

Analytical system for stable carbon isotope measurements of low molecular weight (C₂-C₆) hydrocarbons

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Abstract. We present setup, testing and initial results from a new automated system for stable carbon isotope ratio measurements on C₂ to C₆ atmospheric hydrocarbons. The inlet system allows analysis of trace gases from air samples ranging from a few liters for urban samples and samples with high mixing ratios, to many tens of liters for samples from remote unpolluted regions with very low mixing ratios. The centerpiece of the sample preparation is the separation trap, which is used to separate CO₂ and methane from the compounds of interest. The main features of the system are (i) the capability to sample up to 300 l of air, (ii) long term (since May 2009) operational $\delta^{13}\text{C}$ accuracy levels in the range 0.3–0.8‰ (1- σ), and (iii) detection limits of order 1.5–2.5 ngC (collected amount of substance) for all reported compounds.

The first application of this system was the analysis of 21 ambient air samples taken during 48 h in August 2009 in Utrecht, the Netherlands. Results obtained are generally in good agreement with those from similar urban ambient air studies. Short sample intervals allowed by the design of the instrument help to illustrate the complex diurnal behavior of hydrocarbons in an urban environment, where diverse sources, dynamical processes, and chemical reactions are present.

1 Introduction

A significant amount of the total reactive carbon input (estimated as near 1150 Tg yr⁻¹, Guenther et al., 1995) to the atmosphere consists of non-methane hydrocarbons (NMHCs).

These are emitted to the atmosphere through many processes, both natural as a product of vegetative growth, decay and natural combustion of plant material, and anthropogenic including biomass burning for energy or heating, fossil fuel combustion, and industrial processes. Non-methane hydrocarbons play important roles in atmospheric chemistry contributing to the production of tropospheric ozone and resultant photochemical pollution, the formation of aerosol particles, and the oxidative capacity of the atmosphere (Warneck, 1988; Seinfeld and Pandis, 1998; Goldstein and Galbally, 2007).

Low molecular weight NMHC, consisting of compounds with 2 to 7 carbon atoms (C₂ to C₇), account for the vast majority of anthropogenic emissions to the troposphere (Middleton, 1995). Acetylene, ethylene, propyne, and propylene originate primarily from combustion processes such as fossil fuel combustion and biomass burning; alkanes mainly stem from natural gas leakage and petroleum product evaporation, with significant transportation sources as well; and aromatic compounds mainly from transportation sources and solvent evaporation (Goldstein and Shaw, 2003; Redeker et al., 2007). Oxidative processes provide the atmospheric removal mechanism of NMHC compounds, mainly through reaction with OH, which is by far the dominant process (Conny and Currie, 1996):



Where R stands for any alkyl radical remaining after hydrogen abstraction from the hydrocarbon RH. Other removal mechanisms include NO₃, Cl, or O₃ (Warneck, 1988; Seinfeld and Pandis, 1998; Brenninkmeijer, 2009).

The minor stable isotope of carbon, ¹³C, has an average natural abundance of approximately 1.1%. Biological (e.g. photosynthesis), physical (e.g. diffusion) and chemical



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processes often act slightly differently on isotopologues and thus change the stable isotope ratio, which is expressed as

$$\delta^{13}\text{C} = \left[\frac{\left(\frac{[^{13}\text{C}]}{[^{12}\text{C}]} \right)_{\text{sample}}}{\left(\frac{[^{13}\text{C}]}{[^{12}\text{C}]} \right)_{\text{standard}}} - 1 \right] \quad (2)$$

where measurements are referenced against a standard carbon isotopic ratio, usually VPDB (Vienna Pee Dee Belemnite). Measurements of $\delta^{13}\text{C}$ are commonly multiplied by 1000 ‰ for readability purposes (Goldstein and Shaw, 2003; Brenninkmeijer, 2009).

Isotopically lighter molecules usually react faster than isotopically heavier ones. In the case of hydrocarbons, this is because bonds in molecules containing solely ^{12}C atoms are weaker than those containing one or more ^{13}C atoms. This causes small deviations from the original $^{13}\text{C}/^{12}\text{C}$ ratio during chemical degradation. The ratio of the two rate coefficients of the different isotopologues is known as a kinetic isotope effect (KIE).

$$\text{KIE} = \frac{k_{12}}{k_{13}}. \quad (3)$$

Knowledge of the KIE of relevant chemical reactions can provide a tool to improve the understanding of hydrocarbon atmospheric processing (Rudolph and Czuba, 2000).

Development of the coupled gas chromatography – (combustion interface) – isotope ratio mass spectrometer (IRMS), as pioneered by Matthews and Hayes (1978) for CO_2 and N_2 isotope work, substantially improved upon earlier techniques based on dual-inlet isotope ratio mass spectrometers by greatly reducing necessary sample size and eliminating the need to extract individual compounds from a sample, which is a difficult and time-consuming task. This breakthrough allowed significant research work into the stable isotopic ratios of carbon, nitrogen, oxygen and hydrogen containing compounds in the atmosphere.

Development of instrumentation able to accomplish compound specific measurement of carbon isotope ratios of NMHC is somewhat newer (Rudolph et al., 1997; Goldstein and Shaw, 2003; Brenninkmeijer, 2009). Rudolph et al. (1997) developed the first instrument capable of compound specific stable carbon isotope ratio analysis measurements of multiple NMHCs. This instrument was initially used for observing carbon isotope ratios of emissions from biomass burning and transportation related sources, and urban environment atmospheric samples. The observance of the magnitude of the kinetic isotope effect in hydrocarbon reactions with OH and O_3 was also undertaken in subsequent research with this instrument (Rudolph et al., 1997, 2002; Iannone et al., 2003; Anderson et al., 2004).

The availability of such measurements allowed the subsequent development and application of the so-called isotopic

hydrocarbon clock approach, which is expressed as follows (Rudolph and Czuba, 2000):

$$\delta_Z = t_{\text{av}} \cdot {}^{\text{OH}}k_Z \cdot [\text{OH}] \cdot {}^{\text{OH}}\text{KIE}_Z + {}^0\delta_Z \quad (4)$$

where δ_Z is the measured isotopic ratio of a compound Z , t_{av} the average age of the air mass, ${}^{\text{OH}}k_Z$ the rate of reaction of the compound with OH, $[\text{OH}]$ the concentration of OH, ${}^{\text{OH}}\text{KIE}_Z$ the KIE in the reaction of compound Z with OH, and ${}^0\delta_Z$ the source isotope ratio of compound Z ; it may also be further extended by adding terms representing reactions with e.g. O_3 or Cl. This approach can improve estimates of compound age compared to previous efforts, which relied on ratios of mixing ratios of two compounds emitted at the same time (Rudolph and Czuba, 2000). In the case of light non-methane hydrocarbons, the relatively short lifetime of these compounds in the atmosphere, from mere hours to tens of days, gives the possibility of utilizing the isotopic hydrocarbon clock approach to constrain transport and aging in the atmosphere (Rudolph and Ehhalt, 1981; Rudolph et al., 2002; Goldstein and Shaw, 2003; Redeker et al., 2007).

Other applications of similar instruments that have been subsequently derived include measurements of NMHC $\delta^{13}\text{C}$ in urban, marine and coastal atmospheres and over the north Pacific and east Asia to evaluate atmospheric transport and air mass age (Tsunogai and Yoshida, 1999; Saito et al., 2002, 2009; Nara et al., 2007); of NMHC from biomass burning (Czapiewski et al., 2002; Nara et al., 2006); with some extension, measurements of halocarbons and NMHC (Archbold et al., 2005; Redeker et al., 2007); specific measurement of chloromethane from plants and its atmospheric budget (Bill et al., 2002; Harper et al., 2003; Keppler et al., 2005); and measurement of leaf emissions of acetaldehyde to investigate biochemical reaction pathways (Jardine et al., 2009). Such measurements can be powerful tools to disentangle the relative contribution of different sources to the atmospheric burden of important atmospheric trace gases.

Here we present a new instrument that is capable of high-precision measurements of NMHC stable carbon isotope ratios. It has the unique capacity of being able to process very high volume samples of up to 300l, such as those necessary for stable carbon isotope measurements of NMHC from very clean samples (e.g. stratospheric, firn air samples, or remote high volume air samples) and the flexibility of accepting samples from many other sources. The system is constructed and tested to analyze $\delta^{13}\text{C}$ of non-methane hydrocarbons from C_2 to C_6 , and methyl chloride.

2 Experimental

2.1 System description and procedure

2.1.1 The preconcentration system

The system (Fig. 1) is largely based on well-established cryotrapping techniques and allows for stable isotope analysis

of a variety of different samples. All cryotrap were operated at 77 K and cooled with liquid nitrogen. If not specified otherwise, electrical heating desorbed the trapped compounds. Helium was used as carrier gas to transfer the sample through the different components of the system. To allow the sampling of large volume samples, it is necessary to initially utilize large diameter cryotrap and progressively cryofocus to smaller volumes prior to GC injection. Cryogenic traps, when implemented properly, do not create isotopic fractionation (Archbold et al., 2005; Redeker et al., 2007). The following parts of the preconcentration system are described below: (i) the primary cryogenic sampling trap (referred to as SAMP trap); (ii) the separation trap to separate CO₂ from the NMHCs (referred to as SEP trap); (iii) the W-shaped cryogenic recovery trap (REC trap); and (iv) the final cryogenic focusing trap (FOC trap).

The SAMP trap is a 0.5 m × 4 mm ID stainless-steel tube filled with 100/120 mesh glass-bead packing material, capable of at least 100 standard ml min⁻¹ (standard conditions are 0 °C, 1 bar) flow rates without loss. Typically this trap is operated at a flow of 50 standard ml min⁻¹, which is maintained by a MKS thermal mass flow-controller. A dual-head rotary pump (KNF Neuberger GmbH, Germany) draws the sample through the trap, and provides removal of bulk gases (mainly N₂ and O₂). Desorption of any sample on the trap is accomplished by heating it to 120 °C within 1 min after extraction.

The most innovative design feature of the preconcentration system is the method of CO₂ removal. Whereas other systems (Rudolph et al., 1997; Tsunogai et al., 1999; Archbold et al., 2005) rely on chemical removal of any CO₂ employing Carbosorb, Ascarite II or other sodium hydroxide-on-silica beads, here a packed stainless steel GC-column (Supelco Porapak Q, 3 m × 4 mm ID, 100/120 mesh) acted as a trap for NMHCs and allowed unwanted CO₂ to pass. We designed the SEP trap as a non-chemical removal method to ensure effective separation for large samples, i.e. samples with a high CO₂ content. CO₂ must be removed before IRMS analysis can occur, because the target compounds are oxidized to CO₂ for isotope analysis. In order to do so, the sample is injected on this trap at 70 ml min⁻¹ with helium as the carrier gas. The system procedure developed as a result of SEP trap testing (see Sect. 2.1.3, below) reverses the flow through the column after 10 minutes (any CO₂ having been vented) to retrieve the compounds of interest from the column at a reduced helium flow rate (11.2 ml min⁻¹). During recovery, the column is heated to and kept at 120 °C over a period of 40 min.

Before the sample material is recovered on the REC trap, any small remnant CO₂ and any H₂O is removed in a small glass reactor containing Ascarite II and Mg(ClO₄)₂. The REC trap is a 0.7 m × 2.5 mm ID W-shaped stainless steel cryotrap containing 100/120 mesh glass beads. After the recovery time of 40 min, the REC trap is heated to 100 °C, thereby releasing the sample over the course of 5 min at

Table 1. Mean and standard deviation in δ¹³C (‰) SEP trap evaluation data.

Compound	No SEP trap ^a mean δ ¹³ C	No SEP trap ^a σ δ ¹³ C	Standard config. ^b mean δ ¹³ C	Standard config. ^b σ δ ¹³ C
Ethane	-28.4	0.33	-28.6	0.27
Propane	-34.6	0.49	-34.3	0.49
Methyl Chloride	-46.4	0.69	-48.8	0.72
Benzene	-27.4	0.36	-27.5	0.39

^a SEP trap removed from system, *n*=10 ^b Standard configuration, SEP trap installed, *n*=10.

4.1 ml min⁻¹ to the FOC trap, a 0.5 m × 0.25 mm ID stainless steel-jacketed capillary cryotrap. Sample injection into the GC occurs by extracting and heating the FOC trap to a temperature of over 100 °C within 30 s, at a flow rate of 2.1 ml min⁻¹.

2.1.2 SEP trap verification and testing

Figure 2 displays a total ion abundance chromatogram demonstrating the separation properties of SEP trap under room temperature and aforementioned standard He flow rates of 70 ml min⁻¹, utilizing a 200 ml 50:50 CO₂/natural gas testing mix and a quadrupole mass spectrometer as a detector at the outlet of the SEP trap. Natural gas has a widely varying composition, but generally consists of methane (as bulk gas) and contains significant amounts of nitrogen, CO₂, and higher hydrocarbons such as ethane and propane (Škrbić and Zlatkovič, 1983; Milton et al., 2010). The injected mixture of natural gas and CO₂ as chosen here represents a test of separation column performance of a very demanding sample introduced on the system, representing the CO₂ content of approximately 3001 of ambient air. Figure 2 shows that at 10 min after injection the bulk of methane, remnant nitrogen (peak A) and CO₂ (peak B), has eluted while ethane and other hydrocarbons (peak C) are still in the SEP trap. Therefore the system procedure has been set to reverse the flow through the column after 10 min to retrieve the compounds of interest, after venting all CO₂.

Further, we performed tests to confirm that the SEP trap has no significant effect on the δ¹³C measurements of the selected hydrocarbons. The tests consisted of 10 measurements of calibration gas (working standard gas, AiR Inc., described further in Sect. 2.2) in two configurations: (i) with the system in standard configuration but the SEP trap short-cut (removed), and (ii) with the system in standard configuration, respectively. Table 1 shows that the means and standard deviations are nearly identical for the hydrocarbons. However, there is a consistent shift (-2‰) for methyl chloride, for which a correction is necessary. A similar effect was noted in Archbold et al. (2005), for chemical removal and adsorbance traps. The cause of this shift is as yet unexplained.

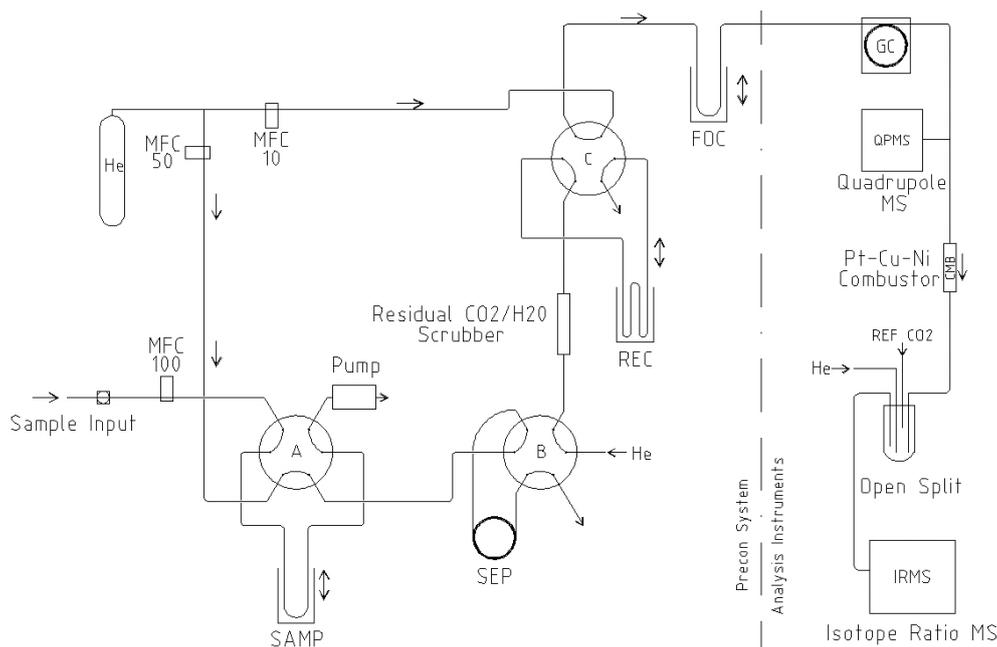


Fig. 1. System diagram. **A**, **B**, **C** indicate Valco 6-port valves; **SAMP**, **SEP**, **REC**, and **FOC** indicate the primary sampling cryotrap, the separation trap, the recovery cryotrap, and the focusing cryotrap, respectively. Mass flow controller (MFC) maximum flow rates are indicated in units of ml min^{-1} (standard conditions).

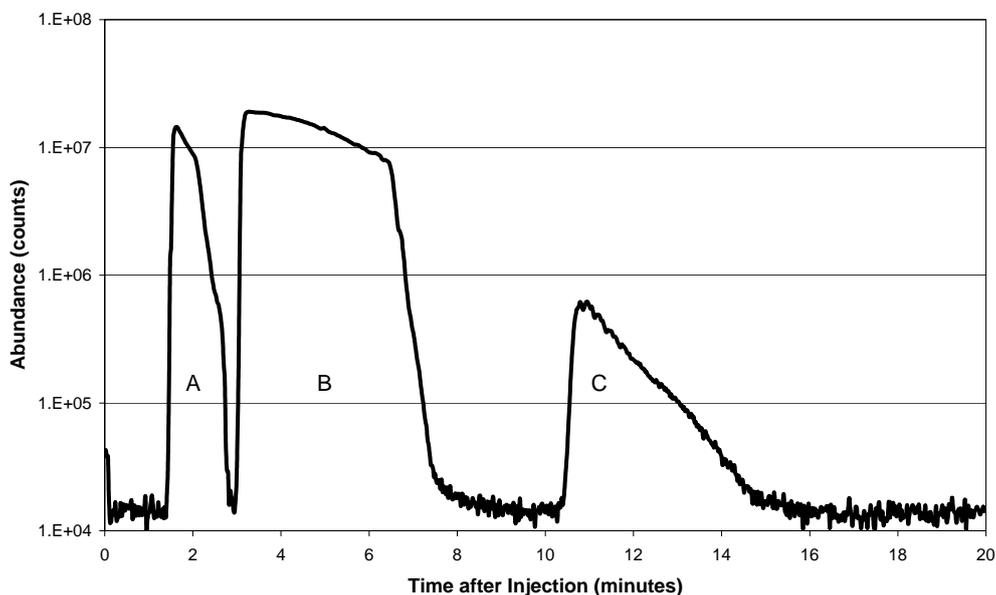


Fig. 2. Performance of the separation trap. The identity of peaks **A** (methane and nitrogen), **B** (bulk carbon dioxide), and **C** (ethane and other hydrocarbons) was confirmed by individual mass signals of the quadrupole mass spectrometer.

2.1.3 GC separation, combustion and detection

Gas chromatographic separation is done on a $52.5 \text{ m} \times 0.25 \text{ mm}$ Varian PoraPLOT Q GC column in a HP 5890 GC. The column is maintained at 40°C for 10 minutes, thereafter being heated at a rate of $12^\circ\text{C min}^{-1}$ to

240°C . This temperature is maintained for 35 min, giving a total run time of 65 min. When not in use, the GC oven is maintained at 150°C . Helium is used as the carrier gas and a constant flow of 2.1 ml min^{-1} is maintained by a mass flow controller (MKS).

The effluent from the GC column is roughly split 1:1 between a quadrupole mass spectrometer (HP5970) for identification of the compounds, and the remainder sent to a ThermoFinnigan Delta⁺ XP IRMS by way of a platinum-copper-nickel ceramic combustor (maintained at 900 °C and restored daily with O₂), a nafion drier, and an open-split interface (Röckmann et al., 2003). The actual flow into the IRMS is approximately 0.5 ml min⁻¹. IRMS δ¹³C drift is monitored through direct injection of CO₂ via the open-split as a working standard. The stable carbon isotope ratio of this CO₂ has been calibrated as -34.0 ‰ ± 0.1 vs. VPDB by Rijksuniversiteit Groningen, The Netherlands. Mixing ratios are calculated from the IRMS *m/z* 44 peak area measurements of each peak in the chromatogram, relative to peak areas from the working standard gas at accuracy levels of ±10 % (see below). Mixing ratios of compounds not contained in the regularly measured working standard gas were estimated by extrapolation based on the number of carbon atoms in the molecules of the species in question and can therefore contain a larger systematic error (±30 %). δ¹³C values are calculated from the individual ion signals of the IRMS, integrated per trace (*m/z* 44, 45, 46; automatic peak detection under normal operation, manual evaluation if necessary), and mathematically corrected for ¹⁷O through the ISODAT isotope ratio analysis package, utilizing the correction from Santrock et al. (1985).

The sample chromatograms shown in Fig. 3 show the IRMS intensity traces at *m/z* 44 of two gas standards and an ambient air sample; and a 44/45 ratio trace for that ambient air sample, respectively, thus demonstrating the separation performance of the GC-IRMS system.

2.1.4 Ambient air sampling unit

As an addition to the basic system described above, a high-flow sampling unit (diagram Fig. 4) was developed allowing ambient air sampling at rates of up to 1 l min⁻¹. The unit is set up as an auxiliary 2-stage cryogenic trapping system consisting of a large diameter stainless steel water trap (0.25 m × 2.1 cm ID) and a stainless steel U-trap (0.5 m × 1.0 cm ID) filled with glass beads (80/100 mesh). The water trap is constructed of 2.54 cm tubular stainless steel with large diameter Swagelok fittings and 0.32 cm (ID) stainless steel lines. The internal volume of this trap (approximately 100 ml) is large enough to freeze out water vapor from very large and humid air samples.

Sampling proceeds as follows: both traps are immersed in liquid nitrogen while flush gas (ultra pure synthetic air or nitrogen) is drawn through the system at 50 ml min⁻¹ by a dual head high-flow rotary pump downstream of the traps. The use of a pump keeps pressure inside the traps low at all times to prevent the condensation of oxygen. Once both traps are at temperature (approximately 2 min), the synthetic air supply is closed, the ambient sample valve is opened, flow rates are increased to 0.5–1 l min⁻¹ and sampling be-

gins. Following the sampling of the desired volume, the flow rate is reduced to 50 ml min⁻¹, the sampling valve is closed, and the flush gas is reintroduced. Subsequently the pump valve is closed and the valve to the preconcentration system is opened and the traps are extracted from the liquid nitrogen in turn: first the water trap is removed and left to warm in laboratory ambient air for 5 min to reduce pressure effects from rapid warm up of such a large volume. Then it is inserted in a warm water bath at 40 °C to release adsorbed volatiles, while retaining water in liquid form at the bottom of the trap. The liberated volatiles are transferred to the large diameter U trap over 5 min. This trap is then extracted from the liquid nitrogen and allowed to warm in ambient laboratory air over 5 min, and is subsequently heated out under a 500 °C air stream for 5 min to transfer all sampled compounds to the preconcentration system.

2.1.5 Automatization

With the exception of the ambient air sampling unit, the system has fully automatic operation. Pneumatic lifters are used to move the traps in or out the Dewar vessels filled with liquid nitrogen. The traps, flow controllers, and valves are operated electronically via a process/time table. Autonomous operation is limited to about 10 h by the supply of liquid nitrogen in the Dewar vessels.

2.2 Performance and stability

For calibration, a 9-compound reference gas (Apel-Riemer, AiR Environmental, Inc.) is used as the primary working standard. Of the compounds in this gas, 4 are monitored in test and calibration runs at the start and end of each measuring day, and during night (automated), namely ethane (206 ppb), propane (103 ppb), methyl chloride (103 ppb) and benzene (103 ppb). Calibration runs with the standard were done with varying volumes, either 50, 100, or 200 ml, to ensure a range of peak areas similar to results in sample measurements and to test for non-linearity effects. Calibration runs using 100 ml of this gas were most commonly done. Usage of low volume high concentration calibration gas as compared to a high volume dilution of the same was found to have no effect in calibration results, similar to previous research (e.g. Archbold et al., 2005; Redeker et al., 2007), further verifying trap performance.

The δ¹³C values of propane, methyl chloride, and benzene in the working standard were established utilizing the method described in Fisseha et al. (2009), at the Forschungszentrum Jülich, Germany, to be -34.8 ± 0.4, -48.7 ± 0.4, and -28.1 ± 0.3 ‰ vs. VPDB, respectively. These calibration results agree (±0.3 to ±0.8 ‰, depending on compound) with all measurements of these compounds obtained by our system when calibrated against the aforementioned injected CO₂, and taking into account the shift in methyl chloride. Unfortunately, no independent measurement of ethane was achieved by the Jülich group. However, calibration results of

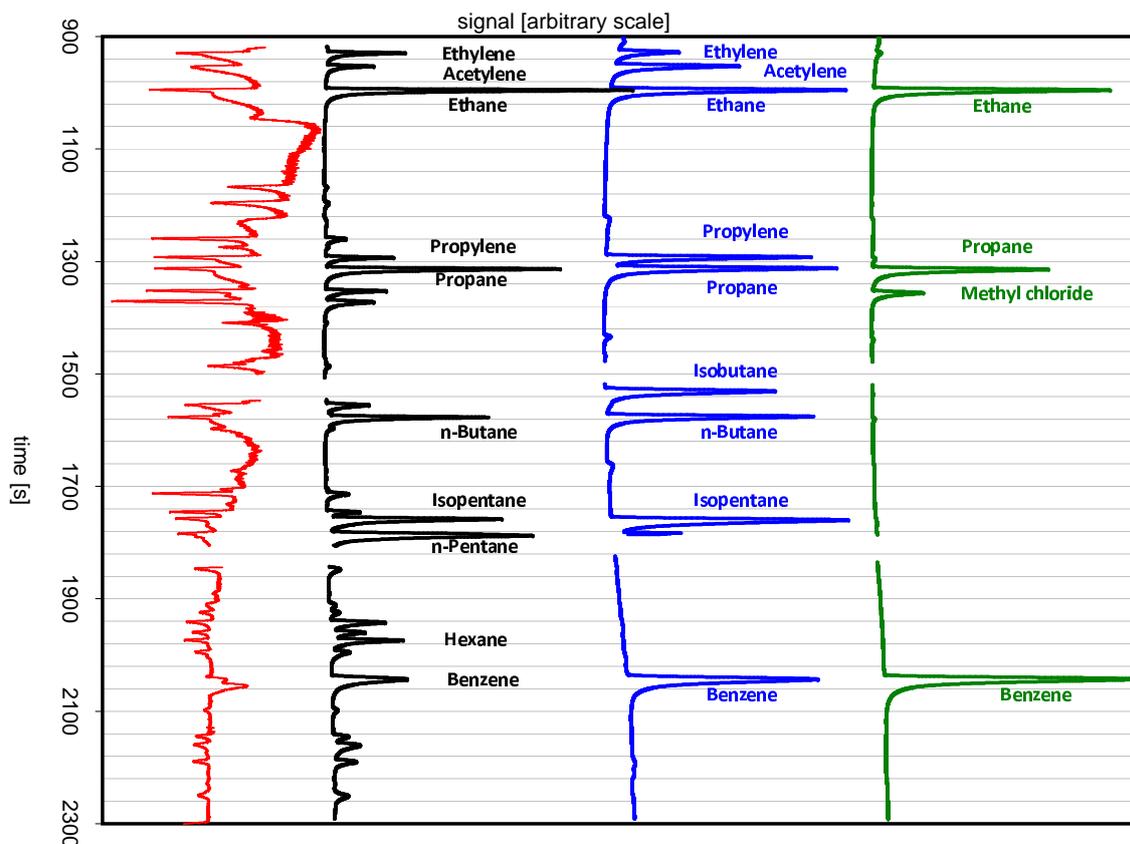


Fig. 3. Example chromatograms (IRMS, m/z 44 signal) of the working gas standard (green trace), the second calibration gas standard (blue trace), and an ambient air sample (black trace), respectively. Peak identification of the ambient sample is based on retention time and the mass spectrum obtained with the quadrupole mass spectrometer. Additionally, the ambient air sample 44/45 ratio trace is provided (red trace) to demonstrate peak separation.

the other tested gases and the reference CO_2 give high confidence that our estimate of -28.6 ± 0.4 ‰ vs. VPDB is valid for ethane.

If the peak area of a given eluted compound was maintained above 0.5 Vs, the IRMS measured $\delta^{13}\text{C}$ values showed no dependency on the sample size. Below this value peak integration can yield inaccurate results and therefore a signal of 0.5 Vs was considered the limit of detection.

Figure 5 shows time series of $\delta^{13}\text{C}$ (‰) and system sensitivity to illustrate the long term stability of the system in the current configuration (since May 2009). The sensitivity was typically in the range 0.2–0.32 Vs ngC^{-1} . Some variability is evident from Fig. 5b and can be attributed to the internal variability of the filament emission in the IRMS. This variation is taken into account by referencing against the aforementioned gas standard. Repeatability of mixing ratio measurements is evaluated to be less than ± 5 % for all compounds. Together with the specified accuracy of ± 5 % for the gas standard this defines the overall error of ± 10 % for measured mixing ratios. The detection limit in terms of collected amount of carbon is calculated to be 1.5–2.5 ngC , based on the limit

of 0.5 Vs for the IRMS signal and the observed sensitivity range. Figure 5a illustrates also a drift of $\delta^{13}\text{C}$ in the system over the selected period. In order to correct for drift in $\delta^{13}\text{C}$, detrending is accomplished by observing weekly averages as compared to long-term calibration measurement means.

To evaluate the overall precision of the system a series of Gaussian-fitted histograms of detrended $\delta^{13}\text{C}$ for the compounds measured in the standard gas are provided in Fig. 6a–d, with a bin size of 0.1 ‰, outliers greater than 3σ rejected. For ethane, propane and benzene the $1-\sigma$ error was below 0.5 ‰ for all volumes tested. For methyl chloride, the standard deviation is ~ 0.8 ‰ for all tested volumes. These values are based on the entire dataset. The same analysis based on sub-samples including only the 50, 100, or 200 ml measurements yield very similar results. For example, for ethane, the mean $\delta^{13}\text{C}$ is -28.9 , -28.9 , -28.6 and -28.9 ‰, for 50, 100, 200 ml data, and all data, respectively; the corresponding standard deviations are 0.308, 0.296, 0.205, and 0.284 ‰. These values show that the sample volume does not influence the measurements. For other tested compounds, behavior is similar.

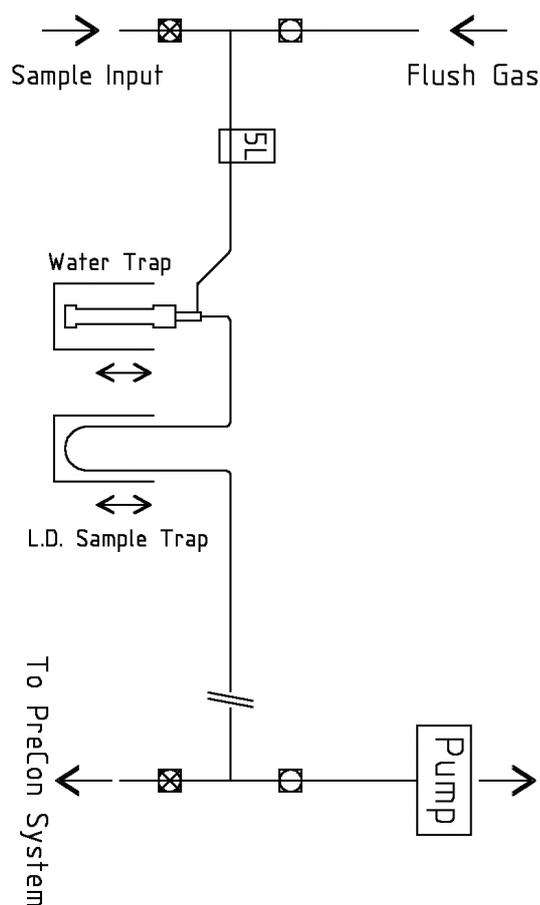


Fig. 4. Ambient air sampling unit. The water trap and the sample trap are large diameter cryogenic stainless steel traps. Flush gas may be He, N₂ or synthetic air. Flows are regulated by a 51 min⁻¹ mass flow controller (MKS instruments). After extraction, the contents of the sample trap are flushed to the preconcentration system (Fig. 1).

The reproducibility for other compounds was tested by introducing another standard gas, containing 20 to 50 ppb of acetylene, ethylene, propylene and C₄ and C₅ saturated hydrocarbons (also see Fig. 3). The results of stability evaluations of these compounds are broadly similar to those of the primary working standard. Table 2 summarizes $\delta^{13}\text{C}$ and sensitivity means and 1- σ errors of all tested compounds.

3 First results

To demonstrate capabilities of this instrument, we present the results of a 48-h measurement campaign of selected non-methane hydrocarbons undertaken over 4–6 August 2009. Samples were taken from an ambient air inlet located ~20 m above ground level at 52°05'14" N, 5°09'57" E. The sampling location is within 500 m of a traffic highway, and is located outside our laboratory on the Utrecht University campus, in a semi-urban environment. Thus, an abundance of

Table 2. Means and 1- σ standard deviations of $\delta^{13}\text{C}$ (‰) and IRMS Sensitivity (Vs ngC⁻¹) for compounds in regularly used calibration gases.

Compound	$\delta^{13}\text{C}$ mean $\pm\sigma$ (‰)	Sensitivity mean $\pm\sigma$ (Vs ngC ⁻¹)
Primary NMHC working standard ^a		
Ethane	-28.898 \pm 0.284	0.249 \pm 0.0053
Propane	-34.716 \pm 0.397	0.254 \pm 0.0063
MeCl	-48.528 \pm 0.795	0.231 \pm 0.0058
Benzene	-27.915 \pm 0.484	0.302 \pm 0.0083
Other tested compounds ^b		
Acetylene	-40.922 \pm 0.441	0.241 \pm 0.0062
Ethylene	-36.307 \pm 0.716	0.239 \pm 0.010
Propylene	-32.955 \pm 0.658	0.258 \pm 0.010
Isobutane	-32.209 \pm 0.542	0.271 \pm 0.0097
Butane	-35.658 \pm 0.476	0.273 \pm 0.0083
Isopentane	-34.927 \pm 0.308	0.33 \pm 0.0095

^a 9-month detrended long-term accuracy levels ^b $n=20$, over period of 1 month.

local sources, dominated by traffic emissions, can be expected for hydrocarbons. Atmospheric conditions at the time of the campaign were characterized by warm stable summer weather. During this period, high surface pressure was located above the North Sea. The sample days were similar meteorologically, with clear skies, light winds, and high temperatures near 30 °C. At night, temperatures decreased to near 20 °C and the winds became near calm.

The samples were taken and processed in situ using the aforementioned ambient sampling unit, with 201 samples (sampling rate 0.5 l min⁻¹) taken at approximately 2-h intervals (excepting necessary calibration runs of the instrument) and processed immediately. The short time interval between samples afforded by the instrument design allowed detailed insight into diurnal evolution of NMHC $\delta^{13}\text{C}$; more so than the majority of previous urban stable carbon isotope studies. The 201 sample size was chosen to ensure IRMS peak areas of >0.5 Vs for the all hydrocarbons of interest.

3.1 Mixing ratio

Broadly, mixing ratios are in line with what may be expected for an urban environment (e.g. Seinfeld and Pandis, 1998), although for some compounds, especially the alkanes, quite high mixing ratios of several ppb were measured. The mixing ratios (Fig. 7a–j and Table 3) show a clear diurnal cycle, which corresponds very well to patterns of urban activity. The unsaturated compounds (acetylene, ethylene, and propylene) exhibit a peak in the morning hours, minimum values in the afternoon, and elevated values at night. Such diurnal cycles agree well with traffic patterns and the development

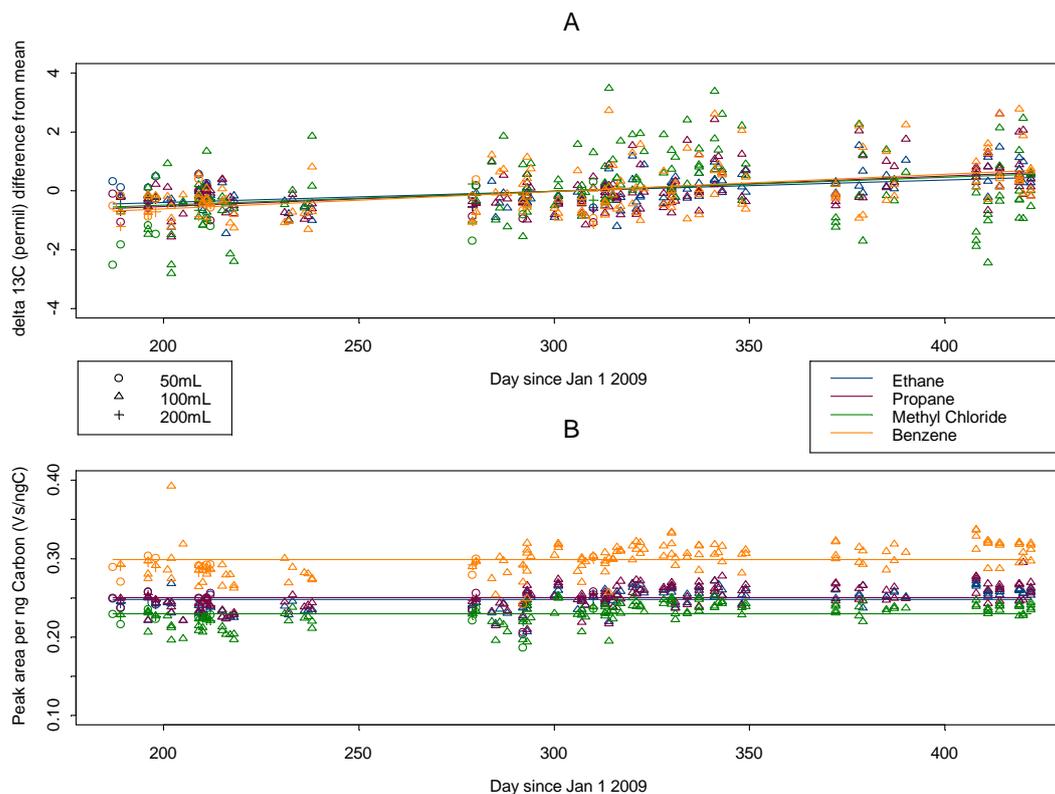


Fig. 5. Time-stability of the system. Panels **A** and **B** show the difference from mean of $\delta^{13}\text{C}$ (‰, panel **A**); and sensitivity (Vs ngC^{-1} , panel **B**) of the 4 tested compounds in the working gas standard, respectively. Data of various injection volumes (50, 100, and 200 ml) are plotted. The lines in panel **A** represent linear fits; the horizontal lines in panel **B** do not represent any trend but are plotted to make the long term variability more visible.

of the boundary layer mixing height. Morning vehicular traffic is intense; heavy congestion on local highways is common in the periods from 07:00 to 09:00 (all times in Central European Summer Time). The afternoon-evening (16:00 to 18:00) peak of traffic, though generally less intense than that of the morning but still notable, is not clearly observed in the data. This is attributed to increased mixing in the afternoon due to the breakup of the nighttime boundary layer, as compared to the morning hours.

Ethane also displays a clear diurnal cycle, but in contrast to the above compounds has peaks in mixing ratio during the night and early morning, far earlier than other compounds. The prevailing meteorological conditions of (near) calm winds during night suppressed mixing and allowed the buildup of continuously emitted gasses. Presuming that the main urban source of ethane is leakage of natural gas, local leakage could cause such an increase of mixing ratio. The daytime decrease may be similarly ascribed to the increase in mixing and dilution.

Isopentane, hexane, and benzene show profiles similar to the unsaturated hydrocarbons mentioned above. The change in mixing during daytime and nighttime can help to explain the afternoon decrease and nighttime buildup in mixing ra-

tio of all alkanes measured, with the exception of n-pentane (Fig. 7h), which exhibits larger daytime than night-time mixing ratios. This implies a different, non-local source that dominates the mixing ratios for this compound. Supporting evidence for a distinct and non-local source can be found in the stable isotope measurements of this compound, of which discussion follows.

3.2 Stable carbon isotope composition

Figure 8a–j shows $\delta^{13}\text{C}$ measurements over the sampling period. In general, $\delta^{13}\text{C}$ averages over the 48-h period (Table 4) agree well with published values from studies of urban air.

Acetylene has a large daily variation (maximum of 5‰ and minimum of -15 ‰), but its mean over the entire period is -9.1 ‰, which falls well in the urban range of -8 ± 4 ‰ as reported in Goldstein and Shaw (2003). The maximum observed in acetylene is more enriched than previous measurements reported in urban environments, but is within the range of daytime summer values reported from rural/marine environments (Redeker et al., 2007).

Ethylene, which shows a very well defined diurnal cycle with minima near -30 ‰ in the early morning hours and maxima near -5 ‰ during the afternoon (24 h mean

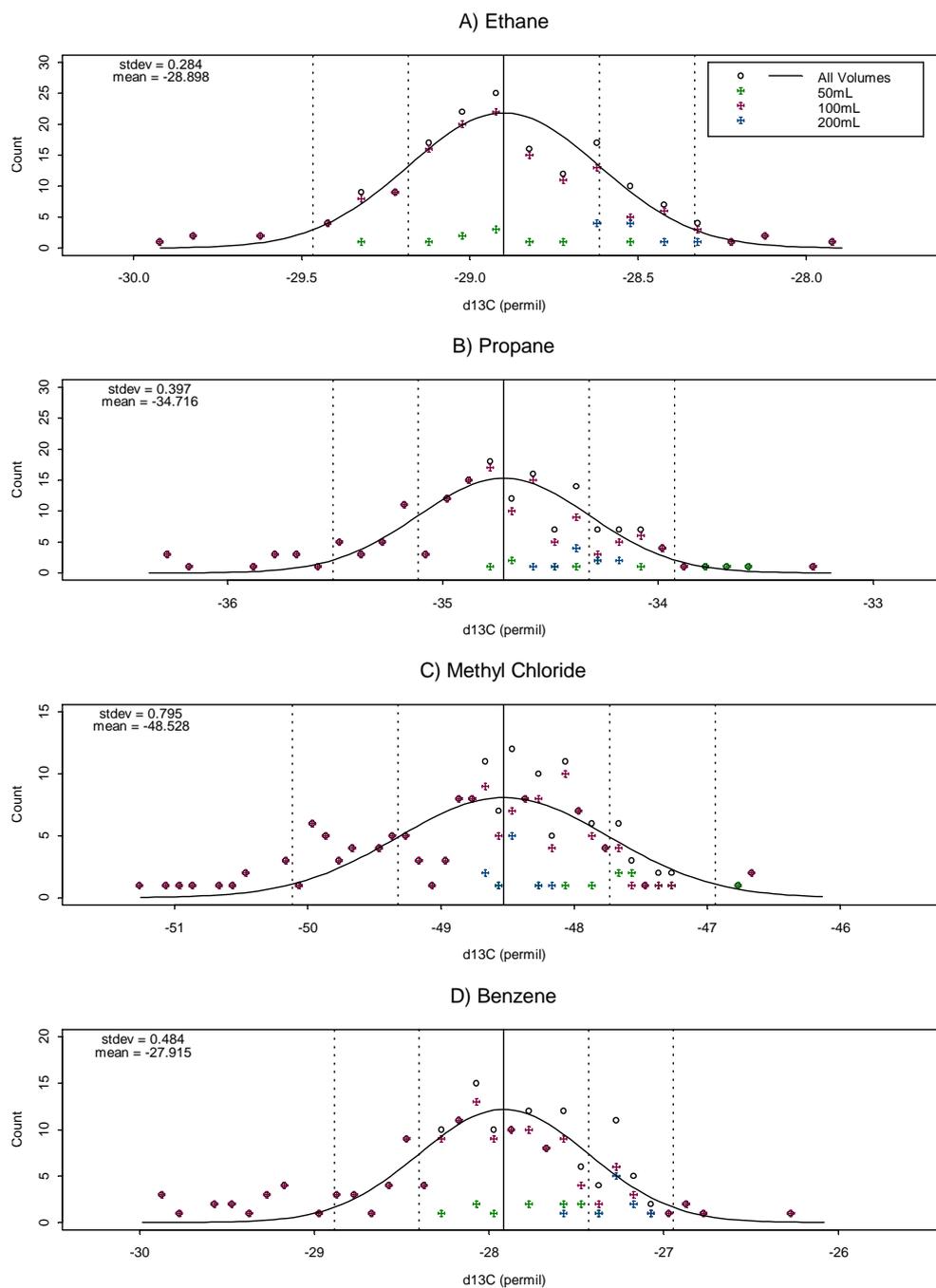


Fig. 6. Histograms of detrended $\delta^{13}\text{C}$ (‰) data, together with Gaussian fit for the Apel-Riemer (AiR) multicomponent NMHC calibration gas, including measurements of various volumes (50, 100, 200 ml) for peak area ranges comparable to measurements. Dashed lines indicate 1 and 2 σ intervals.

–17‰), agrees with expected mean values for C_2 to C_5 alkenes (-22 ± 8 ‰, Goldstein and Shaw, 2003). The large diurnal variation, can be expected for such a reactive compound with a high KIE (18.6‰, Anderson et al., 2004). Strong fractionation occurs during summer daylight hours when OH levels are considerably high. Utilizing the isotopic clock parameterization (Eq. 4, Rudolph

and Czuba, 2000) provides additional support for this: assuming that the nighttime $\delta^{13}\text{C}$ value (mean –27‰) and daytime value (mean –10‰) represent the unoxidized ($\delta_{\text{C}_2\text{H}_4}^0$) and oxidized ($\delta_{\text{C}_2\text{H}_4}$) isotope ratios of ethylene, respectively, a value for $\text{OH KIE}_{\text{C}_2\text{H}_4}$ of 18.6‰ and $\text{OH k}_{\text{C}_2\text{H}_4} = 7.9 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (at 296 K, Atkinson et al., 2006), it is calculated that [OH] required for causing this

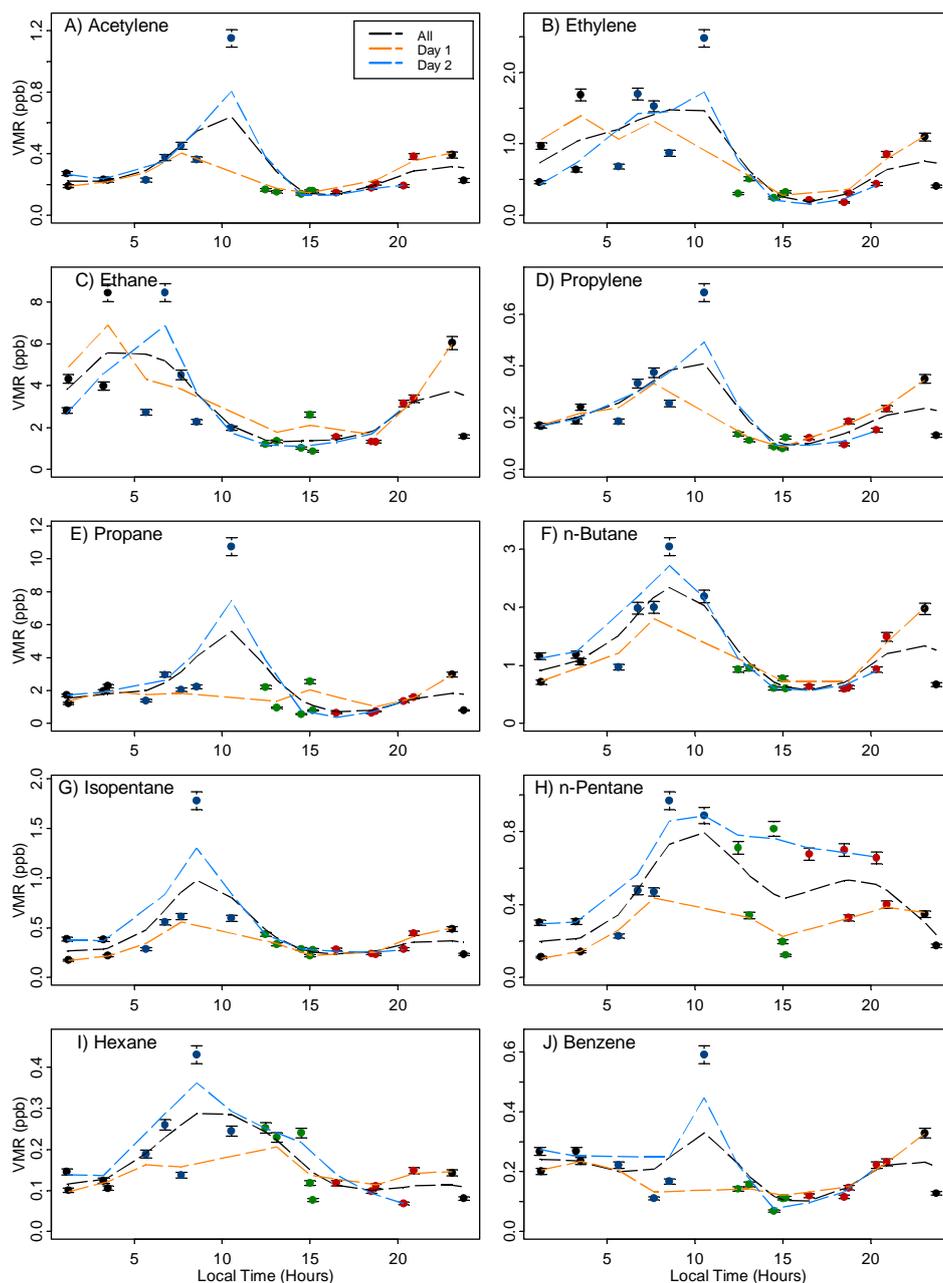


Fig. 7. Mixing ratios (ppb) versus time over 48-h (4–6 August 2009) period, overlapped on one diurnal cycle. Error bars indicate the 10% accuracy levels. Period means in Table 3. Colors indicate time periods: P1 (black): 21:00–05:00; P2 (blue): 05:00–11:00; P3 (green): 11:00–15:30; P4 (red): 15:30–21:00; these correspond to time period colors in Figs. 8 and 9. Period codes correspond to those in Tables 3, 4, and 5. Dashed lines are running averages.

fractionation is 3.6×10^6 molecules cm^{-3} for a 9 h atmospheric processing time. This OH concentration is well within the range for summer tropospheric conditions (e.g., Lu and Khalil, 1991).

The ethane stable isotope ratios we measured are in general more enriched than higher alkanes. This is due to its differing source from natural gas, the ethane in which is known to be relatively enriched. The mean $\delta^{13}\text{C}$ of ethane was mea-

sured to be $-24.5 \pm 0.6\%$ for the entire period. Tsunogai and Yoshida (1999) reported values between -28 to -22% in urban and marine locations. There is almost no diurnal variation in our measurements (with the exception of a slight depletion during the period of highest mixing ratio values, in the morning), which is also reasonable to expect for the most stable and longest-lived non-methane hydrocarbon.

Table 3. Mean mixing ratio and sample standard deviation, 48-h measurements, 4 to 6 August 2009.

Compound	Mean VMR all (ppbv)	σ (ppbv)	Mean VMR P1 ^a (ppbv)	σ (ppbv)	Mean VMR P2 (ppbv)	σ (ppbv)	Mean VMR P3 (ppbv)	σ (ppbv)	Mean VMR P4 (ppbv)	σ (ppbv)
Acetylene	0.29	0.22	0.26	0.07	0.51	0.36	0.15	0.01	0.22	0.09
Ethylene	0.77	0.62	0.88	0.48	1.45	0.71	0.33	0.10	0.40	0.27
Ethane	3.09	2.23	4.52	2.43	3.98	2.68	1.41	0.69	2.14	1.03
Propylene	0.21	0.14	0.21	0.08	0.36	0.19	0.11	0.02	0.16	0.05
Propane	2.02	2.14	1.83	0.77	3.87	3.88	1.41	0.90	0.99	0.45
n-Butane	1.19	0.67	1.13	0.47	2.03	0.74	0.77	0.17	0.85	0.38
Isopentane	0.42	0.34	0.31	0.12	0.76	0.58	0.31	0.08	0.30	0.09
n-Pentane	0.45	0.27	0.23	0.10	0.61	0.31	0.43	0.30	0.55	0.17
Hexane	0.16	0.09	0.12	0.03	0.25	0.11	0.18	0.08	0.11	0.03
Benzene	0.20	0.11	0.24	0.07	0.27	0.21	0.12	0.03	0.17	0.06

^a Period codes are the same as those defined in Fig. 7.

Table 4. Mean $\delta^{13}\text{C}$ (‰) vs. VPDB and sample standard deviation, 48-h measurements, 4 to 6 August 2009.

Compound	Mean $\delta^{13}\text{C}$ (‰) all	σ (‰)	Mean $\delta^{13}\text{C}$ P1 ^a (‰)	σ (‰)	Mean $\delta^{13}\text{C}$ P2 (‰)	σ (‰)	Mean $\delta^{13}\text{C}$ P3 (‰)	σ (‰)	Mean $\delta^{13}\text{C}$ P4 (‰)	σ (‰)
Acetylene	-9.1	4.4	-10.2	1.4	-10.2	4.8	-6.2	6.8	-9.6	2.8
Ethylene	-17.0	7.9	-23.3	3.2	-21.5	5.3	-9.1	4.2	-11.7	6.1
Ethane	-24.5	0.6	-24.1	0.5	-24.6	0.8	-24.6	0.8	-24.6	0.17
Propylene	-21.1	2.3	-21.7	1.3	-19.6	2.5	-20.3	2.5	-22.8	2.1
Propane	-27.9	1.7	-27.0	2.3	-27.8	1.4	-28.6	1.7	-28.3	1.1
n-Butane	-27.6	1.7	-27.0	1.4	-26.2	1.3	-29.3	1.3	-27.8	1.1
Isopentane	-29.0	0.6	-29.0	0.8	-29.0	0.6	-29.4	0.6	-28.9	0.3
n-Pentane	-27.0	1.6	-28.0	1.2	-28.2	0.9	-26.0	2.0	-25.8	0.4
Hexane	-30.4	3.7	-28.6	1.7	-32.1	7.4	-29.4	1.0	-30.7	1.0
Benzene	-26.2	2.3	-25.9	1.4	-26.8	5.1	-25.5	1.6	-26.7	0.2

^a Periods are the same as in Table 3.

The $\delta^{13}\text{C}$ of the C₃ to C₆ alkanes (with the exception of n-butane and n-pentane, see below) show little (clearly apparent) diurnal variation and mean values of -27 to -30‰ during all periods. Previously reported measurements indicated -27 ± 2.5 ‰ (Rudolph et al., 2002; Goldstein and Shaw, 2003). The presence of a single very depleted point (-45‰) in measurements of hexane is notable, but this outlier may be due to an unidentified experimental problem. Apart from this point, standard deviations for these compounds also correspond well to previous results. Benzene also fits well to previous measurements despite some apparent high morning variability: mean -26.2 ± 2.3 ‰, compared to literature values of -27 ± 2 ‰ (Goldstein and Shaw, 2003).

3.3 Source signatures

A common tool for atmospheric isotope research to decipher sources is the Keeling plot analysis, which was first developed for the analysis of stable carbon isotopes of carbon dioxide (Keeling, 1958). This involves correlating $\delta^{13}\text{C}$ against the inverse of the mixing ratio, and linearly fit-

ting the result. The y-intercept of this fit then indicates the isotopic composition of the contaminating source that mixes into background air. This procedure is based on a few assumptions, most importantly: (1) there should be only one source and a stable reservoir into which it is being diluted; and (2) the $\delta^{13}\text{C}$ and inverse mixing ratio should be well-correlated; lest the values calculated become unclear and unreliable (Keeling, 1958). In our dataset, the Keeling plot analysis works well for ethylene, n-butane, and n-pentane (Fig. 9a–c). The isotope source signatures determined this way are given in Table 5. Other measured compounds are not included because of small isotopic variation or low correlation, indicating that the above conditions are violated.

For ethylene the source signatures (~ -27 ‰) derived from this analysis agree well with engine emission measurements (Rudolph et al., 2002; Goldstein and Shaw, 2003). The positive slopes of the Keeling fits are in line with the interpretation of the diurnal variation of the VMR and $\delta^{13}\text{C}$ (see discussion above).

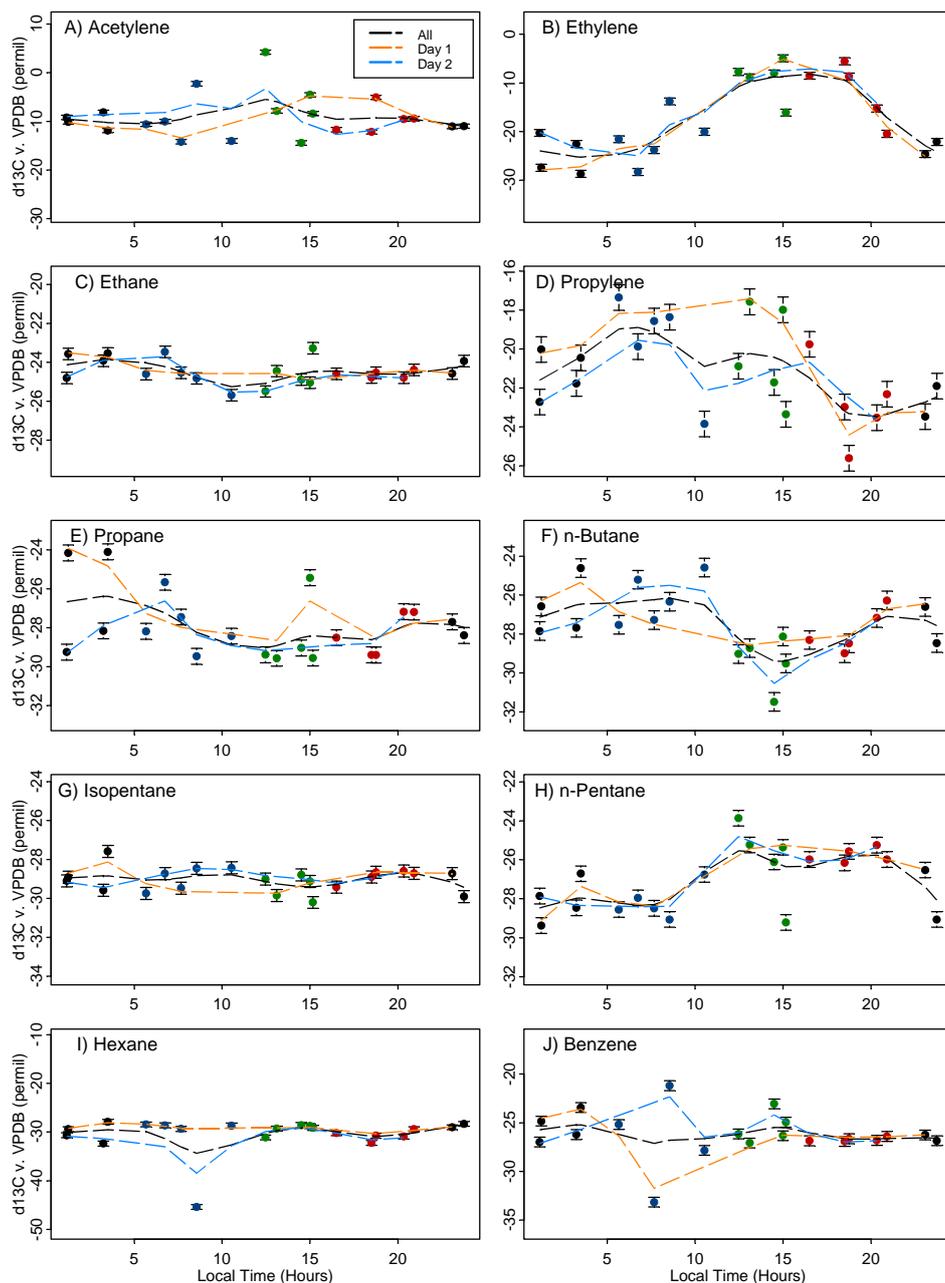


Fig. 8. Compound $\delta^{13}\text{C}$ (‰ vs. VPDB) vs. time (hours) over 48-h (4–6 August 2009) period, overlapped. Error bars indicate $1\text{-}\sigma$ ranges. Period means and standard deviations in Table 4. Colors of points denote the time periods, which are defined in Fig. 7.

The interpretation for n-butane and n-pentane is more complicated because their lifetimes are longer. As a result their mixing ratios are controlled by transport and mixing of different sources. The source signatures of n-butane during periods 3 and 4 (-25.4 and -24.5 ‰, respectively) suggest that emissions from fossil fuel combustion (-27 ± 2.5 ‰, Goldstein and Shaw, 2003) are the dominant local source. However, the reversed slope may indicate that background concentrations of n-butane originate mainly from other sources.

In n-pentane there is a strong departure in source signature values in table 5 period 3: here a strongly correlated source signature of -23.9 ‰ occurs, as compared to more depleted values at other times. This would lend support to the speculation that there is a distinct isotopically different emission occurring at this time as discussed above for the mixing ratios.

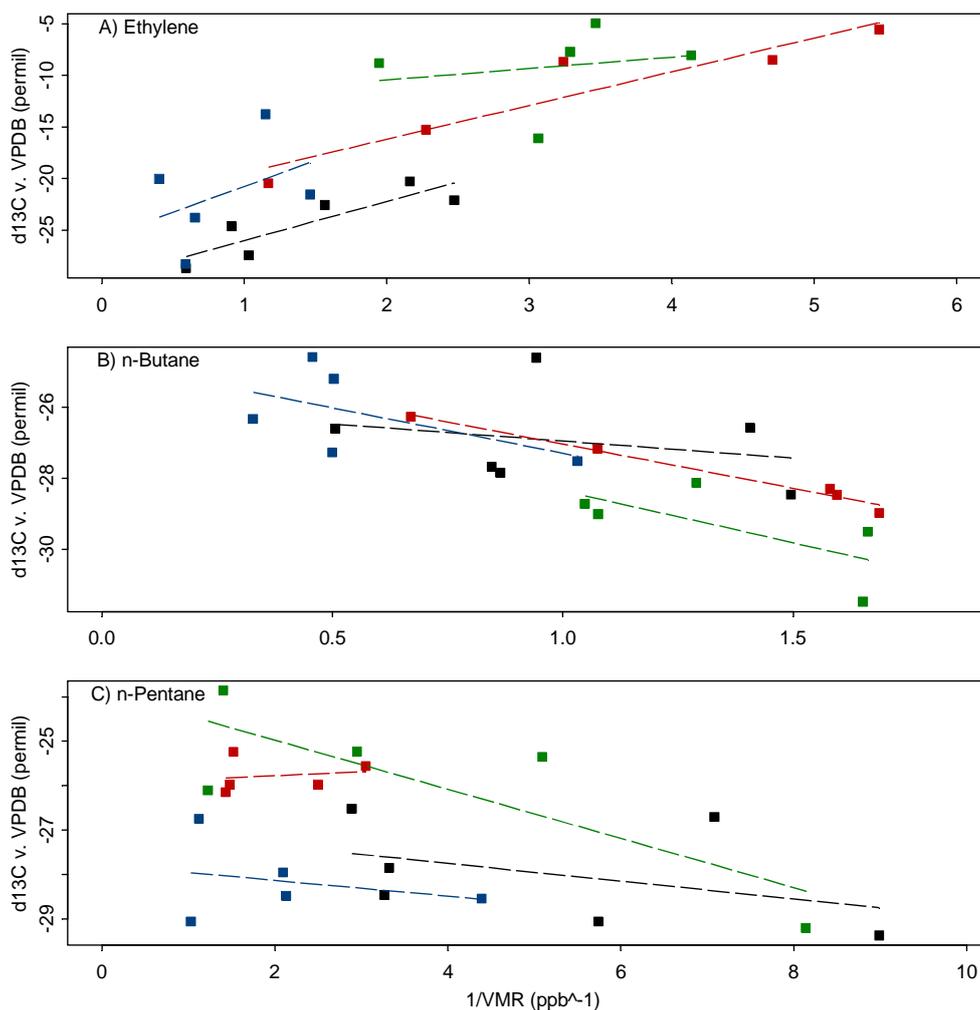


Fig. 9. Ethylene, n-butane, and n-pentane $\delta^{13}\text{C}$ (‰ vs. VPDB) plotted versus inverse mixing ratio (ppb^{-1}) over the 48-h (4–6 August 2009) period, with linear fits to points of each time period. Derived values for isotope source signatures are given in Table 5. Colors indicate periods as indicated in Fig. 7.

Table 5. Source signature (SS, in ‰ vs. VPDB) and r^2 from fits in Fig. 9, 48-h measurements, 4 to 6 August 2009.

Compound	SS all (‰)	R^2 all	SS P1 ^a (‰)	R^2 P1	SS P2 (‰)	R^2 P2	SS P3 (‰)	R^2 P3	SS P4 (‰)	R^2 P4
Ethylene	−26.8	0.68	−29.8	0.76	−25.7	0.17	−12.6	0.04	−22.7	0.89
n-Butane	−24.7	0.52	−26	0.07	−24.7	0.29	−25.4	0.47	−24.5	0.98
n-Pentane	−25.9	0.22	−27	0.17	−27.8	0.08	−23.9	0.65	−26	0.03

^a Periods are the same as in Table 3.

4 Conclusions

We have presented a NMHC stable carbon isotope analysis system capable of high-resolution measurements of many compounds from a large variety of sample sources with small measurement errors (1 ‰ vs. VPDB or less). In particular, the capability to process high volume atmospheric allows examination of samples with large quantities of bulk gases and

CO_2 , without loss of any compounds of interest, and with a short processing time as well. As the first results demonstrate, $\delta^{13}\text{C}$ values measured during a 48-h ambient air measurement campaign agree well with previous research, while highlighting the complex diurnal behavior of hydrocarbons in an urban environment. This on the one hand demonstrates reliable operation of the system and on the other opens the doorway to exciting future measurements.

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