sampled in the studies, the more likely explanation is fractionation associated with atmospheric reactions.

The main atmospheric removal process for VOC is the reaction with OH-radicals. Very recently Rudolph et al. (2000) measured the KIE for reaction of several hydrocarbons with OH-radicals and found that OH-reactions always resulted in an enrichment of ^{13}C in the remaining hydrocarbons. This is fully compatible with our observations. Furthermore, Rudolph et al. (2000) found that the KIE for reaction of alkanes with OH-radicals is substantially lower than for alkenes and

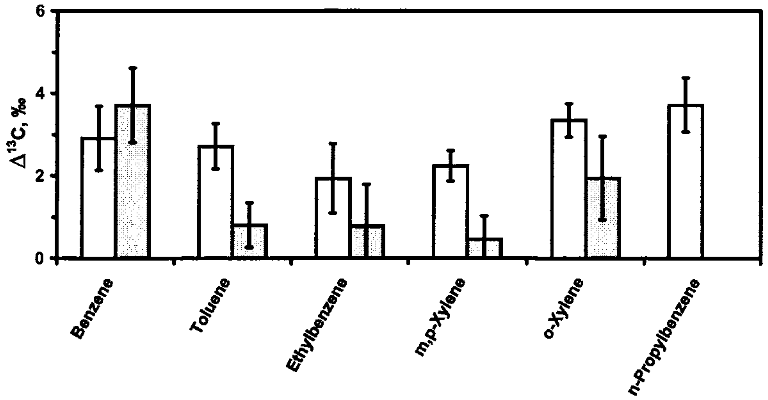

Fig. 2. Difference in $\delta^{13}C$ between average of greater Toronto area source studies and average of ambient observations in winter 97 (shaded bars) and summer 99 (open bars).

aromatic compounds. Again, this is compatible with our finding that changes between source composition and ambient measurements for alkanes are on average lower than for alkenes and aromatic compounds. Finally, the ambient $\delta^{13}C$ values for winter are generally closer to the source composition than for those in summer. The few exceptions, e.g. benzene, are statistically not significant. Qualitatively, this is compatible with smaller OH-radical concentrations in winter, which will result in a slower removal rate and thus a lower fractionation between source and observation.

If removal reactions are sufficiently fast to cause isotope fractionation on a local scale, we can expect that the stable carbon isotope fractionation will to some extent be affected by the diurnal variation of the OH-radical concentration. Since the OH-radical concentration is extremely low or essentially zero at night we expect that during nighttime the $\delta^{13}C$ values of reactive VOC will be closer to the source composition than during daytime and that during daytime the VOC will be somewhat enriched in ^{13}C. Indeed, if we calculate the stable carbon isotope ratios for the nighttime observations (between 11 p.m. and 3 a.m.) for summer 99, we find an average value of −27.4‰; within the uncertainties this is identical to the average values for our source studies. Furthermore, the daytime values (between 9 a.m. and 9 p.m.) in summer are on average by 1.7‰ enriched in ^{13}C. The error of this mean difference is 0.4‰. However, the daytime–nighttime differences for the individual reactive hydrocarbons have substantial uncertainties. For six of the studied compounds the daytime values are on a 2σ significance level heavier than the nighttime measurements. In three cases the significance level exceeds 3σ. Only for *n*-pentane the measurements during nighttime are on average enriched in ^{13}C. However this difference is statistically not significant on the 2σ level. In contrast to the summer measurements, the winter observations give no indication of a systematic day–night change of the stable carbon isotope ratio. The average difference is 0.3‰ with an error of ±0.6‰. It should be noted that the small variations in stable carbon isotope ratios found in ambient air are not necessarily due to the direct influence of chemical processing. Systematic variations in the impact of local or regional sources, e.g. due to diurnal variations of atmospheric stability, will also result in a systematic change in the stable carbon isotope ratios if emitted NMHC and NMHC in background air have different isotopic compositions. However, a detailed study of the relation between atmospheric mixing and stable carbon isotope ratios of NMHC is beyond the scope of this paper.

The number of published studies of the stable carbon isotope ratios of VOC in the urban atmosphere is very limited. Rudolph et al. (1997) measured the stable carbon isotope ratios of some light hydrocarbons at a coastal site close to a major city (Wellington, New Zealand). Tsunogai et al. (1999) presented similar measurements for urban and coastal areas of Japan. This is a very limited data set and conclusions based on such small data sets cannot necessarily be generalized. Nevertheless, a comparison between our results from source studies and ambient observations impacted by local or regional sources will give a better understanding of the representativeness of our findings. In Fig. 3 stable carbon isotope ratios derived from our source studies are compared with urban observations.

In ambient air the light alkanes (C_3–C_5) are slightly enriched in ^{13}C relative to the source values. On average the difference is small, 2.7 ± 0.7‰, but statistically significant. The ambient observations are nearly always higher and never significantly lower than the average of our source studies. The KIEs for reaction of propane and *n*-butane with OH-radicals are known from laboratory studies, they are in the range of 2.5–4‰ (Rudolph et al., 2000). The KIEs for reaction of

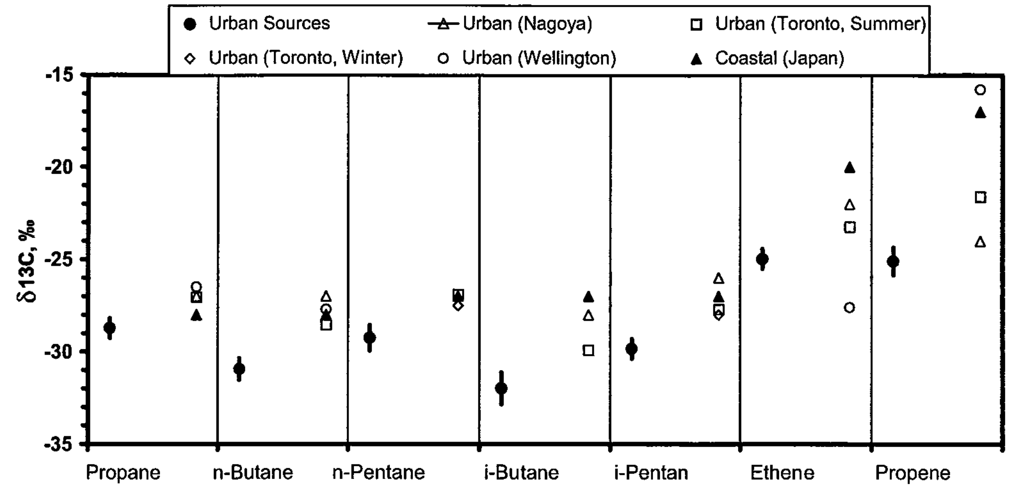

Fig. 3. Comparison of stable carbon isotope ratios of NMHC sources with ambient observations. The value given for man made sources is derived from our source studies in the greater Toronto area and southern Ontario. The error bars indicate the 1σ uncertainty range for all source measurements. The ambient data for Japan are taken from Tsunogai et al. (1999), those for New Zealand from Rudolph et al. (1997).

i-alkanes and *n*-pentane with OH-radicals have not yet been studied, but based on our current understanding of carbon isotope fractionation reactions they most likely will be in the range of 2–5% (Rudolph et al., 2000). Due to these relatively small KIEs, in the case of alkanes we can only expect small fractionation effects for observations influenced by nearby emissions. The stable carbon isotope ratios of crude oil range approximately from −23% to −33‰ (cf. Yeh and Epstein, 1981), with most of the crude oils having δ^{13}C values between −26% and −32%. Thus the δ^{13}C values of alkanes in air impacted by regional sources are fully compatible with emissions having a stable carbon isotope composition close to the average composition of crude oil and a small fractionation due to atmospheric removal. Furthermore, for light alkanes the published ambient δ^{13}C values fall, within the observed scatter, into the range of our observations at York University.

The ambient measurements of ethene and propene show considerably more pronounced variation of the δ^{13}C values and in general ambient alkenes are heavier than the sources. This is fully compatible with their high reactivity and the large KIE for their reaction with OH-radicals (Rudolph et al., 2000).

4. Conclusions

Our studies of traffic related NMHC sources suggest that the stable carbon isotope ratio for compounds is very close to the isotopic composition of the parent fuel. On average these deviations are below 2‰. The only highly significant exception is ethyne, for which substantial enrichment of ^{13}C is observed. The ambient observations in areas strongly impacted by nearby emissions are fully compatible with these findings. Isotope fractionation effects due to atmospheric reactions with OH-radicals can explain the occasional occurrence of small differences between the isotopic compositions of the emission and ambient observations. Still, this does not entirely rule out the emissions of compounds with stable carbon isotope ratios that are significantly different from the composition of the parent material. Indeed, our results for acetylene demonstrate that such cases exist. Furthermore, our studies have been limited to the greater Toronto area and thus we cannot rule out the existence of NMHC sources in other regions with stable carbon isotope ratios that are significantly different from our findings. Specifically, we expect that regional or temporal variations in the stable carbon isotope ratio of fuel result in a corresponding change of the isotopic composition of NMHC emissions. As first approximation this variability should be similar to the variability of the stable carbon isotope ratio of the crude oil that is used as feedstock for fuel production. However, presently there is no experimental evidence that would allow reliably quantifying such variations.

On global average the isotopic composition of crude oil derived fuels is well established and from our results we expect that the average stable carbon isotope ratio for most of the fuel usage derived atmospheric NMHC will be very close to this average. However, the atmospheric residence times of NMHC range from several months to a few hours or less. For NMHC with atmospheric residence times of weeks or more atmospheric mixing and transport will result in substantial averaging, smoothing out many of the possible local variations in the stable carbon isotope ratio of NMHC emissions. However, in the case of short-lived NMHC we expect that atmospheric observations will be strongly impacted by the stable carbon isotope ratios of regional sources.

The kinetic isotope effects for reactions of NMHC with OH-radicals are highly dependent on chemical structure (Rudolph et al., 2000). The KIE for most alkanes is small, comparable in magnitude with the variability of the isotopic composition of NMHC emissions. We expect that for many alkanes the atmospheric stable carbon isotope ratios will maintain a considerable part of the signature of the emissions. The KIE for OH-reactions of alkenes and aromatic compounds is approximately a factor of 5 larger than for alkanes. In this case we expect that atmospheric removal will often have a stronger impact on the stable carbon isotope ratio of these compounds in the atmosphere than the variability of the source composition.

References

Lowe, D.C., Brenninkmeijer, C.A.M., Brailsford, G.W., Lassey, K.R., Gomez, A.J., 1994. Concentration and ^{13}C records of atmospheric methane in New Zealand and Antarctica: evidence for changes in methane sources. Journal of Geophysical Research 99, 16913–16925.

Matthews, D.E., Hayes, A.J., 1978. Isotope ratio monitoring gas chromatography-mass spectrometry. Analytical Chemistry 50, 1465–1473.

McCauley, S.E., Goldstein, A.H., DePaolo, D.J., 1999. An isotopic approach for understanding the CH_3Br budget of the atmosphere. Proceedings of the National Academy of Science, USA 96, 10006–10009.

McLaren, R., Singleton, D.L., 1996. Analysis of motor vehicle sources and their contribution to ambient hydrocarbon distributions at urban sites in Toronto during the Southern Ontario oxidants study. Atmospheric Environment 30, 2219–2232.

Mook, W.G., Koopmans, M., Carter, A.F., Keeling, C.D., 1983. Seasonal latitudinal, and secular variations in the abundance and the isotope ratios of atmospheric carbon dioxide. Journal of Geophysical Research 88, 10915–10933.

Norman, A.L., Ernst, D., Rudolph, J., Blanchard, P., Hopper, J.F., 2000. CF-MS-IRMS: a technique to identify and quantify the source of aerosols and VOCs. Proceedings of the Air and Waste Management Specialty Conference "Recent Advances in the Science and Management of Air Toxics", Banff, Alberta, 10–12 April 2000.

Rudolph, J., 1999. Measurement of nonmethane hydrocarbons in the atmosphere. In: Proceedings of the Workshop on Volatile Organic Compounds in the Troposphere Held in Julich (Germany) from 27–31 October 1997, pp. 11–35.

Rudolph, J., Czuba, E., 2000. On the use of isotopic composition measurements of volatile organic compounds to determine the "photochemical age" of an air mass. Geophysical Research Letters 27, 3865–3868.

Rudolph, J., Lowe, D.C., Martin, R.J., Clarkson, T.S., 1997. A novel method for compound specific determination of δ^{13}C in volatile organic compounds. Geophysical Research Letters 24, 659–662.

Rudolph, J., Czuba, E., Huang, L., 2000. The stable carbon isotope fractionation for reactions of selected hydrocarbons with OH-radicals and its relevance for atmospheric chemistry. Journal of Geophysical Research 105, 29329–29346.

Santrock, J., Studley, S.A., Hayes, J.M., 1985. Isotopic analyses based on the mass spectrum of carbon dioxide. Analytical Chemistry 57, 1444–1448.

Tsunogai, U., Yoshida, N., Gamo, T., 1999. Carbon isotopic composition of C_2–C_5 hydrocarbons and methyl chloride in urban, coastal, and maritime atmospheres over the western North Pacific. Journal of Geophysical Research 104, 16033–16039.

Yeh, H.-W., Epstein, S., 1981. Hydrogen and carbon isotopes of petroleum and related organic matter. Geochimica et Cosmochimica Acta 45, 753–762.