# Carbon isotope analysis for source identification of atmospheric formaldehyde and acetaldehyde in Dinghushan Biosphere Reserve in South China

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## ABSTRACT

Formaldehyde and acetaldehyde are two most abundant carbonyls in ambient air. Biogenic emission has been proposed as a significant source other than anthropogenic emissions and atmospheric secondary formation. Here at a forest site in South China, the carbon isotopic compositions of formaldehyde and acetaldehyde emitted from leaves of three tree species (*Litsea rotundifolia*, *Canarium album* and *Castanea henryi*) were measured in comparison with the bulk carbon isotopic compositions of tree leaves. $\delta^{13}C$ data of the emitted aldehydes (from $-31‰$ to $-46‰$) were quite different for tree species, which were all more depleted in $^{13}C$ than the tree-leaf bulk $\delta^{13}C$ values (from $-27‰$ to $-32‰$). Formaldehyde in ambient air at the forest site had $\delta^{13}C$ values different from those of leaf-emitted formaldehyde, indicating other sources for ambient formaldehyde apart from direct emission from leaves, most probably the photooxidation of biogenic hydrocarbon like isoprene and monoterpene. The $\delta^{13}C$ differences of acetaldehyde between ambient data and those of tree leaves emission were less than 1‰, implying direct biogenic emission as the dominant source.

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## 1. Introduction

Among the oxygenated volatile organic compounds (OVOCs), formaldehyde (HCHO) and acetaldehyde (CH$_3$CHO) are receiving increasing attention as pollutants with potential adverse health effects (Brickus et al., 1998; Gaffney et al., 1997; McLaughlin, 1994; Noisel et al., 2007; Ohura et al., 2006; Timmons et al., 2002), and as ubiquitous components of the background atmosphere at concentrations from low ppbv to sub-ppbv (Brickus et al., 1998; Feng et al., 2004; Gaffney et al., 1997; Grosjean et al., 2002; Ohura et al., 2006). Apart from formation in a variety of important photochemical reactions (Atkinson, 2000; Den Bergh et al., 2004; Kean et al., 2001; Thompson, 1992), they also have direct emissions from anthropogenic (especially auto exhausts) and biogenic source (Fall, 2003; Fracchia et al., 1967; Kean et al., 2001; Martin et al., 1999; Zhang and Smith, 1999). Yet, the relative importance of these sources to their atmospheric budgets is still unclear. Recent estimates suggest that biogenic sources for atmospheric formaldehyde and acetaldehyde are significant and they are the most common low molecular weight carbonyl compounds emitted from some deciduous trees (Fall, 2003; Martin et al., 1999; Rottenberger et al., 2005; Singh

et al., 2001). However, many uncertainties still remain concerning their source strengths, distributions and fates in the atmosphere.

Carbon isotope compositions of atmospheric trace species, e.g. methane (CH$_4$) and non-methane hydrocarbons (NMHCs), have been used to study their budgets and processes (Conny and Currie, 1996; Goldstein and Shaw, 2003; Rudolph et al., 1997). The on-line gas chromatography/combustion/isotope ratio mass spectrometry has been applied to measure the carbon isotopic ratios for atmospheric volatile organic compounds including carbonyls (Goldstein and Shaw, 2003; Johnson and Dawson, 1990; Rudolph et al., 1997; Wen et al., 2005; Yu et al., 2006). These studies indicated that compound specific carbon isotopic analysis could be a powerful tool to complement concentration measurements for the better understanding of their sources and processes.

In previous reports, carbon isotopic compositions of ambient formaldehyde or acetaldehyde in different sites were presented (Johnson and Dawson, 1990; Tanner et al., 1996; Wen et al., 2005), and these results showed that carbon isotope analysis could provide some valuable information for better understanding the sources of aldehyde compounds in ambient air (Johnson and Dawson, 1990; Tanner et al., 1996; Wen et al., 2005). However, no data are available from biogenic emissions. In this paper, three locally familiar tree species in South China are chosen for the carbon isotope measurement of the emitted formaldehyde and acetaldehyde. The study was carried out in Dinghushan Biosphere

Reserve, and the carbon isotopic data of atmospheric formaldehyde and acetaldehyde near the trees were also determined to study their source contribution at such a forest site.

## 2. Experimental

### 2.1. Materials and simulation experiments of sampling

Acetaldehydes (37–40% aqueous solution) were supplied by the Kemiou Chemical Reagent Centre (Tianjin, China) (M1) and Xilong Chemical Factory (Shantou, China) (M2). Chloroform was purchased from Shantou Xilong Chemical Co., Ltd (China) and distilled twice. Cysteamine hydrochloride (97%) was purchased from Fluka (Buchs, Switzerland). Sep-Pak silica gel cartridges (Waters, Millipore Co., USA) were used. Water was double distilled. Sodium bisulfite ($NaHSO_3$) was purchased from United Research Institute of Chengdou (Chengdou, China).

The preparation of $NaHSO_3$-coated Sep-Pak silica gel cartridges and the method for $\delta^{13}C$ measurement of standard acetaldehyde solution were similar to the previous reports (Guo et al., 2007; Wen et al., 2005; Yu et al., 2006). Simulation experiments of sampling were processed to test the carbon isotope fractionation during the air collection and the derivatization process. The experiment was performed using an airtight system, consisted of a sampling pump (Thomas, USA), a $NaHSO_3$-coated sampling cartridge, a ratameter, a three-way-valve, an inlet port and a 100-L Teflon sample bag (SKC Inc.). Simulation experiments for formaldehyde had been done in our previous study (Yu et al., 2006). In this paper, two acetaldehydes with different $\delta^{13}C$ values were used; the typical sampling flow rate was 1.5 L min$^{-1}$. When the concentrations of acetaldehyde were 40 ppb, 200 ppb, 400 ppb, 800 ppb, and 4000 ppb in the simulation experiments (according to our measurements, the range of concentrations for ambient formaldehyde and acetaldehyde was about tens to hundreds of ppb (Feng et al., 2004), in the range of 4000–40 ppb), the respective sampling time was about 4 h, 1.5 h, 1 h, 40 min, 20 min, and the total volume of air for each sampling was about 360 L, 130 L, 90 L, 60 L, and 30 L, respectively, the other operating conditions were the same as that used in simulation experiments of formaldehyde sampling (Yu et al., 2006).

### 2.2. Sampling site description

The sampling site is located on one of main mountaintops of Dinghushan Biosphere Reserve (DHS-BR, 23° 09′ N to 23° 11′ N, and 112° 30′ to 112° 33′ E) with an elevation about 500 m above the sea level in South China. The air sampling was taken on 10–19 December 2006 in the forest of DHS-BR. The DHS-BR is at the southern subtropical edge of South China. It has a southern subtropical monsoon climate and is near the Pacific Ocean to the east and Indian Ocean to the south. The mean annual rainfall of about 1927 mm has a distinct seasonal pattern, with only 6% of its falling from December to February and 75% from March to August (Mo et al., 2003; Yi et al., 2007). The mean annual temperature is about 21.0 °C, ranging from 12.6 °C to 28.0 °C.

The DHS-BR contains three major forest formations: the evergreen broadleaf forest (19%), the mixed pine-evergreen broadleaf forests (44%) and the pine forest (12%) (Mo et al., 2003; Yi et al., 2007). Three familiar tree species indigenous to Dinghushan, including *Litsea rotundifolia*, *Canarium album* and *Castanea henryi* were selected for the collection of formaldehyde and acetaldehyde from leaves. The *L. rotundifolia* and *C. album* are evergreen broadleaf whilst the *C. henryi* is a deciduous tree belonging to families of Lauraceae, Burseraceae and Fagaceae, respectively. Especially, the *L. rotundifolia* is one familiar type of tree species in the mountain forests and suburbs in many provinces in China (e.g. Guangdong

Province, Fujian Province, etc.), and the *C. album* has become familiar for its effect on purifying polluted ambient air and also acts as an ornamental in many cities in China.

### 2.3. Branch enclosure and sample collection

The sample collection in this study was similar to that in previous reports for tree emissions (Martin et al., 1999; Rottenberger et al., 2005). Briefly, a dynamic enclosure system was constructed to collect formaldehyde and acetaldehyde emitted from the tree-leaf using a 100-L Teflon bag (SKC Inc.) modified to slide over target branches and capable of being sealed around the branch with tape or rubber bands (Martin et al., 1999; Rottenberger et al., 2005), and the enclosure volume was less than 35 L in our sampling collection. The branches chosen for collection were enclosed carefully to avoid breaking the leaves, and the branches were about 2 m high. During the period of sampling, the weather was mostly cloudy and the temperature was about 20 °C. All of the branches were shadowed by other taller trees and did not receive direct sunlight in the day. Before each collection, air already existed in the Teflon bag was withdrawn out at a rate of 4 L min$^{-1}$ in order to get rid of carbonyl compounds in it, and the withdrawing time was at least 30 min. Then, purified air without carbonyls and ozone (ambient air was scrubbed via DNPH-coated Sep-Pak silica gel cartridge connected to a potassium iodide (KI) denuder) was introduced at a rate of 1.6 L min$^{-1}$ on one side of the enclosure (Feng et al., 2004; Martin et al., 1999). Simultaneously, the air introduced into the Teflon bag was withdrawn through $NaHSO_3$-coated Sep-Pak silica gel cartridge at a rate of 1.5 L min$^{-1}$ on the opposite side. Previous stability tests showed that no significant degradation occurred for hydrocarbon samples stored at room temperature in the dark for periods up to one week (Martin et al., 1999; Villanueva-Feierro et al., 2004), and our sampling conditions were almost the same to that described above. So, by maintaining a greater introducing rate than withdrawing rate, a positive pressure was obtained within the enclosure to ensure that the compounds sampled were direct plant emissions and not from ambient air or formed via photochemical reactions (Martin et al., 1999).

Especially, when we collected the carbonyls emitted from tree leaves, carbonyls in ambient air at 2 m heights about 1 m away from the test trees were also simultaneously collected to determine their carbon isotopic composition for their data comparison (plant emissions vs. ambient samples). Ambient samples were collected by drawing air with a sampling pump through $NaHSO_3$-coated Sep-Pak silica gel cartridge directly. The typical sampling flow rate was 1.5 L min$^{-1}$. The sampling duration was about 5 h from 10:00 am to 15:00 pm during the daytime, and the respective temperature was ranging from 18 °C to 21 °C. Ambient samples in the nighttime were also collected from 17:30 pm to 8:00 am, and the mean temperature is about 17 °C. After each batch of sampling, sampled cartridges were stored and treated in the laboratory as previous reports (Wen et al., 2005; Yu et al., 2006) before the stable carbon isotopic analysis. Each batch of samples had field blanks that revealed no interference during transport, storage and pretreatment of samples.

In addition, the concentrations of ambient formaldehyde and acetaldehyde were measured by drawing air through silica gel cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) and then analyzed by liquid chromatography in this study (Feng et al., 2004), and the sampling duration of the isotopic and concentration measurements was not the same.

### 2.4. Sample preparation for isotopic analysis

After sampling, the $NaHSO_3$-coated cartridges were processed as described below: the cartridges were eluted with HCl solution (2 mL, pH = 2) into a cuvette (5 mL). The solution was placed in

a water bath at 60 °C for 20 min, and then 20 μL of cysteamine aqueous solution (about 150 μg μL$^{-1}$) were added. The final pH value of the solution was adjusted to 8–9 by adding with about 100 μL of sodium hydroxide solution (200 μg μL$^{-1}$). After 24 h, the solution was extracted three times with chloroform (2 mL) and dried over anhydrous sodium sulfate. The extract was concentrated to about 200 μL using a gentle flow of high-purity $N_2$. Finally, about 1 μL of the concentrated solution with the formed aldehyde–cysteamine adducts was injected for analysis (Guo et al., 2007).

## 2.5. Analytical systems

The $\delta^{13}C$ values of cysteamine hydrochloride and tree leaves were measured using an elemental analyzer/isotope ratio mass spectrometer (EA/IRMS, Thermo Finnigan, Bremen Germany, DEL-TA$^{plus}$XL mass spectrometer). Leaves were dehydrated by liquid $N_2$ and then triturated before analysis. The $\delta^{13}C$ values of acetaldehyde were measured by using an HP6890 GC (Agilent, USA) equipped with an HP-PLOT Q column (30 m × 0.32 mm × 20 μm, Hewlett–Packard, USA) coupled to a combustion furnace and an isotope ratio mass spectrometer (Isoprime, GV Instruments, UK). Details about the analysis for EA/IRMS and GC/C/IRMS were described elsewhere (Guo et al., 2007; Yu et al., 2006).

The $\delta^{13}C$ value of aldehyde–cysteamine derivative was measured by an HP6890 GC system (Agilent, USA) equipped with an HP-5MS column (30 m × 0.32 mm × 0.25 μm, J & W Scientific, USA) coupling to a combustion furnace and an isotope ratio mass spectrometer (Isoprime, GV Instruments, UK). $CO_2$ of known $\delta^{13}C$ value (−26.65‰) was used as the external reference gas. The temperature of the interface between the GC and combustion furnace was set at 200 °C. The combustion furnace containing CuO catalyst and the reduction oven containing Cu catalyst were set at 880 °C and 580 °C, respectively. The other conditions were as follows: the injector temperature was set at 200 °C and splitless model was used; ultrapure helium was used as carrier gas at 1.5 mL min$^{-1}$; the oven temperature programmed was set at 50 °C for 2 min at the start, and then 3 °C min$^{-1}$ to 85 °C. Laboratory isotopic standard contained $C_{12}$, $C_{14}$, $C_{16}$, $C_{18}$, $C_{20}$, $C_{22}$, $C_{25}$, $C_{28}$, $C_{30}$ and $C_{32}$ $n$-alkanes (supplied by Indiana University) with predetermined isotopic values (−31.89‰, −30.67‰, −30.53‰, −31.02‰, −32.24‰, −32.77‰, −28.94‰, −32.11‰, −33.05‰, −29.41‰, respectively) and another laboratory standard GV-mix solution (GV Instruments, UK) contained $C_{10}$, $C_{11}$, $C_{12}$ $n$-alkanes and

a $C_{13}$ compound (methyl decanoate) with $\delta^{13}C$ values of −28.6‰, −26.7‰, −28.6‰ and −30.5‰, respectively, were used for routine analysis to evaluate the accuracy of the GC/C/IRMS system. All $^{13}C/^{12}C$ ratios were expressed in conventional delta ($\delta$) notation, which is the per mil (‰) deviation from the standard Pee Dee Belemnite (PDB).

## 3. Results and discussion

### 3.1. Evaluation of isotopic fractionation during simulation experiments

In this study, $\delta^{13}C$ values of the acetaldehydes from two different suppliers and their respective cysteamine derivatives (collected by sampling cartridges) were determined by GC/C/IRMS (Table 1). The analytical errors (standard deviation) obtained for five GC/C/IRMS analyses of acetaldehyde from the same supplier ranged from 0.05‰ to 0.12‰, and averaged 0.09 ± 0.05‰. Although the acetaldehyde of different concentrations was collected, the derivatization of acetaldehyde from a given supplier was accomplished well, the analytical errors of the derivatives obtained for three GC/C/IRMS analyses were from 0.04‰ to 0.15‰, averaged 0.09 ± 0.04‰. The accuracy of the results was within the technical specifications of the GC/C/IRMS system.

According to the discussion on kinetic isotope effect (Rieley, 1994), if no isotope fractionations occurred during the derivatization process, the carbon isotopic compositions of acetaldehyde, cysteamine and its derivative should comply with the following mass balance equation:

$$\delta^{13}C_{\text{carbonyl-cysteamine derivative}} = f_{\text{carbonyl}}\delta^{13}C_{\text{carbonyl}} + f_{\text{cysteamine}}\delta^{13}C_{\text{cysteamine}} \quad (1)$$

The analytical error of the calculated (or predicted) data for underivatized acetaldehyde (usually expressed as the standard deviation, S), was calculated by the equation listed below:

$$S^2_{\text{carbonyl}} = \left(1/f_{\text{carbonyl}}\right)^2 S^2_{\text{carbonyl-cysteamine derivative}} + \left(f_{\text{cysteamine}}/f_{\text{carbonyl}}\right)^2 S^2_{\text{cysteamine}} \quad (2)$$

Where $f_{\text{carbonyl}}$ and $f_{\text{cysteamine}}$ are the mole fractions of carbon in the carbonyl-derivatives arising from the underivatized carbonyl

**Table 1**
Carbon isotopic composition of measured and predicted acetaldehyde–cysteamine derivatives in simulation experiments of sampling.

| Supplier | Acetaldehyde concentration (ppb) | $\delta^{13}C$ (‰)[a] | | | | $\Delta^i$ | $\Delta^j$ |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | Measured underivatized acetaldehyde[b,c,d] | Measured acetaldehyde derivatives[b,d,e,f] | Predicted acetaldehyde derivatives[g] | Predicted underivatized acetaldehyde[h] | | |
| M1 | 4000 | −25.92 ± 0.12 | −26.77 ± 0.08 | −26.49 | −26.49 ± 0.18 | 0.28 | 0.57 |
| | 200 | | −26.64 ± 0.10 | | −26.23 ± 0.22 | 0.15 | 0.31 |
| | 40 | | −26.78 ± 0.15 | | −26.51 ± 0.31 | 0.29 | 0.59 |
| M2 | 4000 | −29.69 ± 0.05 | −28.49 ± 0.06 | −28.37 | −29.93 ± 0.14 | 0.12 | 0.24 |
| | 800 | | −28.65 ± 0.11 | | −30.25 ± 0.23 | 0.28 | 0.56 |
| | 400 | | −28.58 ± 0.08 | | −30.11 ± 0.18 | 0.21 | 0.42 |
| | 40 | | −28.60 ± 0.04 | | −30.15 ± 0.11 | 0.23 | 0.46 |

[a] Stable carbon isotopic compositions reported in per mil relative to PDB (‰).
[b] $\delta^{13}C$ values determined by GC/C/IRMS.
[c] Five replicate analysis for each sample.
[d] The arithmetic means and standard deviations.
[e] Three replicate analysis for each sample.
[f] Derivatives reacted with cysteamine hydrochloride of $\delta^{13}C$ = −27.05 ± 0.08‰ (determined by five replicate EA/IRMS analysis).
[g] Predicted $\delta^{13}C$ values of acetaldehyde–cysteamine derivative based on mass the balance equation.
[h] Predicted $\delta^{13}C$ values of underivatized acetaldehyde based on mass the balance equation.
[i] Absolute values of the difference between predicted and measured $\delta^{13}C$ values of acetaldehyde–cysteamine derivatives.
[j] Absolute values of the difference between predicted and measured $\delta^{13}C$ values of underivatized acetaldehyde.

and cysteamine reagent, respectively. For example, $f_{carbonyl}$ has the value of 1/2 for the derivatization of acetaldehyde. The $\delta^{13}C$ results of the present study show that the predicted and the measured $\delta^{13}C$ values of acetaldehyde–cysteamine derivative agreed well (Table 1, the difference between them ranged from 0.12‰ to 0.29‰) within the precision limits of the GC/C/IRMS measurements, and the difference between the predicted and the measured $\delta^{13}C$ values of the underivatized acetaldehyde was in the range of 0.24–0.59‰. These results noted that no carbon isotopic fractionation occurred under the study conditions and this method was effective for measuring the $\delta^{13}C$ value of form-aldehyde and acetaldehyde in the atmosphere (Guo et al., 2007; Yu et al., 2006).

### 3.2. Carbon isotope data of formaldehyde and acetaldehyde emitted from the trees

Samples were collected at DHS-BR as described above. The two target compounds in samples were in good separation (Fig. 1). Carbon isotope of formaldehyde and acetaldehyde emitted from three different tree species (L. rotundifolia, C. album and C. henryi) were shown in Table 2. The results were likely to indicate that the $\delta^{13}C$ values of formaldehyde (also acetaldehyde) emitted from a certain tree were almost identical (the differences were all less than 0.50‰). And the carbon isotope data of formaldehyde emitted from different sampled tree species were quite different (about −36.00‰ for L. rotundifolia, −40.00‰ for C. album and −45.50‰ for C. henryi, respectively), for acetaldehyde, larger difference between L. rotundifolia and C. album (about −34.00‰ vs. −31.00‰), and it was nearly no difference between C. album and C. henryi (both about −31.00‰). These results most probably implied that different tree types meant different carbon isotope data of aldehyde.

The $\delta^{13}C$ values for formaldehyde of direct emission showed considerable depletion with respect to that of the tree leaves ($\Delta^{13}C = -4.34‰$ to $-15.96‰$). And the less depletion in $^{13}C$ was shown for acetaldehyde ($\Delta^{13}C = -0.94‰$ to $-3.81‰$). These $\delta^{13}C$ values from this study are more depleted in $^{13}C$ than those of previous investigations on biogenic $CH_3Cl$ ($\Delta^{13}C = -34.50‰$ to $-36.80‰$, with respect to that of plant tissue) and more enriched in $^{13}C$ than that of biogenic isoprene ($\Delta^{13}C = -2.60‰$, comparison to that of plant leaf) (Happer et al., 2001; Rudolph et al., 2003). Overall the formaldehyde and acetaldehyde emitted from L. rotundifolia, C. album and C. henryi were all more depleted in $^{13}C$ with respect to the leaf of tree species, which might come from the complex physiological processes in the produce of the aldehyde compounds.

### 3.3. Different source apportionment patterns of ambient formaldehyde and acetaldehyde: deduction from carbon isotope analysis

In general, carbon isotope data of aldehyde compounds in ambient air near the major sources are heavily influenced by local emissions. These have been proved by the studies on different source types (e.g. sampling near bus station or petroleum refinery) (Johnson and Dawson, 1990; Wen et al., 2005). In forest area, the main sources of aldehyde are direct biogenic emission and photo-oxidation of the biogenic hydrocarbon (Guenther et al., 1995; Kesselmeier, 2001; Rottenberger et al., 2004; Sumner et al., 2001). So the carbon isotope of ambient aldehyde would reflect the mixture of these two sources. From the carbon isotope data listed in Table 2, different source apportionment patterns were shown for ambient formaldehyde and acetaldehyde.

For ambient formaldehyde, as listed in Table 2, there were large deviations of their carbon isotope data between the direct biogenic
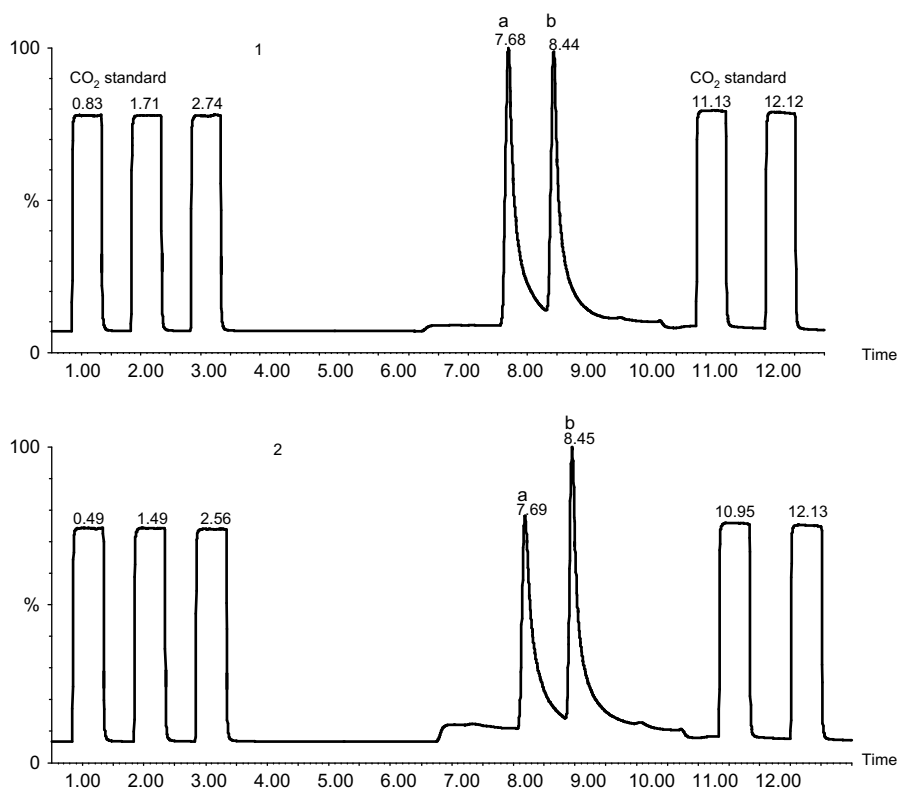


**Fig. 1.** Typical GC/C/IRMS chromatogram for aldehyde–cysteamine derivatives, showing (1) standard sample and (2) sample collected emitted from the leaf of trees. (a) Aldehyde–cysteamine derivative; (b) acetaldehyde–cysteamine derivative.

**Table 2**
Carbon isotopic composition of aldehyde compounds emitted from the leaves of three tree species and ambient measurements.

| Trees and ambient air | $\delta^{13}C$ (‰)[a] | | | | |
|---|---|---|---|---|---|
| | Measured leaf of the trees[b] | Measured formaldehyde derivatives[c,d] | Measured acetaldehyde derivatives[c,d] | Calculated formaldehyde[d,e] | Calculated acetaldehyde[d,e] |
| *Litsea rotundifolia*[f] | −32.07 ± 0.16 | −30.17 ± 0.11 | −30.66 ± 0.14 | −36.41 ± 0.37 | −34.27 ± 0.29 |
| Ambient air[g] | | −30.72 ± 0.14 | −30.79 ± 0.12 | −38.06 ± 0.45 | −34.53 ± 0.25 |
| | | LD | −30.99 ± 0.12 | LD | −34.93 ± 0.25 |
| Ambient air[h] | | −30.62 ± 0.11 | −30.01 ± 0.18 | −37.76 ± 0.37 | −32.97 ± 0.37 |
| *Canarium album*[i] | −27.60 ± 0.13 | −31.52 ± 0.16 | −29.19 ± 0.13 | −40.46 ± 0.51 | −31.33 ± 0.27 |
| | | −31.42 ± 0.11 | −29.23 ± 0.08 | −40.16 ± 0.37 | −31.41 ± 0.18 |
| Ambient air[g] | | −32.67 ± 0.16 | −29.42 ± 0.06 | −43.91 ± 0.51 | −31.79 ± 0.14 |
| | | LD | −29.57 ± 0.18 | LD | −32.09 ± 0.37 |
| Ambient air[h] | | −32.79 ± 0.19 | −29.31 ± 0.00 | −44.27 ± 0.59 | −31.57 ± 0.08 |
| *Castanea henryi*[i] | −29.87 ± 0.08 | −33.31 ± 0.12 | −28.93 ± 0.14 | −45.83 ± 0.39 | −30.81 ± 0.29 |
| | | −33.24 ± 0.10 | −29.04 ± 0.05 | −45.62 ± 0.34 | −31.03 ± 0.13 |
| Ambient air[j] | | −31.24 ± 0.17 | −29.46 ± 0.19 | −39.62 ± 0.53 | −31.86 ± 0.39 |
| Ambient air[h] | | −31.45 ± 0.16 | −29.31 ± 0.08 | −40.25 ± 0.51 | −31.57 ± 0.18 |

[a] Stable carbon isotopic compositions reported in per mil relative to PDB (‰).
[b] $\delta^{13}C$ values determined by EA/IRMS, and six replicate analysis for each sample.
[c] Derivatives reacted with cysteamine hydrochloride of $\delta^{13}C = -27.05 ± 0.08$‰ (determined by five replicate EA/IRMS analysis).
[d] The arithmetic means and standard deviations.
[e] Calculated $\delta^{13}C$ values of underivatized aldehyde compounds based on the mass balance equation.
[f] One sample collected.
[g] Two ambient samples collected near the respective tree species in the daytime.
[h] One ambient sample collected near the respective tree species in the nighttime.
[i] Two samples collected.
[j] One ambient sample collected near the respective tree species in the daytime; LD = lower than detection limit.

emission and the ambient atmosphere: for *L. rotundifolia* and *C. album*, the deviation was −1.35‰ to −4.11‰, and for *C. henryi*, it was about 6.00‰. The large deviation most probably showed that the direct biogenic emission accounted just a small part of the ambient formaldehyde; and the other source (e.g. photooxidation of the biogenic hydrocarbon) would be dominant.

Previous concentration studies had the similar result. It has been shown that the trees had the average (mass-based) emissions of 80–98% hydrocarbons (especially α-pinene, isoprene, β-pinene) and only about 1–8% carbonyls (especially formaldehyde and acetaldehyde) (Martin et al., 1999). The annual global natural VOCs flux was composed of about 44% isoprene and 11% monoterpene (Guenther et al., 1995). Moreover, carbonyl products including formaldehyde were observed in the photochemical reactions of many hydrocarbons with OH-radical (Den Bergh et al., 2004; Grosjean and Grosjean, 1996). And formaldehyde was the dominant initial oxidation product of isoprene with OH-radical or $O_3$, in a high yield of about 63–84% (Duane et al., 2002; Martin et al., 1991; Sumner et al., 2001; Wiedinmyer et al., 2001). Considering the low biogenic carbonyl emission and high rate of formaldehyde transformation coming from biogenic hydrocarbon (Duane et al., 2002; Guenther et al., 1995; Martin et al., 1991, 1999; Padhy and Varshney, 2005; Rottenberger et al., 2005; Villanueva-Feierro et al., 2004; Wiedinmyer et al., 2001), photooxidation of biogenic hydrocarbon would be dominant source of ambient formaldehyde in forest.

What is more, from the previous carbon isotope study of isoprene and the kinetic isotope effect (KIE), the similar result could be achieved. Study had got the carbon isotope data of isoprene from biogenic emission in the range of −27‰ to −32‰ (Rudolph et al., 2003), and for its main atmospheric removal process, the KIE for the reaction of isoprene with OH-radical was about 6.94 ± 0.80‰ (Rudolph and Czuba, 2000). Though no study of carbon isotope effect had been carried out on its main product (mainly formaldehyde), it was expected that a similar positive KIE should occur according to the mass balance equation of $^{13}$C. For its short lifetime of isoprene (about 1.4 h) (Atkinson, 2000), isoprene reacted rapidly

and the formed formaldehyde could have the $\delta^{13}C$ data more negative than −34‰ to −39‰ (this data was according to our forecasted formula: $KIE_{isoprene} = \delta^{13}C_{isoprene} - \delta^{13}C_{HCHO}$), if the trees used were isoprene emitters. Moreover, the lifetimes for formaldehyde with respect to reactions with OH-radical and photolysis were about 1.2 day and 4 h (Atkinson, 2000), respectively. In our sampling situation, weak photolysis reaction was expected, and then small isotope fractionation was expected during a 5-h sampling duration, which was confirmed by the accordance of the $\delta^{13}C$ values for ambient formaldehyde collected in the daytime and the nighttime (Table 2). All the measured $\delta^{13}C$ data of ambient formaldehyde ranged from −37.76‰ to −44.27‰, more depleted in $^{13}$C than the predicted data (−34‰ to −39‰), and also considerably more negative than the data of the other related sources such as transportation and petrochemical refinery (ranged from −16.68‰ to −26.69‰) in our previous study (Wen et al., 2005). Photolysis reaction of aldehydes with OH radial was weak and so it could be omitted during our sampling processes which was confirmed by the isotope data of aldehydes between the daytime and the nighttime (Table 2), but the photochemical reactions for many reactive hydrocarbons (e.g. isoprene) with OH-radical could not be omitted during so long sampling time (Den Bergh et al., 2004; Duane et al., 2002; Grosjean and Grosjean, 1996; Martin et al., 1991; Sumner et al., 2001; Wiedinmyer et al., 2001). This accordance also indicated that the secondary formations of formaldehyde were the main source of ambient formaldehyde in DHS-BR.

Especially, some tree species were monoterpene (α-pinene and β-pinene) rich emitters (He et al., 2000; Kesselmeier et al., 1996; Kesselmeier and Staudt, 1999), and also the formaldehyde was important product in the photochemical reaction of β-pinene with OH-radical (Den Bergh et al., 2004), with the yield of about 54–57% (Atkinson, 1997; Sumner et al., 2001); the reaction was also rapid with the monoterpene lifetime of about 2.6 h (Atkinson, 2000). So, may be the different kinds of the hydrocarbon emission resulted in the different carbon isotope data of ambient formaldehyde. Unfortunately, no $\delta^{13}C$ data of biogenic monoterpene and photo-reaction KIE data were reported, further discussion was impossible.

**Table 3**
Comparison of $\delta^{13}$C ratios for atmospheric formaldehyde and acetaldehyde in different sampling sites.

| Location | $\delta^{13}$C[a] | | |
| --- | --- | --- | --- |
| | Formaldehyde | Acetaldehyde | References |
| DHS-BR, China, rural site, at a main mountaintop | −44.27‰ to −37.76‰ | −34.93‰ to −31.57‰ | This study |
| Guangzhou, China, urban site, at a petrochemical refinery | −28.51‰ to −26.69‰ | −29.28‰ to −29.20‰ | Wen et al., 2005 |
| Guangzhou, China, urban site, at a bus station | −18.99‰ to −16.68‰ | −21.00‰ | Wen et al., 2005 |
| Chebogue Point, Nova Scotia, at a coastal site | −24.27‰ to −18.00‰ | | Tanner et al., 1996 |
| Mt. Lemmon, Arizona, at a continental site | −17.00‰ | | Johnson and Dawson, 1990 |
| Baring Head, New Zealand, at a marine site | −28.30‰ | | Johnson and Dawson, 1990 |

[a] Stable carbon isotopic compositions reported in per mil relative to PDB (‰).

However, for ambient acetaldehyde, the measured $\delta^{13}$C data of ambient acetaldehyde ranged from −31.57‰ to −34.93‰, considerably more negative than the data of the transportation and petrochemical refinery related sources (ranged from −21‰ to −29.2‰) (Wen et al., 2005), which meant that these related sources of the ambient acetaldehyde were impossible. And the carbon isotope data were very close to that of biogenic emission (Table 2). In the daytime, differences between the carbon isotope data of the emission and ambient were from 0.26‰ to 1.05‰, and in the nighttime, they were from 0.16‰ to 1.30‰; and the total averaged difference is 0.62‰. The data comparison (daytime vs. nighttime) showed that the isotopic compositions of ambient acetaldehyde between the daytime and nighttime were almost the same, and the isotopic compositions of ambient acetaldehyde (in the daytime or nighttime) were also very close to those of emissions from the trees. The accordance between these data showed that the direct biogenic emission most probably was the main source of the ambient acetaldehyde.

Moreover, ambient formaldehyde and acetaldehyde in different sites were reported in previous studies (Johnson and Dawson, 1990; Tanner et al., 1996; Wen et al., 2005) and their carbon isotope data were listed in Table 3. Large variation range could be seen (from −17‰ to −44‰). These distinctions in carbon isotopic composition of aldehyde might indicate their different sources, and carbon isotope analysis could provide valuable information for understanding their sources of aldehyde compounds in the atmosphere.

Although we measured the concentrations of ambient formaldehyde and acetaldehyde together with isotopic measurements, the sampling duration was not the same, and it's hard to find the relationship between the isotopic and concentration measurements. According to us, this method developed is a novel method to analyze $\delta^{13}$C values of formaldehyde and acetaldehyde, and further work is needed to apply it to sampling together with concentration measurements in the future.

Overall, the carbon isotope analysis of formaldehyde and acetaldehyde in this study showed the different source identification of the ambient aldehydes in DHS-BR in South China. For formaldehyde, the photooxidation of the biogenic hydrocarbon was likely to be dominant, but for acetaldehyde, the direct emission from the tree species would be dominant.

## 4. Conclusions

For the first time, the carbon isotopic analysis of formaldehyde and acetaldehyde emitted from trees (*L. rotundifolia*, *C. album* and *C. henryi*) were proceeded at a forest site in DHS-BR in South China. Method was developed to allow accurate measurements of carbon isotopic compositions of aldehyde compounds, the uncertainty and reproducibility of the measurements were both good enough for the environmental analysis.

It was showed that the $\delta^{13}$C data of the emitted aldehyde compounds (from −31‰ to −46‰) were quite different for different measured tree species, and they were all more depleted in $^{13}$C than the tree-leaf bulk $\delta^{13}$C values (from −27‰ to −32‰). The larger $\delta^{13}$C value differences of formaldehyde between ambient and direct biogenic emission indicated other major source for ambient formaldehyde (probably the photooxidation of biogenic hydrocarbon like isoprene and monoterpene). However, the accordance in $\delta^{13}$C values of acetaldehyde between ambient and biogenic emissions indicated the latter as the dominant source. The result showed that carbon isotope method might be a valuable indicator for sources identification of atmospheric aldehyde compounds.

## References

Atkinson, R., 1997. Gas-phase tropospheric chemistry of volatile organic compounds: 1. alkanes and alkenes. Journal of Physical and Chemical Reference Data 26 (2), 215–290.

Atkinson, R., 2000. Atmospheric chemistry of VOCs and NOx. Atmospheric Environment 34, 2063–2101.

Brickus, L.S.R., Cardoso, J.N., de Aquino Neto, F.R., 1998. Distributions of indoor and outdoor air pollutants in Rio de Janeiro, Brazil: implications to indoor air quality in bayside offices. Environmental Science and Technology 32, 3485–3490.

Conny, J.M., Currie, L.A., 1996. The isotopic characterization of methane, non-methane hydrocarbons and formaldehyde in the troposphere. Atmospheric Environment 30 (4), 621–638.

Den Bergh, V.V., Vankerckhoven, H.C.H., Vinckier, F.C.C., 2004. Study of the carbonyl products of terpene/OH radical reactions: detection of the 2, 4-DNPH derivatives by HPLC–MS. Analytical and Bioanalytical Chemistry 379, 484–494. doi:10.1007/s00216-004-2629-7.

Duane, M., Poma, B., Rembges, D., Astorgs, C., Larsen, B.R., 2002. Isoprene and its degradation products as strong ozone precursors in Insubria, Northern Italy. Atmospheric Environment 36, 3867–3879.

Fall, R., 2003. Abundant oxygenates in the atmosphere: a biochemical perspective. Chemical Reviews 103, 4941–4951.

Feng, Y., Wen, S., Wang, X., Sheng, G., He, Q., Tang, J., Fu, J., 2004. Indoor and outdoor carbonyl compounds in the hotel ballrooms in Guangzhou, China. Atmospheric Environment 38, 103–112. doi:10.1016/j.atmosenv.2003.09.061.

Fracchia, M.F., Schuette, F.J., Mueller, P.K., 1967. A method for sampling and determination of organic carbonyl compounds in automobile exhaust. Environmental Science and Technology 1 (11), 915–922.

Gaffney, J.S., Marley, N.A., Martin, R.S., Dixon, R.W., Reyes, L.G., Popp, C.J., 1997. Potential air quality effects of using ethanol–gasoline fuel blends: a field study in Albuquerque, New Mexico. Environmental Science and Technology 31, 3035–3061.

Goldstein, A.H., Shaw, S.L., 2003. Isotopes of volatile organic compounds: an emerging approach for studying atmospheric budgets and chemistry. Chemical Reviews 103, 5025–5048.

Grosjean, D., Grosjean, E., Moreira, L.F.R., 2002. Speciated ambient carbonyls in Rio de Janeiro, Brazil. Environmental Science and Technology 36, 1389–1395.

Grosjean, E., Grosjean, D., 1996. Carbonyl products of the gas reaction of ozone with 1, 1-disubstituted alkenes. Journal of Atmospheric Chemistry 24, 141–156.

Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R.,

Taylor, J., Zimmerman, P., 1995. A global model of natural volatile organic compound emissions. Journal of Geophysical Research 100 (D5), 8873–8892.

Guo, S., Wen, S., Wang, X., Sheng, G., Fu, J., Jia, W., Yu, Y., Lu, H., 2007. Carbon isotope analysis of acetaldehyde and acetone by cysteamine derivatization. Rapid Communications in Mass Spectrometry 21, 1809–1812. doi:10.1002/rcm.3015.

Happer, D.B., Kalin, R.M., Hamilton, J.T.G., Lamb, C., 2001. Carbon isotope ratios for chloromethane of biological origin: potential tool in determining biological emissions. Environmental Science and Technology 35 (18), 3616–3619.

He, C., Murray, F., Lyons, T., 2000. Monoterpene and isoprene emissions from 15 Eucalyptus species in Australia. Atmospheric Environment 34, 645–655.

Johnson, B.J., Dawson, G.A., 1990. Collection of formaldehyde from clean air for carbon isotopic analysis. Environmental Science and Technology 24 (6), 898–902.

Kean, A.J., Grosjean, E., Grosjean, D., Harley, R.A., 2001. On-road measurement of carbonyls in Caledonian light-duty vehicle emissions. Environmental Science and Technology 35, 4198–4204.

Kesselmeier, J., 2001. Exchange of short-chain oxygenated volatile organic compounds (VOCs) between plants and the atmosphere: a compilation of field and laboratory studies. Journal of Atmospheric Chemistry 39, 219–233.

Kesselmeier, J., Schafer, L., Ciccioli, P., Brancaleoni, E., Cecinato, A., Frattoni, M., Foster, P., Jacob, V., Denis, J., Fugit, J.L., Dutaur, L., Torres, L., 1996. Emission of monoterpenes and isoprene from a Mediterranean oak species *Quercus iles* L. measured within the bema (biogenic emissions in the Mediterranean area) project. Atmospheric Environment 30 (10/11), 1841–1850.

Kesselmeier, J., Staudt, M., 1999. Biogenic volatile organic compounds (VOCs): an overview on emission, physiology and ecology. Journal of Atmospheric Chemistry 33, 23–88.

Martin, R.S., Westberg, H., Allwine, E., Ashman, L., Farmer, J.C., Lamb, B., 1991. Measurement of isoprene and its atmospheric oxidation products in a central Pennsylvania deciduous forest. Journal of Atmospheric Chemistry 13, 1–32.

Martin, R.S., Villanueva, I., Zhang, J., Popp, C.J., 1999. Nonmethane hydrocarbon, monocarboxylic acid, and low molecular weight aldehyde and ketone emissions from vegetation in central New Mexico. Environmental Science and Technology 33, 2186–2192.

McLaughlin, J.K., 1994. Formaldehyde and cancer: a critical review. International Archives of Occupational and Environmental Health 66, 295–301.

Mo, J., Brown, S., Peng, S., Kong, G., 2003. Nitrogen availability in disturbed, rehabilitated and mature forests of tropical China. Forest Ecology and Management 175, 573–583.

Noisel, N., Bouchard, M., Carrier, G., 2007. Evaluation of the health impact of lowering the formaldehyde occupational exposure limit for Quebec workers. Regulatory Toxicology and Pharmacology 48, 118–127. doi:10.1016/j.yrtph.2007.02.001.

Ohura, T., Amagai, T., Senga, Y., Fusaya, M., 2006. Organic air pollutants inside and outside residences in Shimizu, Japan: levels, sources and risks. Science of the Total Environment 366, 485–499. doi:10.1016/j.scitotenv.2005.10.005.

Padhy, P.K., Varshney, C.K., 2005. Isoprene emission from tropical tree species. Environment Pollution 135, 101–109. doi:10.1016/j.envpol.2004.10.003.

Rieley, G., 1994. Derivatization of organic compounds prior to gas chromatographic–combustion–isotope ratio mass spectrometric analysis: identification of isotope fractionation processes. Analyst 119, 915–919.

Rottenberger, S., Kuhn, U., Wolf, A., Schebeske, G., Oliva, S.T., Tavares, T.M., Kesselmeier, J., 2004. Exchange of short-chain aldehydes between Amazonian vegetation and the atmosphere. Ecologic Applications 14 (4), S247–S262.

Rottenberger, S., Kuhn, U., Wolf, A., Schebeske, G., Oliva, S.T., Tavares, T.M., Kesselmeier, J., 2005. Formaldehyde and acetaldehyde exchange during leaf development of the Amazonian deciduous tree species *Hymenaea courbaril*. Atmospheric Environment 39, 2275–2279. doi:10.1016/j.atmosenv.2004.12.027.

Rudolph, J., Czuba, E., 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 (D24), 29329–29346.

Rudolph, J., Lowe, D.C., Martin, R.J., Clarkson, T.S., 1997. A novel method for compound specific determination of $\delta 13C$ in volatile organic compounds at ppt levels in ambient air. Geophysical Research Letters 24 (6), 659–662.

Rudolph, J., Anderson, R.S., Czapiewski, K.V., Czuba, E., Ernst, D., Gillespie, T., Huang, L., Rigby, C., Thompson, A.E., 2003. 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. Journal of Atmospheric Chemistry 44, 39–55.

Singh, H., Chen, Y., Staudt, A., Jacob, D., Blake, D., Heikes, B., Snow, J., 2001. Evidence from the Pacific troposphere for large global sources of oxygenated organic compounds. Nature 410, 1078–1081.

Sumner, A.L., Shepson, P.B., Couch, T.L., Thornberry, T., Carrol, M.A., Sillman, S., Pippin, M., Bertman, S., Tan, D., Faloona, I., Brune, W., Young, V., Cooper, O., Moody, J., Stockwell, W., 2001. A study of formaldehyde chemistry above a forest canopy. Journal of Geophysical Research 106 (D20), 24387–24405.

Tanner, R.L., Zielinska, B., Uberna, E., Harshfield, G., McNichol, A.P., 1996. Concentrations of carbonyl compounds and the carbon isotopy of formaldehyde at a coastal site in Nova Scotia during the NARE summer intensive. Journal of Geophysical Research 101 (D22), 28961–28970.

Thompson, A.M., 1992. The oxidizing capacity of the earth's atmosphere: probable past and future changes. Science 256, 1157–1165.

Timmons, S.R., Nwankwo, J.O., Domann, F.E., 2002. Acetaldehyde activates Jun/AP-1 expression and DNA binding activity in human oral keratinocytes. Oral Oncology 38, 281–290.

Villanueva-Feierro, I., Popp, C.J., Martin, R.S., 2004. Biogenic emissions and ambient concentrations of hydrocarbons, carbonyl compounds and organic acids from ponderosa pine and cottonwood trees at rural and forested sites in Central New Mexico. Atmospheric Environment 38, 249–260.

Wen, S., Feng, Y., Yu, Y., Bi, X., Wang, X., Sheng, G., Fu, J., Peng, P., 2005. Development of a compound-specific isotope analysis method for atmospheric formaldehyde and acetaldehyde. Environmental Science and Technology 39 (16), 6202–6207.

Wiedinmyer, C., Fridefeld, S., Baugh, W., Greenberg, J., Guenther, A., Fraser, M., Allen, D., 2001. Measurement and analysis of atmospheric concentrations of isoprene and its reaction products in central Texas. Atmospheric Environment 35, 1001–1013.

Yi, Z., Fu, S., Yi, W., Zhou, G., Mo, J., Zhang, D., Ding, M., Wang, X., Zhou, L., 2007. Partitioning soil respiration of subtropical forests with different successional stages in south China. Forest Ecology and Management 243, 178–186. doi:10.1016/j.foreco.2007.02.022.

Yu, Y.X., Wen, S., Feng, Y.L., Bi, X.H., Wang, X.M., Peng, P.A., Sheng, G.Y., Fu, J.M., 2006. Development of a compound-specific carbon isotope analysis method for atmospheric formaldehyde via $NaHSO_3$ and cysteamine derivatization. Analytical Chemistry 78 (4), 1206–1211.

Zhang, J., Smith, K.R., 1999. Emissions of carbonyl compounds from various cook-stoves in China. Environmental Science and Technology 33 (14), 2311–2320.