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Atmospheric volatile organic compounds (VOC) at a remote tropical forest site in central Amazonia

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Abstract

According to recent assessments, tropical woodlands contribute about half of all global natural non-methane volatile organic compound (VOC) emissions. Large uncertainties exist especially about fluxes of compounds other than isoprene and monoterpenes. During the Large-Scale Biosphere/Atmosphere Experiment in Amazonia – Cooperative LBA Airborne Regional Experiment 1998 (LBA-CLAIRE-98) campaign, we measured the atmospheric mixing ratios of different species of VOC at a ground station at Balbina, Amazonia. The station was located 100 km north of Manaus, SE of the Balbina reservoir, with 200–1000 km of pristine forest in the prevailing wind directions. Sampling methods included DNPH-coated cartridges for carbonyls and cartridges filled with graphitic carbons of different surface characteristics for other VOCs. The most prominent VOC species present in air were formaldehyde and isoprene, each up to several ppb. Concentrations of methylvinyl ketone as well as methacroleine, both oxidation products of isoprene, were relatively low, indicating a very low oxidation capacity in the lower atmospheric boundary layer, which is in agreement with a daily ozone maximum of < 20 ppb. Total monoterpene concentration was below 1 ppb. We detected only very low amounts of VOC species, such as benzene, deriving exclusively from anthropogenic sources. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Volatile organic compounds; VOC; Tropical atmosphere; LBA

1. Introduction

Biogenic nonmethane volatile organic compounds (NMVOC) including isoprenoids such as isoprene and terpenes, as well as a large number of other species from the groups of alkanes, alkenes, alcohols, esters, carbonyls, and acids (for a review see Kesselmeier and Staudt, 1999), are found in the atmosphere ranging between some ppb up to several ppb. Some species, including isoprene and some monoterpenes, sesquiterpenes, and other reactive VOC (ORVOC) species can be quite reactive under atmospheric conditions, as reflected by their short chemical lifetimes between some minutes and hours. Thus, the emission of biogenic VOCs plays a central role in the atmosphere, influencing the oxidative capacity of the atmosphere. Furthermore, they contribute to the

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production of air pollutants as well as to greenhouse gases such as acids, carbonyls, ozone, carbon monoxide, and methane. They can directly or indirectly increase the acidity of the atmosphere and provide the starting material for much of the natural atmospheric aerosol (Graedel, 1979; Altshuller, 1983; Yokouchi and Ambe, 1985; Trainer et al., 1987; Chameides et al., 1988; Warneck, 1988; Kotzias et al., 1989; Atkinson, 1990; Brasseur and Chatfield, 1991; Pandis et al., 1991; Fehsenfeld et al., 1992; Andreae and Crutzen, 1997; Christoffersen et al., 1998; Kavouras et al., 1998, 1999; Calogirou et al., 1999). 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, especially in the tropics where our knowledge is poorest.

The dominant sources of VOCs are forests worldwide, most important among them the Amazonian rainforest representing the largest continuous forest. Despite its enormous dimensions, little is known about the release of VOC species from the Amazonian rainforest, or any tropical rainforest. There have been a few studies of oxygenated VOC species (Andreae et al., 1988; Khare et al., 1999; Sanhueza and Andreae, 1991; Sanhueza et al., 1996; Trapp and Deserves, 1995) as well as a small number of publications dealing with isoprenoids (Rasmussen and Khalil, 1988; Zimmerman et al., 1988; Helmig et al., 1998.) Isoprenoid emissions have been studied in a few other tropical forest regions including central Africa and central America (Lerdau and Keller, 1997; Klinger et al., 1998; Keller and Lerdau, 1999; Guenther et al., 1999). Due to the insufficient data base, we still depend on model extrapolation to discuss the chemical processes in the tropical atmosphere (Guenther et al., 1995). However, such extrapolations are based on algorithms developed for extratropical plants and may not accurately simulate emissions in the tropics (Keller and Lerdau, 1999). Therefore, to understand the atmospheric chemistry in the tropics, data of atmospheric VOC speciation and biogenic release under tropical conditions are needed. This can only be derived from field experiments in or over the pristine tropical forest. As a first step, concentration measurements of as many VOC species as possible will increase our knowledge significantly, as atmospheric concentrations are the product of diverse factors such as biological sources or sinks, meteorology, chemical reactivity, and deposition. As oxidation products of some of these compounds, especially terpenoids, can condense into aerosol particles and form the bulk of the natural aerosol (Christoffersen et al., 1998; Kavouras et al., 1998, 1999; Calogirou et al., 1999) it is obvious that we need a detailed data set on the release of VOCs, covering as many hydrocarbon species as possible. Combining such directly measured emissions with

atmospheric VOC concentrations, the loss of reactive VOC species into oxidation products and aerosols may be assessed.

As a first step, we measured the concentration of a large number of VOC species, such as isoprene, monoterpene species, aldehydes and several other VOCs at a ground station at Balbina, Amazonia, Brazil, together with diel courses of ozone and meteorological conditions. The station was located 100 km north of Manaus, SE of the Balbina reservoir, facing between 200 and 1000 km of pristine forest in the prevailing wind directions and hence representing a remote site with only a very low anthropogenic influence. Concentrations of VOC species were measured with different sampling and analysis techniques in order to cover a large variety of biogenic VOCs.

2. Materials and methods

2.1. Site description

The measurements were performed as part of the Large-scale Biosphere Atmosphere Experiment in Amazonia – Cooperative LBA Airborne Regional Experiment 1998 (LBA-CLAIRE-98) mission in March and April 1998 at a ground station at Balbina, Amazonia. The station was located $\sim$ 100 km north of Manaus (1°59′S, 59°12′W, 470 m asl), SE of the Balbina reservoir, with large areas of pristine forest in the prevailing wind directions. Measurements were conducted in a large forest clearing near an airstrip (closed to traffic during the campaign) and inside the surrounding forest. A second air sampling site was the Instituto Nacional de Pesquisas da Amazônia (INPA) forest tower (ZF2), which is located at 2°28′S, 60°09′W, $\sim$ 50 km north of Manaus, some kilometers west of the highway Manaus to Caracas and, hence, potentially influenced by traffic.

2.2. Climate and ozone data

Monitoring of light, relative humidity, temperature, rainfall, wind speed and direction was performed with an automated weather station equipped with standard sensors at a height near 2 m above ground. Ozone was monitored with a Daisibi instrument. Sampling occurred at 2 m above ground. All data were recorded as 10 min averages on a data logger (CSI Ltd. UK, model 21X).

2.3. VOC measurements

Mixing ratios of isoprene, monoterpenes and other VOC were measured by two different laboratories, which we refer to here as NCAR/IPEN and CNR/MPIC. Samples were collected at a standard sampling height

of 1.5 m. All laboratories collected samples on solid adsorbent traps and used GC/MS for sample separation, identification and quantification. The CNR/MPIC samples were collected on two-stage traps consisting of glass tubes (15 cm × 0.3 cm ID) filled with Carbotrap C (0.034 g) and Carbotrap (0.17 g) particles ranging between 20 and 40 mesh. Both adsorbents were supplied by Supelco (Bellefonte, PA, USA). Before sample collection, traps were cleaned by passage of a stream of ultra-pure helium at a flow rate of 300 ml min^{-1} and under heating up to 250°C. Separation, identification as well as quantification was done by GC/MS. A detailed description is given by Ciccioli et al. (1992). For VOC sampling and analysis by NCAR/IPEN see Greenberg et al. (1999). Using the tethered balloon system samples were typically collected at heights between 200 and 500 m above ground level (Greenberg et al., 1999). Some co-located samples were collected in order to compare the results of the two laboratories. All cartridges were analyzed under controlled conditions in the laboratories at home.

Aldehydes (Form- and Acetaldehyde) were trapped on C-18 coated silica particles in glass cartridges (C-18 Baker bond). The C-18 phase was coated with an acidified solution of 2,4-dinitrophenylhydrazine (DNPH). Trapping efficiency was found to be better than 95% for formaldehyde and acetaldehyde. All samples were stored at 4–6°C and were analyzed within 24 h after sampling. Trapped aldehydes were eluted with 2 ml of acetonitrile and analyzed by high performance liquid chromatography (HPLC) with a UV/VIS-detector set at a wavelength of 365 nm and compared with standard calibration mixtures. A detailed description is given by Kesselmeier et al. (1997).

Blank values were obtained for all VOC species by opening and closing sampling cartridges without loading.

3. Results and discussion

3.1. Meteorological conditions

The field campaign took place in March/April 1998 during the wet season. Diurnal fluctuations of light, temperature, and humidity as well as rain events are shown in Fig. 1. Winds were generally from the SE or NE. Fig. 2 gives an overview about the daytime and nighttime wind directions during the measurement period. Wind from north east traveled over more than 1000 km of untouched forest, wind from south east traveled over more than 200 km. In both cases, we found only minor anthropogenic influences (see below). Ozone mixing ratios (Fig. 3) were always low (< 20 ppb), reflecting the low oxidation capacity of the atmosphere, which is in agreement with the hydrocarbon data as shown below.
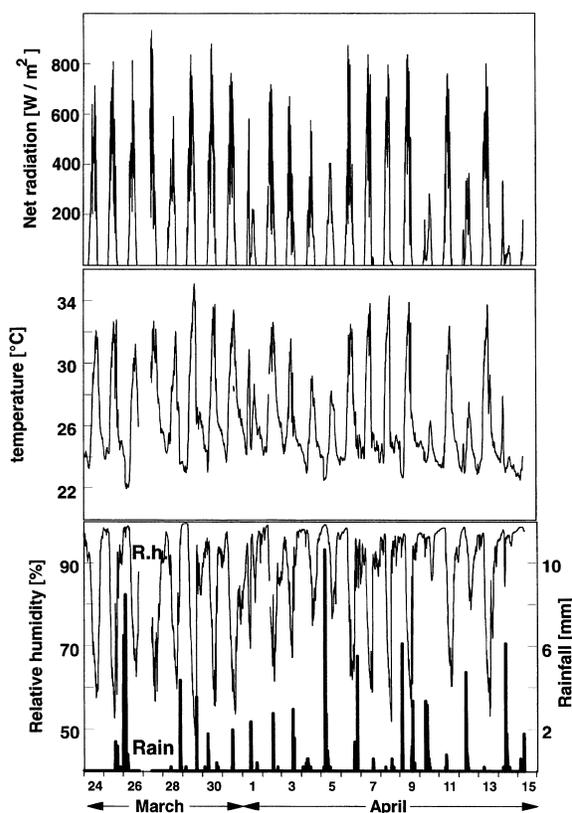

Fig. 1. Light, temperature, humidity and rainfall events during the measurement period in March and April 1998 at the Balbina site. All data given as 10 min means.
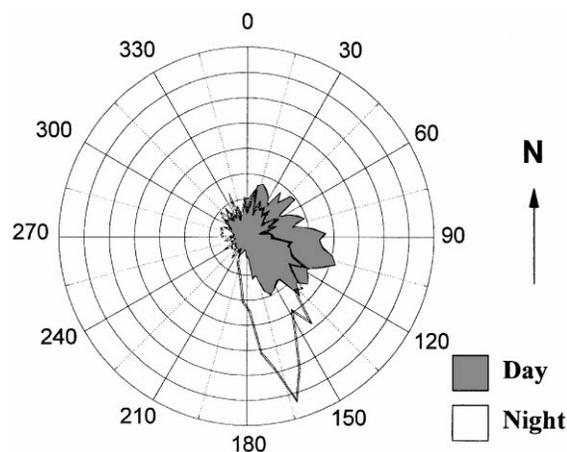

Fig. 2. Frequency distribution of prevailing wind directions under daytime and nighttime conditions. Scale: 0–35 events.
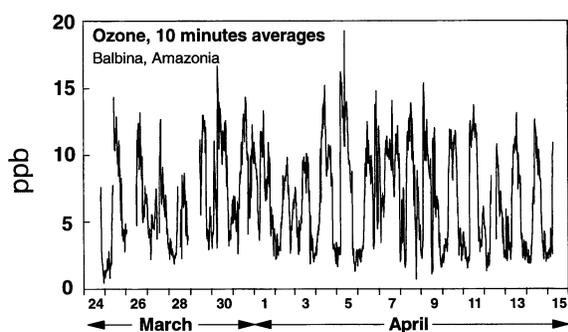
Fig. 3. Atmospheric ozone mixing ratios (10 min means) measured at the Balbina site in March and April.

3.2. Atmospheric levels of isoprene and monoterpenes

The main hydrocarbon species identified at the Balbina site was isoprene with mixing ratios between 4 and 10 ppb. Total monoterpene concentrations ranged one order of magnitude lower, between 0.5 and 1 ppb. Fig. 4 gives an overview of speciation and mixing ratios observed throughout one day in the atmosphere outside the forest. A large number of monoterpene species were identified, with α-pinene, β-pinene, limonene and p-cymene as dominant species. Among the minor monoterpene species several highly reactive ones were detected, such as myrcene, terpinolene, α-phellandrene and α-terpinene. The low concentrations of some species can be interpreted as a result of low emission rates and/or their fast decomposition after emission. According to Neeb et al. (1997) this unknown decomposition rate might mask the real amount released biogenically into the air. Likewise, Ciccioli et al. (1999) report on an in-canopy decomposition of reactive terpene species in the Mediterranean area. Though the ozone values at the Balbina site were found to be extremely low, we cannot exclude an OH-derived decomposition of the more reactive terpene species over the Amazon rain forest. The VOC composition at forest floor inside the forest was comparable to the air outside the forest but atmospheric mixing ratios of all terpenoids were significantly reduced by 30–60% inside the forest (Fig. 5).

At the ZF2 tower site near Manaus, which was visited for a short sampling period, concentration ranges were found to be very similar to the ground based site at Balbina. Here, we were able to perform a preliminary "profiling" of VOC compounds at different sampling heights (Fig. 6). It should be noted that sampling at the different heights was not simultaneous, but sequential. Therefore, these data cannot be interpreted as gradient reflecting transport. Nevertheless, we may compare them to the larger data set obtained near the surface at Balbina. The oxidation product of isoprene, MVK, shows higher amounts in the air above the forest, due to ongoing oxidation in the upper atmosphere. A comparison made at the 50 m level (Fig. 6) shows that general agreement in VOC concentrations was obtained by the two different laboratories NCAR/IPEN and CNR/MPIC, although large discrepancies in concentrations were found for the monoterpenes limonene (100%), β-pinene (500%), and α-pinene (200–300%). An explanation for these differences cannot be given now, further intercomparison is necessary.

Profiles of isoprene and some major monoterpene species were measured by tethered balloon soundings (Fig. 7). These data are compiled from soundings during day and night and give a rough overview of the range of mixing ratios at altitude levels between 200 and 500 m. Mixing ratios of isoprene as well as the dominant monoterpene species α- and β-pinene and limonene are highest near the surface with a large diurnal variation due to the diurnal behavior of emission and decomposition and/or transport. The lowest mixing ratios, and only a small concentration variation were observed at higher altitudes. This is typical for observations of mixed layer concentrations, which also remain fairly constant in the middle of the day (Greenberg et al., 1999).

3.3. Atmospheric levels of other VOCs

In contrast to isoprene and monoterpene species only a limited data set on the biogenic emission of other VOC (OVOC) exists up to now, although a large number of different VOC species are known to have at least some biogenic sources (Kesselmeier and Staudt, 1999). Plant species dependencies as well as technical difficulties such as the need for a large set of different sampling techniques are the main reasons. We combined two techniques for the OVOC sampling, the trapping on the same carbotrap cartridges as used for the isoprenoids plus DNPH-coated cartridges for low molecular carbonyls. The results show that there are very low levels of benzene and toluene, both regarded as markers for anthropogenically influenced air pollution. Benzene values in blanks were one order of magnitude lower than in the samples, toluene was not detectable. Therefore, we believe that the presented data are not affected by contamination but represent the true atmospheric concentration. This demonstrates that the air sampled has passed over large areas of quite pristine forest and that Balbina can be considered a very remote site.

The most prominent OVOCs were methacrolein (MACR) and methyl vinyl ketone (MVK), both oxidation products of isoprene (Fig. 4). Their presence was accompanied by 3-methylfuran, described by Ruppert et al. (1995) as a minor product of isoprene degradation by OH radicals in NO_x limited conditions. Their mixing ratios were always significantly below 1 ppb, hence summing up to < 10% of the isoprene mixing ratios. This
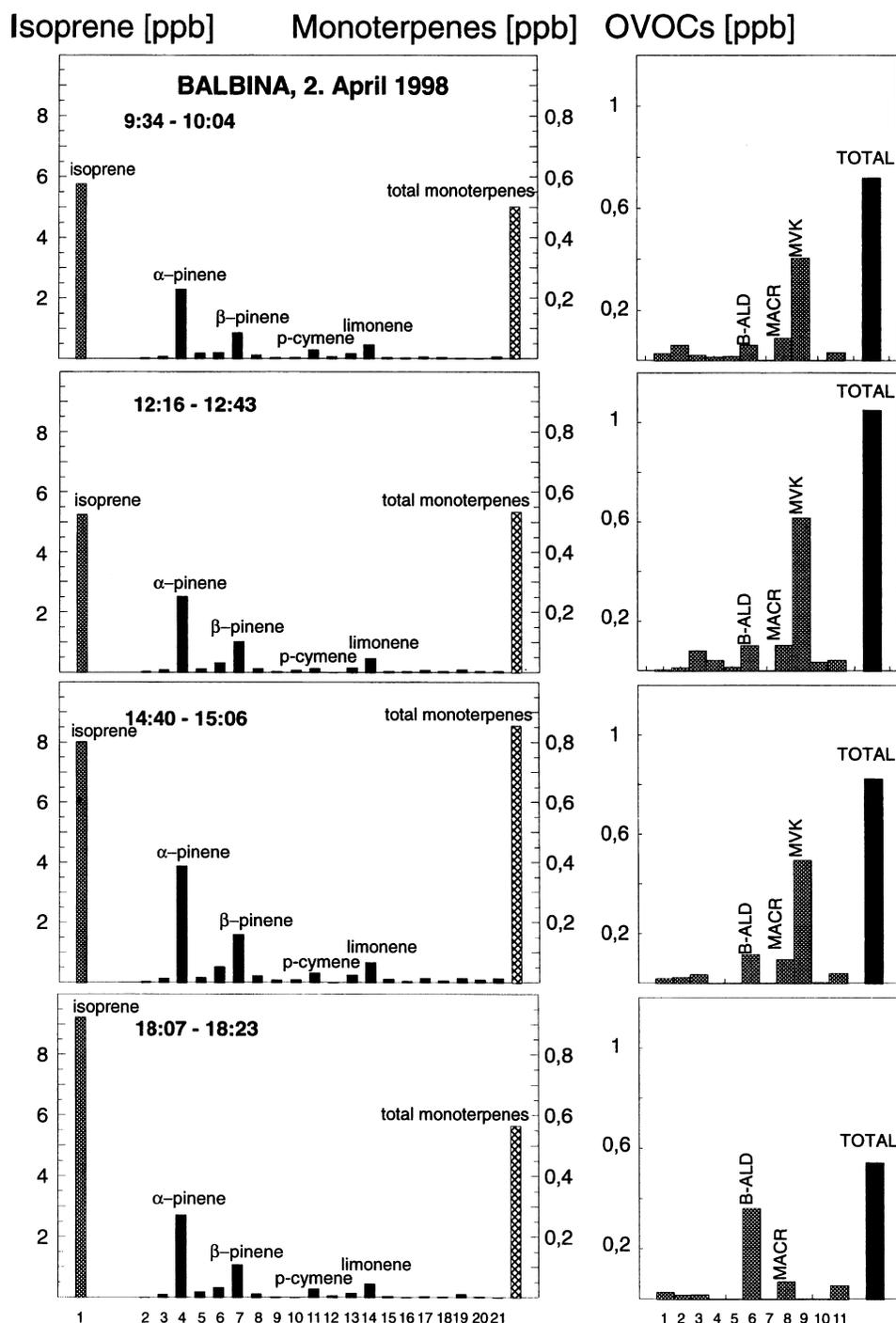
Fig. 4. Speciation and atmospheric mixing ratios of terpenoid species and OVOC species in the course of one day in the atmosphere outside the forest. Terpenoids: (1) isoprene, (2) tricyclene, (3) thujene, (4) α-pinene, (5) camphene, (6) sabinene, (7) β-pinene, (8) myrcene, (9) α-phellandrene, (10) α-terpinene, (11) *p*-cymene, (12) 1,8-cineol, (13) β-phellandrene, (14) limonene, (15) *cis*-β-ocimene, (16) *trans*-β-ocimene, (17) γ-terpinene, (18) terpinolene, (19) linalool, (20) 4-terpineol, (21) (α + γ)-terpinenol; OVOCs: (1) benzene, (2) toluene, (3) 6-methyl-5-hepten,2-one. (4) nonanal, (5) decanal, (6) benzaldehyde, (7) *n*-C-13, (8) metacrolein (MAC), (9) 3-buten-2-one (MVK), (10) 2-methyl furan, (11) 3-methyl furan.
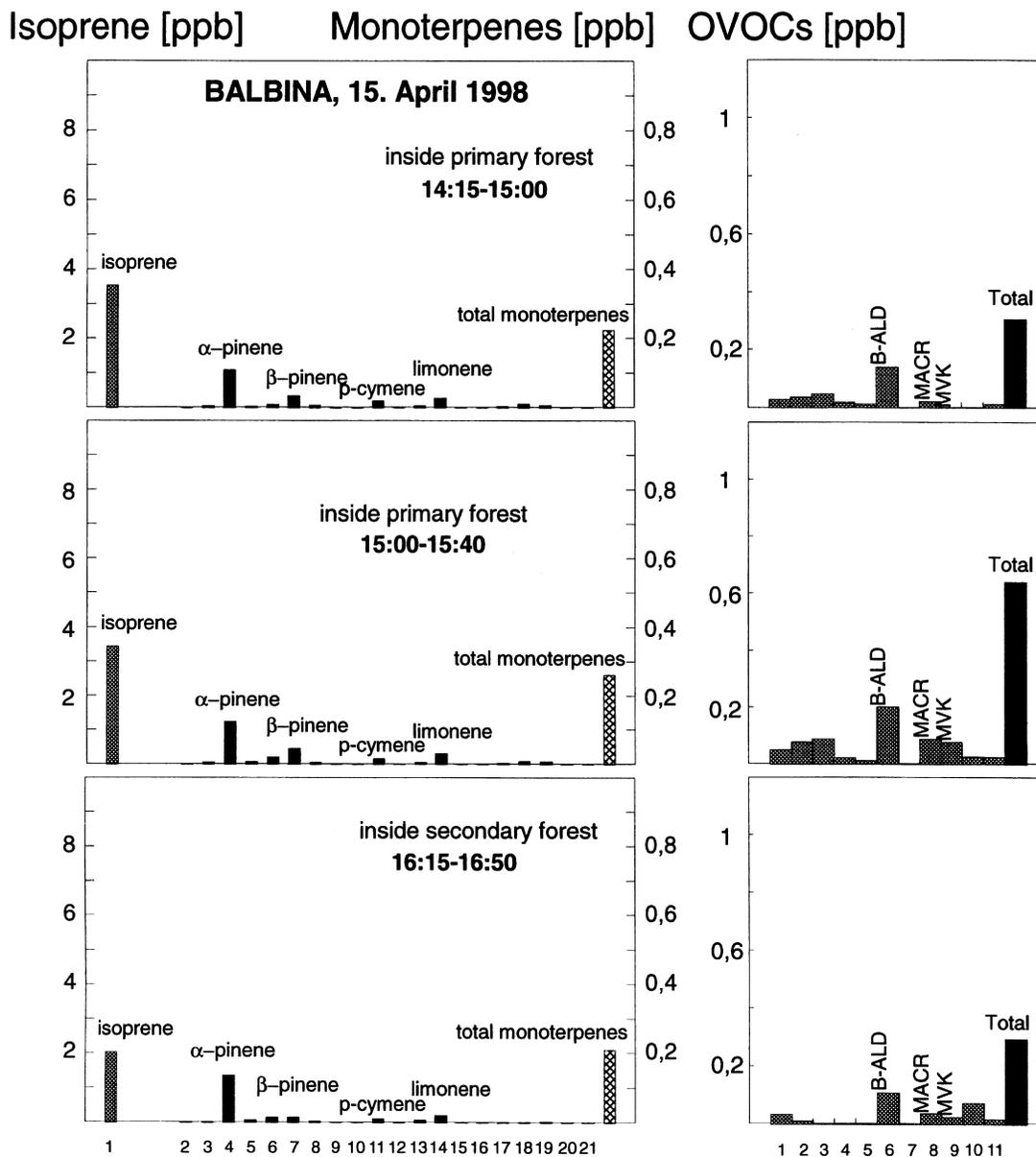
Fig. 5. Speciation and atmospheric mixing ratios of terpenoid species and OVOC species in the air inside the primary (untouched) and secondary (disturbed, re-grown)forest. Species numbers see Fig. 3.

low ratio MVK + MACR/isoprene point to a very low oxidation capacity of the pristine atmosphere over the Amazon rainforest, which is in agreement with ozone concentrations that are always below 20 ppb (Fig. 3). Another prominent VOC species was benzaldehyde, ranging between 0.1 and 0.4 ppb in the atmosphere outside the forest. Measurements within the forest canopy showed a significant decrease of concentrations of MVK as well as MACR, resulting from a lower oxidation potential as well as deposition. In contrast, other OVOC species were found in concentrations in the air within the forest canopy in still detectable amounts (Fig. 5). The dominant one was benzaldehyde, but also benzene as well as toluene were also present in levels similar to that outside the forest. We cannot explain the presence of benzene inside the canopy in terms of biogenic emission. Toluene might be of biogenic origin (Heiden et al., 1999). The relative increase of benzaldehyde mixing ratios within the forest as compared to outside might indicate a release from biological sources. Benzaldehyde emission
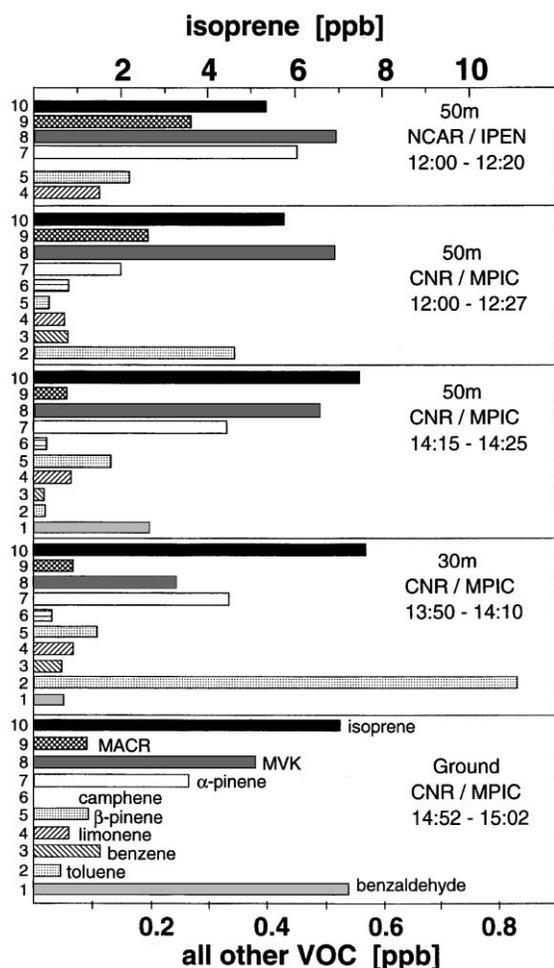
Fig. 6. Main VOC species inside and above the canopy, measured on the ZF2 tower on 7 April 1998. Note different sampling times.
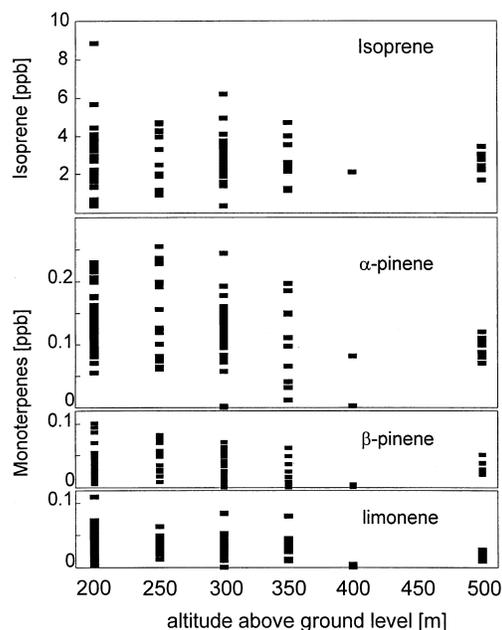

Fig. 7. Isoprene and dominant monoterpene species in the atmosphere around Balbina as measured by tethered balloon soundings between 19 and 28 March 1998. Data shown are compiled from sounding over days and nights giving the ranges of mixing ratios.

from plants has for example been found for grasses (Kirstine et al., 1998), but a release might also occur by decomposition processes due to the activity of bacteria and fungi equipped with relevant enzymes such as a lignin-decomposing enzyme, the lignostilben-α,β-dioxygenase (EC 1.13.11.43; Harwood and Parales, 1996; Watillon et al., 1998). Hence, a release of benzaldehyde from wood litter or from other decomposing compounds of the plant shikimate pathway (production of aromatic compounds) is plausible and would explain the increase of benzaldehyde inside the forest canopy. However, such a release has to be confirmed.

In addition to the VOC and OVOC species trapped on carbotrap cartridges we investigated the diel fluctuations of the low-molecular carbonyls, formaldehyde and acetaldehyde by trapping on DNPH-coated C-18 cartridges. A compilation of all data obtained during three weeks of

measurements is given in Fig. 8. Acetone and some other small carbonyl peaks with higher molecular weights were observed sometimes. However, as we did not check sampling efficiency on our cartridges, we are not able to quantify the acetone data. The peaks were small and, assuming the same calibration factor as for formaldehyde, the mixing ratios for acetone were below 0.5 ppb. Though scattering owing to climatic variations in the course of the experiments was found, for formaldehyde a clear diurnal cycle is seen with formaldehyde concentrations ranging between 0.5 and 3 ppb. Thus, after isoprene, formaldehyde is the most abundant VOC species in the pristine tropical forest air. In contrast, acetaldehyde concentrations are much lower and do not show a significant cycle. The diurnal behavior of formaldehyde is somewhat correlated with light but more strongly correlated with temperature (Fig. 9). Diel cycles of formaldehyde concentrations in the air could be caused by photochemical processes (oxidation of terpenes and isoprene) and/or by exchange processes with the vegetation. Results obtained by two tethered balloon soundings suggest that there are sources of formaldehyde at the surface as implied by the afternoon sounding in Fig. 10. The morning sounding was partly affected by slight rain. However, these data are insufficient to confirm the suggestion and need further experimental support in the future. Such an observed profile may be caused either by
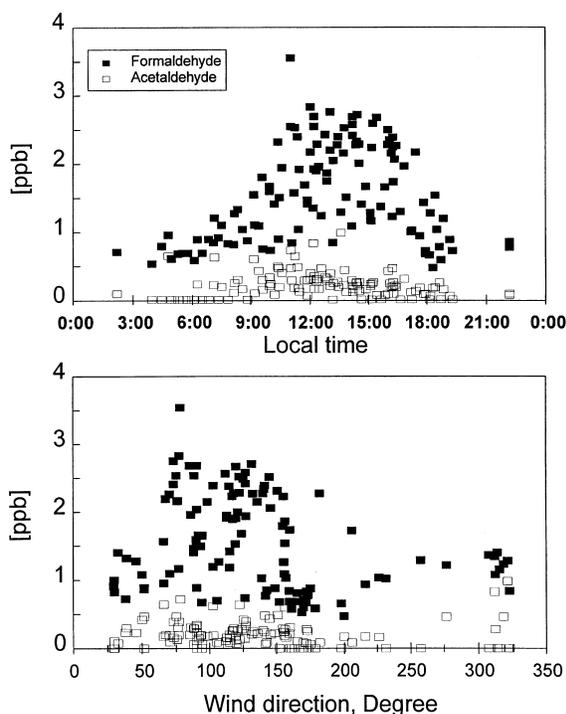
Fig. 8. Diurnal cycles of formaldehyde and acetaldehyde and concentrations related to wind directions as measured at Balbina (sampling time 60–120 min) in the course of the experiment during 25 March to 10 April 1998.
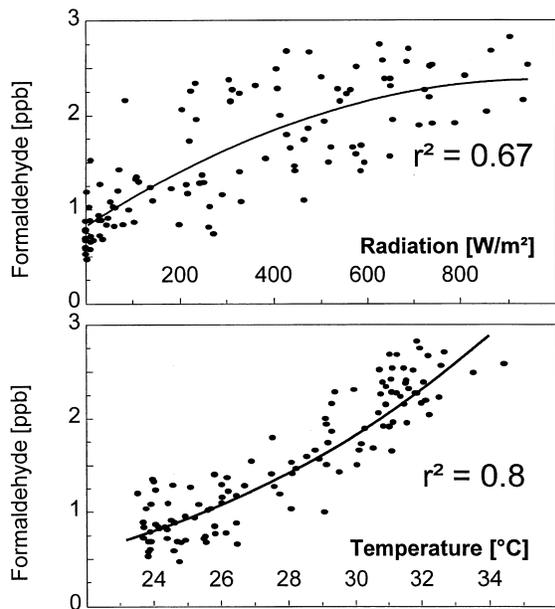

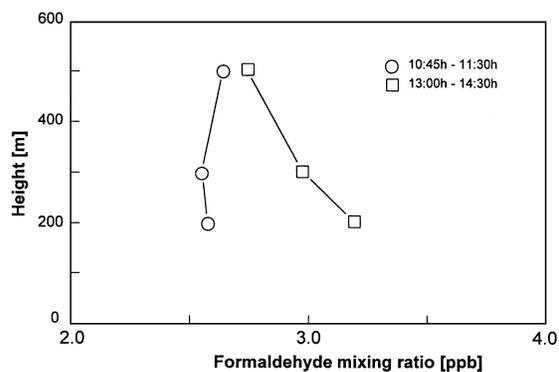Fig. 9. Correlation of formaldehyde atmospheric mixing ratios with light and temperature.

Fig. 10. Formaldehyde atmospheric mixing ratios observed during two tethered balloon soundings.

increased photochemical production near the ground due to emission of the chemical precursors and/or by the exchange with biological sources. The emission of carbonyls has recently been reported by Kesselmeier et al. (1998) from two main Mediterranean tree species. However, the authors found that the actual ambient concentrations have an important influence on the exchange direction, and that uptake instead of emission can occur in cases where the ambient concentration is above the compensation point, which was found as low as 1 ppb for two European oak species under field conditions (Bode et al., 1996). Questions regarding the role of the tropical vegetation can only be answered by future direct measurements of fluxes and emission rates within pristine forest.

4. Conclusions

The data set presented gives an overview of a large number of different VOC species measured at a remote site in the Amazonian rainforest. Isoprene and formaldehyde are the dominant compounds, but other species such as monoterpenes were also found in detectable amounts ranging up to 10% as compared to the isoprene level. Hence, isoprene chemistry can be regarded as the dominant process within this area. Furthermore, isoprene may be discussed as the major source for formaldehyde. However, as we found several reactive monoterpenes, other alkenes might also contribute to the formaldehyde formation. The low but detectable amounts of monoterpene species will also have some impact on aerosol formation, as for example, reactive terpenes can be primary targets for oxidants and hence can end up in source compounds for organic aerosol particles. Direct emission analysis (enclosures) combined with flux and atmospheric concentration measurements covering the widest range of VOC species are needed in

the future. In this way, the simultaneous detection of the direct biogenic emission of organics and their secondary products can provide useful information for assessing the oxidation capacity of the atmosphere as well as for aerosol formation.

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