J. Chem. Chem. Eng. 5 (2011) 1097-1106

First Measurements of Biogenic Hydrocarbons in Air in a Tropical Cloudy Forest, Monteverde, Costa Rica

Germain Esquivel-Hernández[1*], Sergio Madrigal-Carballo[2], Rosa Alfaro-Solís[1], José Pablo Sibaja-Brenes[1] and Juan Valdés-González[1]

1. Atmospheric Chemistry Laboratory, National University, Escuela de Quimica, Heredia 86-3000, Costa Rica

2. Polymers Research Group, National University, Escuela de Quimica, Heredia 86-3000, Costa Rica

Received: August 23, 2011 / Accepted: September 20, 2011 / Published: December 10, 2011.

Abstract: Measurements of biogenic hydrocarbons in ambient air were carried out during 2008 in a cloudy tropical forest in Monteverde, Costa Rica. Isoprene, α-pinene, β-pinene, 3-carene, d-limonene and γ-terpinene were sampled by adsorption cartridges filled with graphitized carbon and Tenax TA and analyzed by GC-FID. Parallel samples were collected using 2 liters canisters and analyzed by GC-MS. *In situ* ozone measurements were done by using a UV absorption instrument. Increasing mixing ratios of isoprene, related to photosynthetic activity and ambient temperature, were observed during the morning and afternoon hours. Maximum isoprene's mixing ratio reached 30 ppbv in March. An increment in the emissions of monoterpenes during high humidity periods and after rain events was also observed. Average mixing ratios of monoterpenes were between 0.3 and 3 ppbv. During the dry season (December to April), most abundant hydrocarbons were isoprene and d-limonene, whereas in the rainy season (May to November) isoprene and *α*-pinene were dominant. Hydrocarbons mixing ratios were used to estimate the OH and NO_3 densities. Average OH density was calculated in $(4.87 \pm 0.17) \times 10^6$ mol/cm^3. Average NO_3 density was calculated in $(1.39 \pm 0.09) \times 10^8$ mol/cm^3. Average O_3 mixing ratio was 30.9 ppbv.

Key words: Biogenic hydrocarbons, ambient air, atmospheric oxidation, cloudy forest.

1. Introduction

Vegetation emits a variety of volatile organic compounds (VOCs) into the air. Among these compounds, monoterpenes and isoprene together make up 55% of the estimated 1150 TgC (1 Tg = 10^{12} g) of biogenic volatile organic compounds emitted each year into our atmosphere. Monoterpenes alone are comparable to the 150 TgC per year total emissions estimated from all anthropogenic sources including fossil fuel usage and biomass burning [1-2]. These compounds play an important role in the chemistry of the atmosphere, playing a central role in influencing the oxidative capacity of the atmosphere and were predicted to have a particularly strong impact on tropical regions [3].

Monoterpenes and isoprene react quickly with OH radical, ozone and radical NO_3. These reactions lead to the formation of by-products such as ozone, hydrogen peroxide, organic peroxides, aldehydes, ketones and secondary organic aerosols (SOA), including carboxylic acids (C_6-C_{34}), sesquiterpenes and the fatty diterpenes. The formation of these compounds affects the local and regional dynamics of some processes, such as cloud formation, the production of organic aerosols and wet deposition processes [4]. Having in mind this important role of VOCs, a detailed description of the atmospheric concentrations and the exchange processes on a local and regional scale as well as a better understanding of the biological production and the chemical fate of all these compounds in the atmosphere is urgently needed,

---

[*] **Corresponding author:** Germain Esquivel-Hernández, M.Sc., research fields: atmospheric chemistry, environmental chemistry. E-mail: gesquiveher@gmail.com.

especially in the tropics where our knowledge is poorest [5]. In this study, we selected a cloudy tropical forest located in Monteverde, Costa Rica, which is an excellent site for studying the biogenic release under tropical conditions and in or over the pristine tropical forest.

Under these pristine conditions, one interesting topic to study is the combined efficiency of the physical and chemical removal processes. This is defined as the atmospheric residence time, i.e. the time needed for a compound's initial concentration in the atmosphere to be reduced to 1/e times the initial concentration [6]. In order to evaluate these removal processes, gas chromatography (GC) has been used extensively to determinate the concentration of reactive VOCs in ambient air, allowing to investigate the emission, distribution, and oxidation of these VOCs in the atmosphere [7-11]. It has been shown that the atmospheric variability of short lived VOCs measured by gas chromatography can be used to estimate OH and NO_3 densities [6, 12]. The authors proposed an empirical formula, with an inverse relationship between the variability of short lived VOCs, expressed by the standard deviation, and atmospheric lifetime. In the proposed expression:

$$\sigma(\ln(X)) = A\tau^{-b} \tag{1}$$

$\sigma((\ln(X))$ is the relative standard deviation of the natural logarithm of mixing ratios, τ is the residence time and A and b are empirical fitting parameters [6, 12]. This expression has been used to determinate average OH and NO_3 densities along the back trajectory and to estimate the remoteness of sampling locations [6, 12].

In this study, the seasonal trends and diurnal cycles of five biogenic VOCs will be presented and discussed in terms of sources and local meteorology. The variability of these VOCs as function of their atmospheric residence time will be also presented. This variability was used to estimate OH and NO_3 densities under known ozone concentrations and by using the measured concentrations of five biogenic hydrocarbons during 2008 in Monteverde, Costa Rica.

2. Materials and Methods

2.1 Sampling Site

Air samples were collected in the Monteverde Cloud Forest Reserve, in the Cordillera de Tilaran, in west central Costa Rica and located in the province of Puntarenas (10'18" N, 84'48" W). This reserve is a private protected area, established in October 1972, and belongs to the Tropical Science Centre, a Costa Rican NGO.

In Monteverde, the three distinct seasons are differentiated primarily by the seasonal migration of the intertropical convergence zone: (I) a dry season (mid-January to April), characterized by moderate northeasterly tradewinds and wind-driven cloud and mist, (II) a wet season (May to October), characterized by convective precipitation, and (III) a transition season (November to mid-January), characterized by strong tradewinds and wind-driven precipitation and mist [13].

The study site is located ca. 2.2 km southeast of the continental divide, inside a laboratory facility located in a clearing surrounded by tropical forest, closed to the Monteverde Cloud Forest Reserve Headquarters. Average elevation at the study site is 1529 m. a. s. l.

2.2 Sampling and Analysis

In this study, we report on seven two days sampling periods between March and November 2008 of six speciated biogenic hydrocarbons mixing ratios inside the cloud forest of Monteverde (isoprene, α-pinene, β-pinene, 3-carene, d-limonene and γ-terpinene). Temperature and wind speeds were measured using a HOBO weather station (Onset, Bourne, MA), mounted ca. 15 m above ground level and installed closed to the laboratory facility. Ozone concentration was measured continuously by using a UV absorption instrument DKK, Model GUX-113-J (DKK, Japan).

Air was continuously pulled from the roof of the laboratory facility through an impregnated inlet filter for particulate and ozone removal [8]. The filter material used was Teflon impregnated with glass fiber. The filters were impregnated with sodium thiosulfate, which was used as ozone scrubber. The ozone removal efficiency was better than 90% and was tested regularly in the laboratory. As reported by Jüttner [10], high humidity often leads to water deposition in the adsorption cartridges, which may interfere in the chromatographic separation. Therefore, it was used a 70 cm × 5 mm I.D. glass column, positioned in a Dewar vessel and cooled with crushed ice [10]. The air was pulled through a 0.32 cm I.D. Teflon line with a total length of 5 m.

Two types of adsorption cartridges connected in series were used in this study. The front adsorption cartridge was 80 mm × 3 mm I.D. glass tube filled with 0.4 mL of Tenax (60-80 mesh). The back cartridge (same length and I.D.) was filled with 0.4 mL Carbotrap C, 60-80 mesh. The sampling system was connected to a diaphragm pump. Air flow was regulated by using a flow controller and a calibrated rotameter. The average air volume was 6.0 L collected in one hour. After completion of the sampling, the cartridges were returned to glass vials and transported to the laboratory inside a container with a ground glass joint. This sampling methodology has been reported by several authors in the past [7, 9-10].

In the laboratory, thermal desorption was carried out in a modified injector of a Perkin Elmer Autosystem XL gas chromatograph. Cryogenic preconcentration was done in the first 20 cm of the analytical column by using liquid nitrogen as coolant. The analytical column was a fused silica capillary column 60 m long × 0.32 mm I.D., with a 1.0 µm thick crosslinked methylsilicone DB-1 as stationary phase (Phenomenex, USA). After transfer was complete, analytes were separated using the following temperature program: 30 °C (3 min), 30 °C to 50 °C at 4.0 °C/min, 50 °C to 200 °C at 5.0 ° C/min (7 minutes). Detection was by flame ionization detector (FID). The FID response was set equal for all hydrocarbons. The detection limit of the method was estimated as a chromatographic peak three times the noise for each compound, and was 25 pptv for isoprene and 8 pptv for monoterpenes for a 6.0 L sample volume. Identifications were made from retention data, using different temperature programs, and were confirmed by mass spectrometric studies on parallel samples collected in 2 L canisters. The canisters were analyzed in the Rowland-Blake Group, Department of Chemistry, University of California, Irvine, USA.

3. Results and Discussion

3.1 Meteorological Conditions and Ozone Concentrations

This study was conducted in the three distinct seasons in Monteverde during 2008. In the dry season, sampling was done at the end of March and April. Average temperature in March and April was 19.4 °C, with a minimum and maximum of 18.2 and 21.9 °C, respectively. Sampling in the wet season was done in September and the last week of October. It was registered an average temperature of 16.3 °C, with values ranged from 14.3 and 19.8 °C. Late in the year, sampling in the transition season was done in the first week of November. Average temperature was 16.0 °C, with a minimum and maximum of 14.1 and 18.3 °C. A high relative humidity along the sampling periods in the three seasons, with a consistent average of 90% and maximum values reaching 99% in some periods of the day, was observed. As expected, the minimum relative humidity was observed around noon, where the temperature was the highest. During the dry season sampling period, six rain events were registered in March, with an average value of 0.59 mm. In October and November, 11 rain events per day were registered in Monteverde, with an average precipitation at the study site of 0.69 mm.

Representative back trajectories for Monteverde in 2008 are shown in Fig. 1 [14]. In the dry season, air masses are dominantly transported from the Caribbean Sea by the trade winds, with a main wind direction

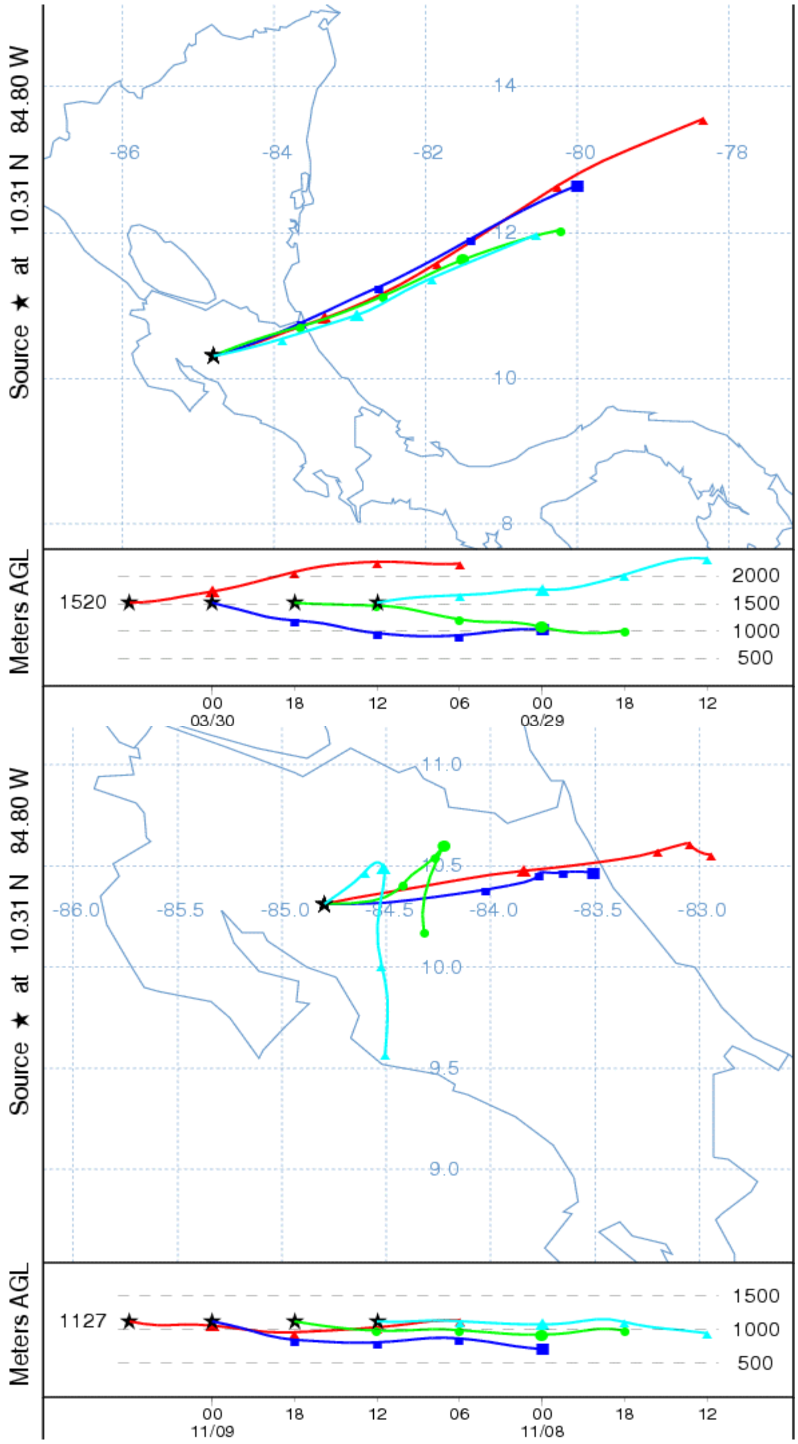

Fig. 1 24 h backward trajectory for March 29 (top) and for November 08 (bottom) [14].

northeast to southwest. In the wet and transition seasons, some air masses intrusions from south and southeast was observed, as result of air masses transported by continental winds. However, air masses transported from the Caribbean Sea are still dominant. In the study site, average wind speed in March-April was 2.2 m/s, and in October-November were 5.4 m/s, with a main direction from east.

Mean hourly ozone concentrations in Monteverde in March-April and in October-November are illustrated in Fig. 2. Mean ozone concentration in 2008 was 30.9, where the higher ozone concentrations were registered in March-April, with an hourly mean concentration of 32 ppbv. During the sampling periods, ozone mixing ratios were below 40 ppbv, which allow us to classify Monteverde as a remote site. This finding will be discussed later together with the hydrocarbon data presented in this work.

3.2 Biogenic Hydrocarbons Mixing Ratios

The mean monthly mixing ratios of the six species measured in Monteverde in 2008 are shown in Table 1. The higher mean concentrations of BVOCs were found in March and October. In March the mixing ratios were between 7.1 ppbv (isoprene) and 0.5 ppbv (γ-terpinene), whereas in October, the range of concentrations was 6.5 ppbv (isoprene) to 0.4 ppbv (β-pinene). This seems to indicate an influence of local meteorological conditions (temperature and rainfall) on the mixing ratios of the six biogenic hydrocarbons. It has been demonstrated that isoprene emissions are controlled by temperature and light [15-16]. Besides these factors, the ambient levels are dependent on the mixing within the boundary layer and the atmospheric oxidation by ozone and OH and NO_3 radicals. The influence of temperature has been also reported for monoterpenes, where the higher mixing ratios are usually observed during the day [15]. Rainfall has also a positive influence on monoterpenes emissions from plants, which has been attributed to physical stress and to the change of environmental parameters [8, 16]. The influence of these factors on the mixing ratios of the most abundant hydrocarbons is observed in Fig. 3 and Fig. 4. The mixing ratio of the most abundant hydrocarbon, isoprene, is clearly influenced by temperature, as increasing mixing ratios were observed during the noon hour and the afternoon. Isoprene's mixing ratio reached 30.0 ppbv during the warmer hours in March. Increasing concentrations of isoprene after sunrise was also observed, which may indicate a linkage between isoprene concentrations and photosynthesis [16]. An influence of precipitations on the mixing ratios of some monoterpenes, like d-limonene, was also observed, which is illustrated in Fig. 4 and Fig. 5. This effect has been reported in studies carried out in deciduous forests [8]. Increasing concentrations of monoterpenes at night may attributable to a strongly reduced vertical mixing and the height of the boundary layer in Monteverde. This effect has been reported by other authors [6, 8].

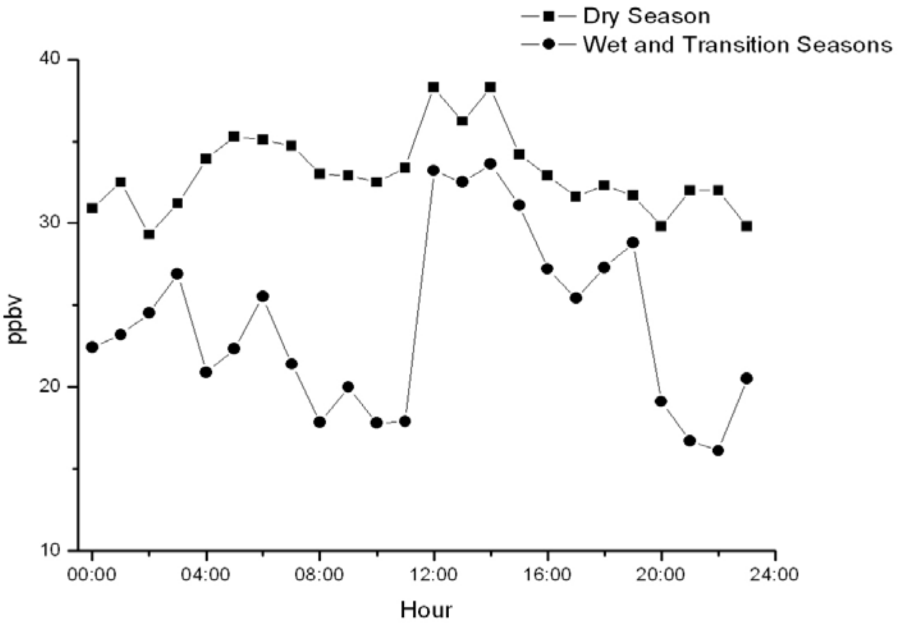

Fig. 2 Average hourly ozone concentration at the Monteverde sampling site during 2008.

Table 1 Mean monthly concentrations of the six biogenic hydrocarbons measured in Monteverde during the dry season (March and April 2008) and the wet and transition seasons (September, October and November 2008).

Compound	Mean concentration (ppbv)				
	March	April	September	October	November
Isoprene	7.1	1.7	1.1	6.5	2.4
α-pinene	0.6	0.1	0.1	2.9	0.1
β-pinene	0.8	0.2	0.1	0.4	0.1
3-carene	0.7	0.2	0.2	1.1	0.1
d-limonene	5.6	0.3	0.2	1.3	0.1
γ-terpinene	0.5	0.2	< 0.1	1.5	< 0.1

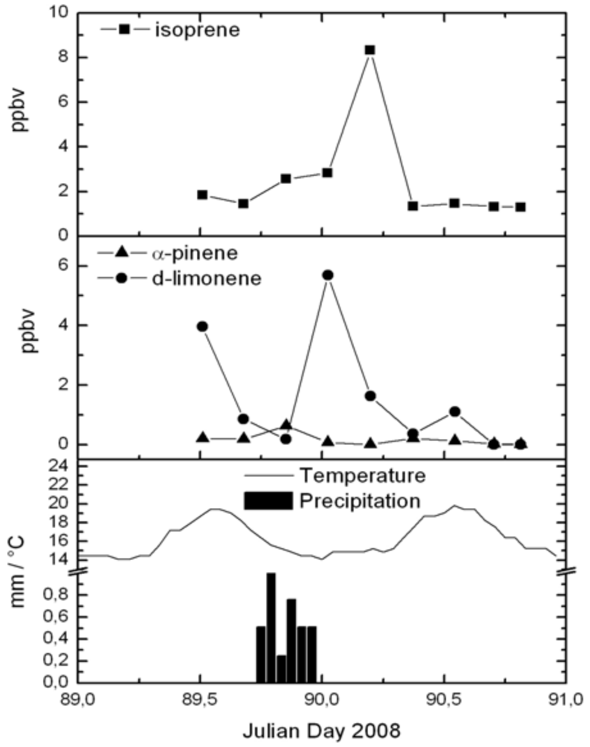

Fig. 3 Mixing ratio time series of isoprene (top), α-pinene, d-limonene (middle), and temperature and precipitation (bottom) from 29 to 30 March 2008.

The mean daily mixing ratios of the three most abundant species is shown in Fig. 5. During the dry season, most abundant hydrocarbons were isoprene and d-limonene. Isoprene and d-limonene daily average mixing ratio was 4.4 and 2.8 ppbv, respectively. Other monoterpenes species mean mixing ratios were between 0.3 and 0.5 ppbv. The highest isoprene's concentrations were registered in March, with a daily average mixing ratio of 16.6 ppbv measured on March 15. These mixing ratios can be related with the relative high temperatures in Monteverde during March, where maximum temperatures can reach 20 °C or higher. In the wet and transition seasons, isoprene and α-pinene were the dominant species. Average isoprene and α-pinene mixing ratios were 3.1 and 1.0 ppbv, respectively. Similarly to the dry season, other monoterpenes concentrations were between 0.3 and 0.6 ppbv. The increase in the hydrocarbons mixing ratios observed in October can be related to the influence of precipitations on hydrocarbons emission, as discussed before. However, average mixing ratios of monoterpenes measured in the wet and transition season were about 1.6 times smaller than the values measured in the dry season. For isoprene, this ratio was practically the same as for the monoterpenes (1.5), which may indicate that the influence of temperature is the most important environmental factor on controlling the emissions of these compounds in Monteverde, although this conclusion must be corroborated by other studies, such as *in situ* enclosure measurements.

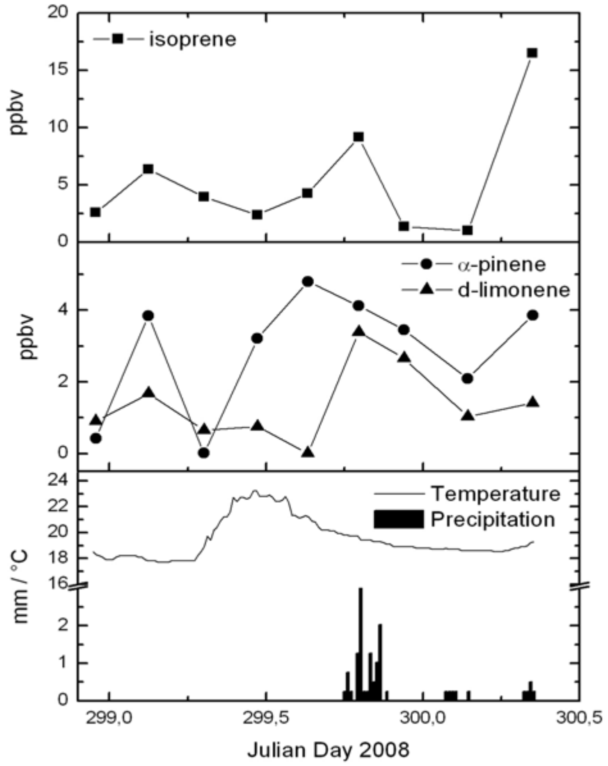

Fig. 4 Mixing ratio time series of isoprene (top), α-pinene, d-limonene (middle), and temperature and precipitation (bottom) from 26 to 27 October 2008.

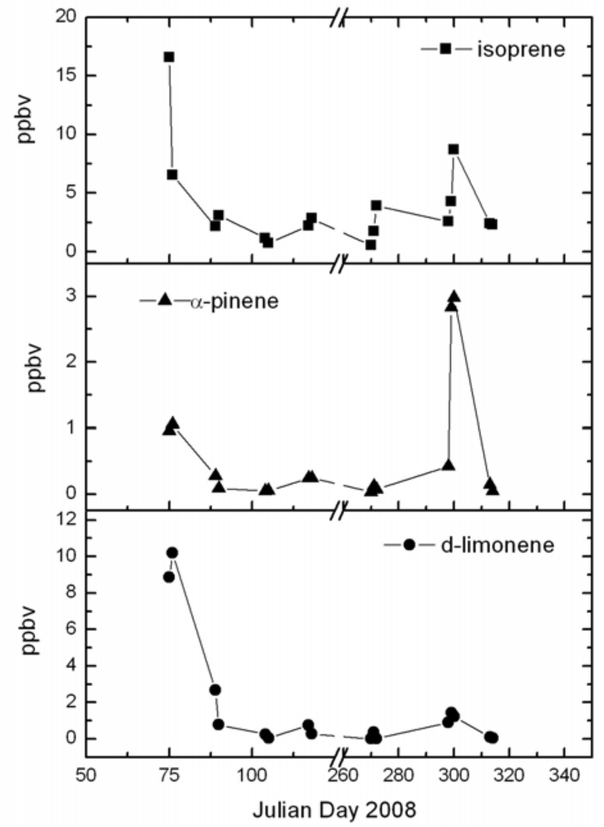

Fig. 5 Mean daily concentration of selected biogenic hydrocarbons with isoprene (top), α-pinene (middle) and d-limonene (bottom) during 2008.

3.3 Estimation of OH and NO_3 Radical Concentrations

In order to estimate the OH and NO_3 concentrations in Monteverde, we followed the method previously described by other authors [6, 12]. In this procedure, it is assumed that the variability in the dataset of VOCs species is controlled by the O_3 and OH concentration during the day, whereas during the night, this variability is controlled by the O_3 and NO_3 concentration. Because measured VOCs react with more than one oxidant (e.g. HO and O_3) and the atmospheric concentration of either one is known (e.g. O_3), OH and NO_3 concentration can be estimated by using Eq. (1). The standard deviation of the gradient *b* (Eq. (1)) is then used to express the uncertainty in the HO and NO_3 estimate. For the application of this method, it is also important that the hydrocarbon data are separated into day-time concentrations and night-time concentrations, in order to minimize the influence of different sources and different radical chemistry on the data analysis [6]. According to this method, the problem of finding the average HO and NO_3 radical concentrations can be solved by a simple linear programming, where by varying the HO and NO_3 densities, it is possible to estimate an average lifetime and iteratively find the optimal value for OH and NO_3 average, yielding either the maximum correlation in Eq. (1) [12].

The relationship between the diurnal variability of the measured hydrocarbons and their atmospheric lifetime according to Eq. (1) is shown in Fig. 6. The lifetimes were calculated using the reaction rate coefficients from Atkinson and co-workers [17-19]. During the day, the hydrocarbon with the highest variability was d-limonene, in agreement with its relative high reaction rate coefficient with O_3 and OH, thus can be removed more rapidly than the other monoterpenes. γ-terpinene variability can be also attributed to the chemical reactions during the day (this compound has similar O_3 and OH reaction rates coefficients as d-limonene), but also to its low mixing ratios compared to the other species, which contributes to a more efficient removal process. At nights, the hydrocarbons with the highest variability were d-limonene, 3-carene and α-pinene, which also correlate well with the reaction rate with O_3 and NO_3. It has been also demonstrated that the exponent b in Eq. (1) indicates the proximity of the sampling site to the source region, where $b = 0$ indicates a nearby source and no dependence of variability on chemistry; whereas $b = 0.5$ or greater, indicates a remote source, where the variability is significantly influenced by the chemistry [6, 20]. The mean b exponent for the biogenic hydrocarbons diurnal oxidation is 0.55, which indicates that the variability depends on lifetime of the measured species and therefore the chemistry and the transport are determining the ambient concentrations. This result is consistent with the geographical position of the study site inside the Monteverde Cloud Forest Reserve.

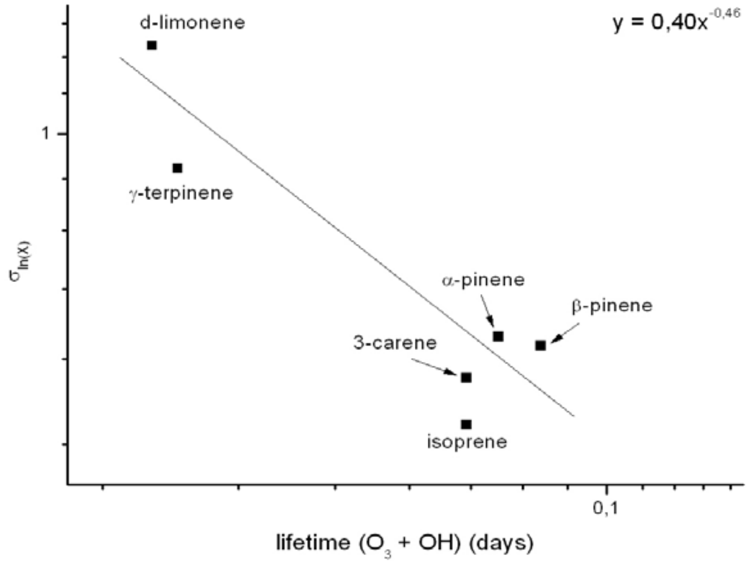

Fig. 6 Average diurnal atmospheric variability versus the lifetime of the biogenic hydrocarbons for the Monteverde sampling site in 2008.

The study site is located in the southwest area of the Reserve, where the air masses reaching the sampling site have traveled over a high density vegetation area of about 3500 ha. The ambient concentrations of the emitted compounds, transported by the trade winds with a main wind direction northeast to southwest, are mainly controlled by the oxidation processes during the day (e.g. reactions with OH and O_3). The mean b exponent calculated for the night-time oxidation reactions (e.g. reaction with $NO_3 + O_3$) is 0.24. When this value is compared with the *b* exponent calculated for the OH + O_3 reactions, the decrease in the *b* exponent can be attributed to a weaker oxidation process by nights. This may also be related to a less efficient mixing process in the boundary layer during nights, which contributes to a stronger influence of the local emissions on the ambient concentrations (Fig. 4). Similar results have been reported by Bartenbach et al. [6]. It has been also demonstrated that the A factor in Eq. (1) can be interpreted as a range factor for sampled air mass ages [13]. Mean of the factors for Monteverde were 0.22-0.44, which are relative small factors. This observation is in agreement with the short-lived and reactive biogenic VOCs included in the variability-lifetime analysis that were mainly removed by reaction with OH radicals from similar air masses and not diluted by mixing [13].

According to the variability-lifetime plot shown in Fig. 6, the calculated mean OH radical density in Monteverde is $4.87 \pm 0.17 \times 10^6$ mol/cm^3. This value is 2.5 times greater than the mean OH radical density predicted by the models for Central America of 1.8-2.0 $\times$ 10^6 mol/cm^3 [21-22]. This observation has been reported recently in other tropical regions, e.g. Suriname and Borneo [23-24] and has been suggested that may be linked to high emissions of isoprene and the production of organic peroxides (RO_2) in low NOx atmospheres [23]. However, Whalley and co-workers [24] suggested that an additional OH source from isoprene oxidation cannot reconcile both the OH and HO_2 observations in tropical atmospheres, unless an additional HO_2 sink mechanism is also included. For Monteverde, the calculation of the OH radical density included only high reactive biogenic VOCs, under the assumption that the selected VOCs were emitted from similar sources types inside the forest. As suggested by Bartenbach et al. [6], the variability-lifetime analysis may be influenced by other factors than chemistry, e.g. source variability or distribution, which may require the use of other high resolution analytical techniques than GC, for example PTR-MS [6]. However, the observed ozone concentrations in Monteverde and the high concentrations of some biogenic VOCs, like isoprene, may indicate that the calculated OH density may reflect chemical processes similar to those reported in other tropical regions. For the calculation of NO_3 radical density, we used the biogenic VOCs data measured during nights (18:00 to 05:00 CST). Under the assumption that by night, NO_3 and O_3 are the most important oxidising species, the calculated mean NO_3 radical density for Monteverde is $1.39 \pm 0.09 \times 10^8$ mol/cm^3. Karl et al. [25] calculated the NO_3 radical concentration in a tropical rain forest at La Selva Biological Station (10.43 N, 83.93 W), situated in the lowland tropical wet forests of Costa Rica. NO_3 radicals were calculated to reach concentrations up to 4 pptv (0.95×10^8 mol/cm^3) with low NOx concentrations. The calculated density for Monteverde is in general agreement with the measurements carried out in the lowland forests of Costa Rica [25].

4. Conclusions

Although we report first measurements of a limited number of biogenic hydrocarbons in Monteverde, some preliminary conclusions regarding the daily and seasonal patterns of these VOCs at this tropical forest may be drawn. The mixing ratios of the biogenic species are influenced by environmental conditions, e.g. temperature, relative humidity and precipitation. In agreement with previous studies, cool and cloudy conditions (wet and transition seasons) showed generally less biogenic hydrocarbons emission than warm and sunny days (dry season), except when precipitations were registered. The variability-lifetime analysis seems to indicate that although the biogenic hydrocarbons sources are relative close to the sampling site, atmospheric chemical reactions play a significant influence in determining the mixing ratios, according to the increasing variability in the most reactive species, like d-limonene. The variability-lifetime analysis was used to estimate the OH and NO_3 concentrations. The mean day OH concentration thus calculated is $4.87 \pm 0.17 \times 10^6$ mol/cm^3, which is about 2.5 times higher compared to the mean OH density estimated for Central America. This finding has also been reported in other tropical forests studies and may be related to other oxidation process than OH reactions. By using this analysis in the night data, the mean NO_3 concentration is calculated to be $1.39 \pm 0.09 \times 10^8$ mol/cm^3. According to the temporal resolution and amount of compounds in our data, we limited our work to estimate the OH and NO_3 concentrations. However, these preliminary radical concentrations are of great value because they were calculated at a rural site with an extensive area of pristine vegetation and unaffected by pollution.

Acknowledgments

The authors are grateful for access to the field sites and logistical support by the Tropical Science Center and the Monteverde Cloud Forest Reserve. We also thank Prof. Dr. Donald Blake, University of California, Irvine, for his help in the GC-MS analysis of air samples collected in Monteverde.

References

[1] Williams, J.; Yassaa, N.; Bartenbach, S.; Lelieveld, J. Mirror Image Hydrocarbons from Tropical and Boreal Forests. *Atmos. Chem. Phys. Discuss.* **2006,** *6,* 9583-9602.

[2] Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; et al. A Global Model of Natural Volatile Organic Compound Emissions. *J. Geophys. Res.* **1995,** *100,* 8873-8892.

[3] Kuhn, U.; Rottenberger, S.; Biesenthal, T.; Wolf, A.; Schebeske, G.; Ciccioli, P.; Brancaleoni, E.; et al. Isoprene and Monoterpene Emissions of Amazonian Tree Species during the Wet Season: Direct and Indirect Investigations on Controlling Environmental Functions. *J. Geophys. Res.* **2002,** *107,* 8071-8083.

[4] Seinfeld, J.; Pandis, S. *Atmospheric Chemistry and Physics from Air Pollution to Climate Change;* Wiley Interscience Publication: USA, 1998; pp 234-292.

[5] Kesselmeier, J.; Ciccioli, P.; Kuhn, U.; Stefani, P.; Biesenthal, T.; Rottenberger, S.; Wolf, A.; et al. Volatile Organic Compound Emissions in Relation to Plant Carbon Fixation and the Terrestrial Carbon Budget. *Global*

Biogeochem. Cycles **2002,** *16,* 1126-1134.

[6] Bartenbach, S.; Williams, J.; Plass-Dülmer, C.; Berresheim, H.; Lelieveld, V. In-situ Measurement of Reactive Hydrocarbons at Hohenpeissenberg with Comprehensive Two-Dimensional Gas Chromatography (GC×GC-FID): Use in Estimating HO and NO_3. *Atmos. Chem. Phys.* **2007,** *7,* 1-14.

[7] Hoffmann, T.; Jacob, P.; Linscheid, M.; Klockow, K. Measurements of Biogenic Hydrocarbons and Their Atmospheric Degradation in Forests. *Intern. J. Environ. Anal. Chem.* **1993,** *52,* 29-37.

[8] Helmig, D.; Greenberg, J.; Guenther, A.; Zimmerman, P. Volatile Organic Compounds and Isoprene Oxidation Products at a Temperate Deciduous Forest Site. *J. Geophys. Res.* **1998,** *103,* 22414-23397.

[9] Strömvall, A. M.; Petersson, G. Protection of Terpenes Against Oxidative and Acid Decomposition on Adsorbent Cartridges. *J. Chromatogr.* **1992,** *589,* 385-389.

[10] Jüttner, F. A Cryotrap Technique for the Quantitation of Monoterpenes in Humid and Ozone-rich Forest air. *J. Chromatogr.* **1988,** *442,* 157-163.

[11] Brancaleoni, E.; Scovaventi, M.; Frattoni, M.; Mabilia, R.; Ciccioli, P. Novel Family of Multi-Layer Cartridges Filled with a New Carbon Adsorbent for the Quantitative Determination of Volatile Organic Compounds in the Atmosphere. *J. Chromatogr. A.* **1999,** *845,* 317-328.

[12] Karl, T.; Crutzen, P. J.; Mandl, M.; Staudinger, M.; Guenther, A.; Jordan, A.; Fall, R.; Lindinger, W. Variability-Lifetime Relationship of VOCs Observed at the Sonnblick Observatory 1999: Estimation of HO-densities. *Atmos. Environ.* **2001,** *35,* 5287-5300.

[13] Clark, K.; Nadkarni, N.; Schaefer, D.; Gholz. H. Cloud Water and Precipitation Chemistry in Tropical Montane Forest, Monteverde, Costa Rica. *Atmos. Environ.* **1998,** *32,* 1595-1603.

[14] Draxler, R. R.; Rolph, G. D. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) [Online]; NOAA Air Resources Laboratory: Silver Spring, MD, 2003; http://www.arl.noaa.gov/ready/hysplit4.html.

[15] Atkinson, R.; Arey, J. Atmospheric Chemistry of Biogenic Organic Compounds. *Acc. Chem. Res.* **1998,** *31,* 574-583.

[16] Kesselmeier, J.; Staudt, M. Biogenic Volatile Organic Compounds (VOC): An Overview on Emission, Physiology and Ecology. *J. Atmos. Chem.* **1999,** *33,* 23-88.

[17] Atkinson, R.; Aschmann, S. M.; Pitts, J. N. Rate Constants for the Gas-Phase Reactions of the OH Radical with a Series of Monoterpenes at 294 K. *Int. J. Chem. Kinet.* **1986,** *18,* 287-299.

[18] Atkinson, R. Gas-Phase Tropospheric Chemistry of Organic Compounds. *J. Phys. Chem. Ref. Data.* **1997,** *26,* 215-290.

[19] Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; et al. Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Volume II-Gas Phase Reactions of Organic Species. *Atmos. Chem. Phys.* **2006,** *6,* 3625-4055.

[20] Jobson, B. T.; Parrish, D. D.; Goldan, P.; Kuster, W.; Fehsenfeld, F. C. Spatial and Temporal Variability of Nonmethane Hydrocarbon Mixing Ratios and Their Relation to Photochemical Lifetime. *J. Geophys. Res.* **1998,** *103,* 13557-13567.

[21] Lelieveld, J.; Peters, W.; Dentener, F. J.; Krol, M. C. Stability of Tropospheric Hydroxyl Chemistry. *J. Geophys. Res.* **2002,** *107,* ACH 17-01-17-11.

[22] Wang, Y.; Jacob, D. J. Anthropogenic Forcing on Tropospheric Ozone and OH Since Preindustrial Times. *J. Geophys. Res.* **1998,** *103,* 31123-31135.

[23] Kubistin, D.; Harder, H.; Martinez, M.; Rudolf, M.; Sander, R.; Bozem, H.; Eerdekens, G.; et al. Hydroxyl Radicals in the Tropical Troposphere over the Suriname Rainforest: Comparison of Measurements with The Box Model MECCA. *Atmos. Chem. Phys.* **2010,** *10,* 9705-9728.

[24] Whalley, L. K.; Edwards, P. M.; Furneaux, K. L.; Goddard, A.; Ingham, T.; Evans, M. J.; Stone, D.; et al. Quantifying the Magnitude of a Missing Hydroxyl Radical Source in a Ttropical Rainforest. *Atmos. Chem. Phys. Discuss.* **2011,** *11,* 5785-5809.

[25] Karl, T.; Potosnak, M.; Guenther, A.; Clark, D.; Walker, J.; Herrick, J. D.; Geron, C. Exchange Processes of Volatile Organic Compounds above a Tropical Rain Forest: Implications for Modeling Tropospheric Chemistry above Dense Vegetation. *J. Geophys. Res.* **2004,** *109(D18306),* 1-19.