

Concentrations and species composition of atmospheric volatile organic compounds (VOCs) as observed during the wet and dry season in Rondônia (Amazonia)

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[1] We measured atmospheric gas-phase volatile organic compounds (VOCs) at the end of the wet and end of the dry season at a tropical rainforest site in Rondônia, Brazil, using various sampling techniques such as trapping on different adsorbents or cryogenic trapping combined with appropriate analysis techniques. The measuring sites were located inside the forest of a biological reserve near Ji-Paraná. Sampling was performed from 3 May 1999 to 17 May 1999 and from 24 September 1999 to 2 November 1999 during the “wet-to-dry season transition” and “dry-to-wet season transition” periods in Rondônia, respectively. Samples were obtained at the canopy top close to the potential sources/sinks for these compounds as well as above the forest. We report the measured concentrations of a large number of different VOCs and their oxidation products, such as isoprenoids, organic acids, carbonyls, aromatics, and alcohols. The most prominent VOCs present in air over the last part of the wet season were isoprene, formaldehyde, and formic acid, with mixing ratios of each ranging up to several parts per billion (ppb). Methyl vinyl ketone as well as methacrolein, both oxidation products of isoprene, ranged around 1 ppb. The sum of the measured monoterpene concentrations was below 1 ppb. At the end of the dry season, the amount of C₁–C₂ organic acids and C₁–C₂ aldehydes increased significantly up to 17 and 25 ppb, respectively, which is thought to result significantly from vegetation fire emissions. High methanol concentrations also support this scenario. At the same time, however, atmospheric mixing ratios of biogenic compounds such as isoprene increased up to 30 ppb near the crown region and well above 10 ppb at 10–20 m over the forest, whereas monoterpene species seem to decrease. We discuss seasonal development of the vegetation and climatological factors to be responsible for such concentration pattern. The results give an impression about the variability and concentration of VOCs during the different seasons. *INDEX TERMS*: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS*: volatile organic compounds, isoprene, monoterpenes, acids, carbonyls

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1. Introduction

[2] Volatile organic compounds (VOCs) are of high interest for atmospheric chemistry and biogeochemistry as they

contribute to the oxidative capacity of the atmosphere, to particle production and to the carbon cycle. Although global emission budgets for vegetation exist, our knowledge on the role of some dominant ecotypes of the world is insufficient. Large regions of the world are still poorly investigated, namely tropical rainforest ecosystems (among them the largest one, the Amazonian rainforest). Relatively few studies exist regarding atmospheric VOC concentrations, fluxes and emission rates within the tropics [Rasmussen and Khalil, 1988; Zimmerman *et al.*, 1988; Lerdau and Keller, 1997; Helmig *et al.*, 1998; Klinger *et al.*, 1998; Keller and Lerdau, 1999; Guenther *et al.*, 1999]. Nearly all of these studies deal with the investigation of isoprene emission. Monoterpenes

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and other VOC species, especially oxygenated VOCs, have only been rarely examined [Andreae *et al.*, 1988; Sanhueza and Andreae, 1991; Trapp and Deserves, 1995; Sanhueza *et al.*, 1996; Kesselmeier and Staudt, 1999; Khare *et al.*, 1999; Kesselmeier *et al.*, 2000].

[3] VOCs comprise a large number of different species belonging to the isoprenoids (isoprene and terpenoids) as well as alkanes, alkenes, carbonyls, alcohols, acids, esters and ethers. For vegetation emissions, the most prominent compounds are ascribed to be isoprene and monoterpenes. As such, these compounds have been the focus of much of the research effort, with relatively little examination of the occurrence and release of other compounds (e.g. OVOCs among them oxygenated VOCs). For some of these compounds, initial studies have provided evidence of vegetative emissions of methanol, organic acids and aldehydes [Fall and Benson, 1996; Kesselmeier *et al.*, 1997, 1998]. Emission strategies and patterns may change according to changing environmental conditions for example acetaldehyde emissions due to anaerobic fermentation caused by flooding [Kreuzwieser *et al.*, 1999; Holzinger *et al.*, 2000; Wilske *et al.*, 2001]. Also dead plant matter may contribute [Warneke *et al.*, 1999]. Another complicating factor with oxygenated compounds is that both emission and deposition are possible, depending on the environmental conditions [Kesselmeier *et al.*, 1997; Kesselmeier, 2001; Staudt *et al.*, 2000; Kuhn *et al.*, 2002a]. As a consequence, the understanding of the exchange of these compounds needs more field and mechanistic studies. These examples show that we need to know more about VOCs in the atmosphere, especially in the tropics, to fully understand their sources and fates within the fields of atmospheric chemistry and biogeochemistry. Recently, Kesselmeier *et al.* [2000] reported on VOC studies within the Amazon region, showing isoprene as the most prominent compound and formaldehyde as the most predominant OVOC species. Short-chain oxygenated compounds are of special interest because they are released directly from vegetation as well as being intermediates of the breakdown of other biogenic VOCs. Within our studies spanning the final stages of both the wet and dry seasons 1999 in the southwestern part of Amazonia, we performed new measurements combining different kinds of VOC sampling and analysis and can now report about a substantial number of different compounds in the atmosphere of a tropical rainforest.

2. Material and Methods

2.1. Measuring Sites

[4] The field experiments were performed during the “wet-to-dry season transition” and “dry-to-wet season transition” (LBA-EUSTACH-1, April/May 1999, and LBA-EUSTACH-2, September/October 1999) within an well preserved ecological reserve 100 km north of Ji-Parana in the state of Rondônia, southwest Amazonia, Brazil. VOC samples were collected at two sites: a tower within the primary open rainforest of Rebio Jaru nature reserve (tower A [Andreae *et al.*, 2002]; 10°04'55"S, 61°55'48"W, 110 m a.s.l.; canopy height 25–45 m, mean 32 m) and at a scaffold built up at the edge of secondary forest of the Rebio Jaru nature reserve (10°08'43"S, 62°54'27"W, 107 m a.s.l.; canopy height 8–15 m) at the camp site of the Brazilian

Environmental Protection Agency IBAMA (Instituto Brasileiro de Meio Ambiente e Recursos Renováveis) surrounded by primary forest. Sampling heights were 25–54 m and 8–10 m, respectively. For an overview see Andreae *et al.* [2002].

2.2. Sampling of VOCs; General Remarks

[5] Sampling occurred through 1/4" Teflon lines (maximum length 5 m) shielded by Zefluor Teflon filters (47 mm diameter, 2 µm pore size) to remove particulate matter from the sample air stream. All lines were equipped with ozone scrubbers consisting of MnO₂ coated copper nets (Type ETO341FC003, Ansynco, Karlsruhe, Germany). Airflow was continuously monitored during sampling using electronic mass flowmeters.

2.2.1. Sampling and Analysis of Organic Acids

[6] Organic acids were cryogenically cotrapped with atmospheric water at -70°C. Sampling efficiency was 100%. Sampling times were 35–45 minutes with flow rates of 4–5 l min⁻¹. Samples were transferred into small vials and temporarily stored at -18°C before analysis by ion chromatography. The detection limit is <10 ppt. The technique is described in detail by Hofmann *et al.* [1997]. Analyses were usually performed within 48 h.

2.2.2. Sampling and Analysis of Aldehydes

[7] Aldehydes (form- and acetaldehyde) were trapped on C-18 coated silica particles in glass cartridges (C-18 Baker bond). Sampling times were 40–60 minutes with flow rates of 300 ml min⁻¹. 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 hours after sampling. Trapped aldehydes were eluted with 2 ml of acetonitrile and analyzed by high performance liquid chromatography (HPLC) with an UV/VIS-detector set at a wavelength of 365 nm. Identification and quantification of C1–C2 aldehyde-hydrazones was through comparison with standard calibration mixtures. Detection limit was <0.3 ppb. A detailed description is given by Kesselmeier *et al.* [1997].

[8] An additional series of measurements used slightly modified sampling and analysis techniques. Formaldehyde and acetaldehyde were sampled on C-18 coated silica SEP-PAK cartridges (Waters). Cartridges were coated similarly to the above described method (acidified solution of pre-purified 2,4-dinitrophenylhydrazine-DNPH, dried with a stream of nitrogen from liquid nitrogen and stored for a maximum period of 30 days. Sampling rate was 12–30 l h⁻¹ for 1h, depending on expected levels. Separation was accomplished by HPLC using an Axiom ODS (5 µm, 150 mm × 4.7 mm) column and a gradient elution of water: acetonitrile varying from 45:55 to 25:75 within 12 min. Eluent flow was 1.4 ml min⁻¹. Quantification utilised a standard reference (ERA-013K, Radian International, Texas, USA) using a UV/VIS detector at λ = 360 nm [Hewlett Packard 1090]. Quantification limits were 0.1 and 0.4 ppb for formaldehyde and acetaldehyde, respectively.

2.2.3. Sampling and Analysis of Methanol

[9] The same samples of atmospheric water obtained by cryogenically trapping for organic acid determinations were also analyzed for methanol. Samples were kept frozen in 5 ml vials until analysis after the field campaign. Methanol

determination was carried out by HPLC chromatographic separation using a 120 mm × 4.0 mm Hypersil ODS 3 μm column, followed by enzymatic derivatization using a Biometra EP 45 (immobilised alcohol oxidase) and electrochemical detection of the H₂O₂ formed at +0.5 V, employing 0.1 M sodium phosphate buffer (pH 7.4) as eluent at a flow rate of 0.3 ml min⁻¹, with a relative error of 1.5%. Limit of quantification obtained for methanol samples in the conditions of the Amazon forest was <0.9 ppb.

2.2.4. Sampling and Analysis of VOCs by GC/FID

[10] VOCs were collected on sequential adsorbent beds packed into fused-silica-lined stainless steel cartridges (Silcosteel[®] (Restek (USA) 89mm*5.33mm I.D.)). The following adsorbents were used: for the wet season, 180 mg Tenax TA 60/80 (35 m²/g) followed by 130 mg of Carbograph 1 (90 m²/g); and for the dry season, 130 mg of Carbograph 1 followed by 130 mg of Carbograph 5 (560 m²/g). The size of the Carbograph particles was in the range of 20–40 mesh. Tenax TA was provided by Alltech (Deerfield, IL, USA). Carbographs 1 and 5 were provided by Lara s.r.l. (Rome, Italy). Sampling flow rates were 100 mL min⁻¹. In the wet season, two different sample volumes were collected to avoid breakthrough problems: 0.8 L (for isoprene and other <C₅ compounds) and 4.0 L (for >C₅ compounds). For the adsorbents used in the dry season sampling there were no breakthrough problems, and the sample volume was 4.0 L for all compounds. For subsequent analysis, the adsorbent cartridges were thermally desorbed under helium flow at 260° C for 10 min (using a Perkin Elmer ATD400). In this instrument, desorbed species are refocused on a small quartz tube packed with 20 mg Carbograph 1 and held at -30°C. The quartz tube was then rapidly heated to 280°C and the desorbed compounds were transferred through a heated line to the GC for separation and FID detection (Perkin Elmer Autosystem XL GC/FID). Separations were accomplished on two capillary columns connected in series: (Supelco SPB-5, 30 m × 0.25 mm I.D., 0.25 μm film thickness, followed by Hewlett Packard HP-1, 30 m × 0.25 mm I.D., 0.25 μm film thickness). The temperature program was as follows: -50°C to 10°C at 20°C/min followed by 2.0°C/min to 20°C and finally 5.0°C/min to 180°C.

2.2.5. Sampling and Analysis of VOCs by GC/MS

[11] VOCs were collected on traps consisting of glass tubes (16 cm × 0.3 cm I.D.) packed with 118 mg of Carbopack C (12 m²/g), 60 mg of Carbograph 1 (90 m²/g), and 115 mg of Carbograph 5 (560 m²/g) in sequential beds. This adsorbent configuration was based on the data recently obtained by *Brancaleoni et al.* [1999]. Carbopack C was supplied by Supelco (Bellefonte, PA, USA) whereas Carbograph 1 and 5 were provided by Lara s.r.l. (Rome, Italy). In all cases the size of the particles was in the range of 20–40 mesh. We sampled for 20 minutes with sampling flow rates of 250 ml min⁻¹. After sampling, the cartridges were thermally desorbed at 250°C and the desorbed compounds were refocused on a fused-silica liner at -180°C. Rapid heating of the liner (to 200°C at a rate of 15°C/s) served to inject the compounds into the GC (HP 5890). Separations were done on a fused silica capillary column (50 m × 0.32 I.D.) chemically bonded for mass spectrometry (CB-MS) with a thin film (0.4 μm) of CP-Sil 5 (Chrompack, Middelburg, The Netherlands). The temperature program was as follows: 0°C for 3 min, then 3°C/min to 50°C, followed by

5°C/min to the final temperature of 220°C. Compounds were detected using an HP 5970B mass selective detector. The MS unit was operated in the scan mode (m/z 20 to 300). Reconstructed chromatograms with selected ions were used for the quantification of individual components [*Ciccioli et al.*, 1993].

2.3. Climate and Ozone Data

[12] Atmospheric ozone was photometrically monitored with a Daisibi instrument (model 1003). Monitoring of light, relative humidity, temperature, rainfall, wind speed and direction was performed with standard sensors. All parameters were measured at the top of the scaffold (8–10 m) in the IBAMA camp. Data were recorded as 5 min averages on a data logger (CSI Ltd. (UK), model 21X).

3. Results and Discussion

3.1. Meteorological Conditions

[13] Diurnal fluctuations of ozone, light, temperature, and humidity as well as wind speed and wind directions were measured at the top of the Ibama camp scaffold (Figures 1a and 1b). The data are comparable to those obtained at the forest tower (U. Rummel, personal communication, 2000). At the end of the dry season temperature, light, wind speed and ozone mixing ratios were principally higher during daytime and relative humidity dropped to much lower values than in the wet season. Also, ozone mixing ratios showed pronounced differences comparing the two seasons. Wind at daytime was dominant from North and South directions. During nighttime, directions exhibited a shift to SE (wet season) and SE to NE (dry season).

3.2. VOC Species as Identified by GC/MS

[14] Numerous different VOCs were found in both seasons. However, conventional sampling and analysis techniques such as those used in this study cannot be regarded as sufficient to identify all of the VOCs in this environment. Table 1 shows an overview of the large number of different compounds determined via adsorbent sampling and GC/MS analysis. Samples were taken at two different sites: a tower site with sampling heights at the canopy top (25–35 m) and above, and a scaffold site at the edge of the forest near the canopy top (8–10 m) adjacent to the IBAMA camp. Biogenic VOCs were observed, as well as VOCs of anthropogenic origin (indicated by the combined presence of Freon 11, 113, benzene and toluene). However, Table 1 represents a limited number of one-sample “snapshots” of the atmospheric VOC composition. The range of concentrations of some of the main compounds is described in more detail in later sections describing the GC/FID samples, which were much more numerous. Under wet season conditions, the most prominent VOC species was isoprene followed by its oxidation product methyl vinyl ketone (MVK). Monoterpene species were found at concentrations which were as a sum one order of magnitude lower. Several other VOCs with biogenic origins could be identified, such as acetone, some higher aldehydes and 6-methyl-heptenone (6-MHO). Under dry season conditions, isoprene was still found to be a main compound, the ratio of isoprene versus MVK and MACR shifted slightly toward its oxidation products (see below), pointing to an atmosphere with a

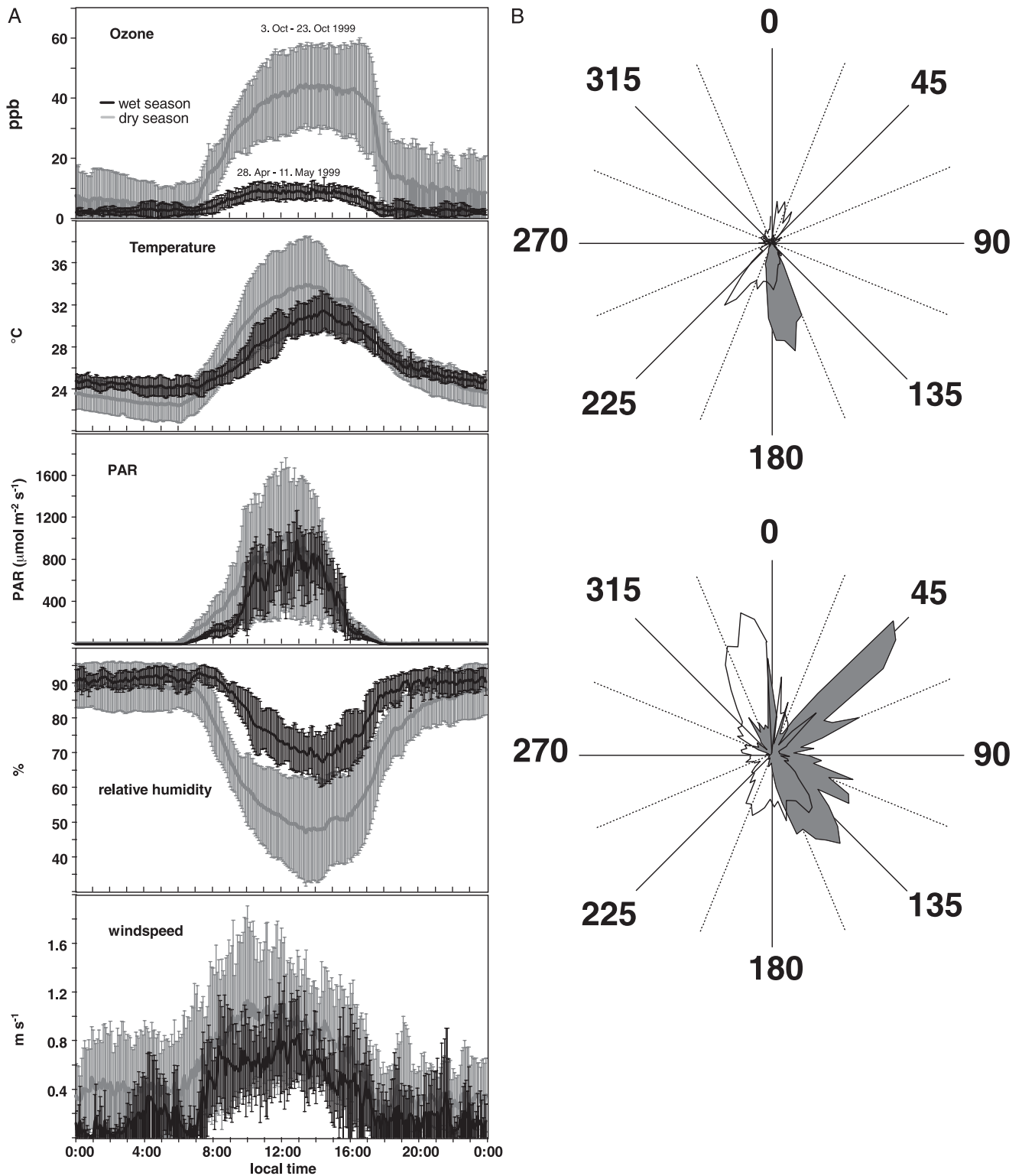


Figure 1. Meteorological conditions: (a) Diurnal cycle of ozone, air temperature, photosynthetic active radiation (PAR), relative humidity and wind speed as measured at the scaffold site in the Rebio Jaru at the edge of the canopy top (8–10m) near the IBAMA camp at the end of the wet and dry season 1999. All data are given as mean values of 5 min averages over several days (continuous lines) and the standard deviations (1σ); $n = 8-9$ days (wet season) and $19-20$ days (dry season). (b) Frequency distribution of prevailing wind directions in the wet (top) and dry (bottom) under daytime (white) and nighttime (gray) conditions. Scale : 0–150 events.

Table 1. VOC Species Composition (%) During the End of Wet and End of Dry Season as Observed by Sampling on Carbotrap and After GC/MS Identification in Samples at and Above Canopy Top^a

Sampling Height, m Site	End of Wet Season						End of Dry Season						
	25		46		10		25		45		52		
	Tower 16 May 1999 1500–1520	Tower 17 May 1999 1430–1450	Tower 16 May 1999 1500–1520	Tower 17 May 1999 1430–1450	Scaffold 10 May 1999 1450–1510	Tower 29 October 1999 1400–1440	Tower 29 October 1999 1400–1440	Tower 29 October 1999 1400–1440	Tower 29 October 1999 1400–1440	Tower 29 October 1999 1400–1440	Scaffold 11 October 1999 1500–1540	Scaffold 11 October 1999 1430–1510	Scaffold 18 October 1999 1430–1510
Carbon tetrachloride	0.65	0.78	0.83	2.64	0.98	1.49	1.58	1.92	1.92	1.04	1.04	0.97	1.06
Freon 11	0.57	0.76	0.57	3.54	0.98	1.66	1.70	1.41	1.41	0.93	0.93	0.62	0.85
Freon 113	0.39	0.70	0.59	2.62	0.48	0.80	0.91	0.95	0.95	0.57	0.57	0.79	0.50
Acetone	7.81	10.03	9.11	23.04	8.58	...	8.61	2.10	2.10	2.62	2.62
Methacrolein	4.24	5.05	5.64	5.85	3.33	5.70	9.43	8.24	8.24	8.02	8.02	8.35	6.61
3-Buten,2-one (MVK)	22.27	22.66	27.74	17.61	15.70	17.22	29.77	26.72	26.72	26.23	26.23	24.60	21.22
2-Methyl furane	0.72	0.78	0.87	0.79	0.78	2.13	2.79	3.18	3.18	2.59	2.59	1.80	2.26
3-Methyl furane	0.13	0.04	0.12	...	0.07
Tetrahydrofurane	5.32	3.17	2.98	2.53	4.28	28.75	17.07	9.15	9.15	11.84	11.84	16.18	21.11
Butanal	2.32	3.39	3.94	5.71	3.10
Pentanal	1.68	1.55	2.85	2.14	1.49	0.06	0.06
Hexanal	1.15	0.53	1.98	0.97	0.68	2.19	2.19	0.25	0.25
Heptanal	0.58	0.23	0.81	0.81	0.28	0.67	...	0.98	0.98	1.23	1.23	0.66	0.19
Octanal	0.43	0.16	0.42	0.56	0.19	0.66	...	1.51	1.51	1.12	1.12	...	1.02
Nonanal	0.31	0.21	0.59	0.78	0.22	0.97	...	0.89	0.89	0.56	0.56	...	0.33
Decanal	0.18	0.07	0.22	0.37	0.11	1.03	0.18	0.18
Benzaldehyde	0.52	0.20	0.54	0.90	0.47	1.88	...	2.26	2.26	0.77	0.77	...	0.98
Benzene	0.68	1.90	0.80	3.34	0.53	0.97	1.45	1.56	1.56	2.21	2.21	2.84	2.08
Toluene	0.16	0.22	0.17	0.70	0.17	0.36	0.28	0.66	0.66	0.63	0.63	1.00	0.75
2-Butanone	4.19	5.55	6.14	6.14	3.55	3.55	3.57	4.45
Styrene	1.81	...	1.09	1.09	0.39	0.39	0.28	2.00
6MHO	2.09	0.12	0.41	0.21	0.11	1.19	...	0.68	0.68	0.12	0.12
Isoprene	45.34	45.38	35.72	23.72	52.51	23.82	20.86	23.36	23.36	31.90	31.90	35.39	29.23
α-Pinene	1.61	1.44	1.94	1.09	3.26	3.06	...	3.09	3.09	1.72	1.72	1.70	2.93
Sabinene	0.42	...	0.60	0.60	0.34	0.34	0.30	0.57
β-Pinene	0.13	0.08	0.15	...	0.30	0.90	...	1.06	1.06	0.85	0.85	0.83	1.34
Myrcene	0.02	0.07	0.07	0.04	0.15
β-Phellandrene	0.02	...	0.02	...	0.05	0.12	...	0.11	0.11	0.10	0.10	0.04	0.15
Limonene	0.25	0.25	0.30	0.07	0.23	0.17	...	0.14	0.14	0.07	0.07	0.04	0.15
cis-β-Ocimene	0.04
trans-β-Ocimene	0.02	0.02	...	0.02
Linalool	0.03	0.03
Camphene	0.27	0.12	0.30	...	0.57
p-Cymene	0.22	0.17	0.27	...	0.57
Total, %	100	100	100	100	100	100	100	100	100	100	100	100	100
Total, ppb	11.5	9.4	7.4	2.7	8.0	7.3	6.6	6.4	6.4	11.1	11.1	8.6	9.5

^a Tower, sampled at the forest tower within the Rebio Jaru (canopy height 25–30 m); Scaffold, sampled at top of a small tower (8–10 m) at the edge of the canopy (canopy height 8–15 m) in the Rebio Jaru near the IBAMA camp.

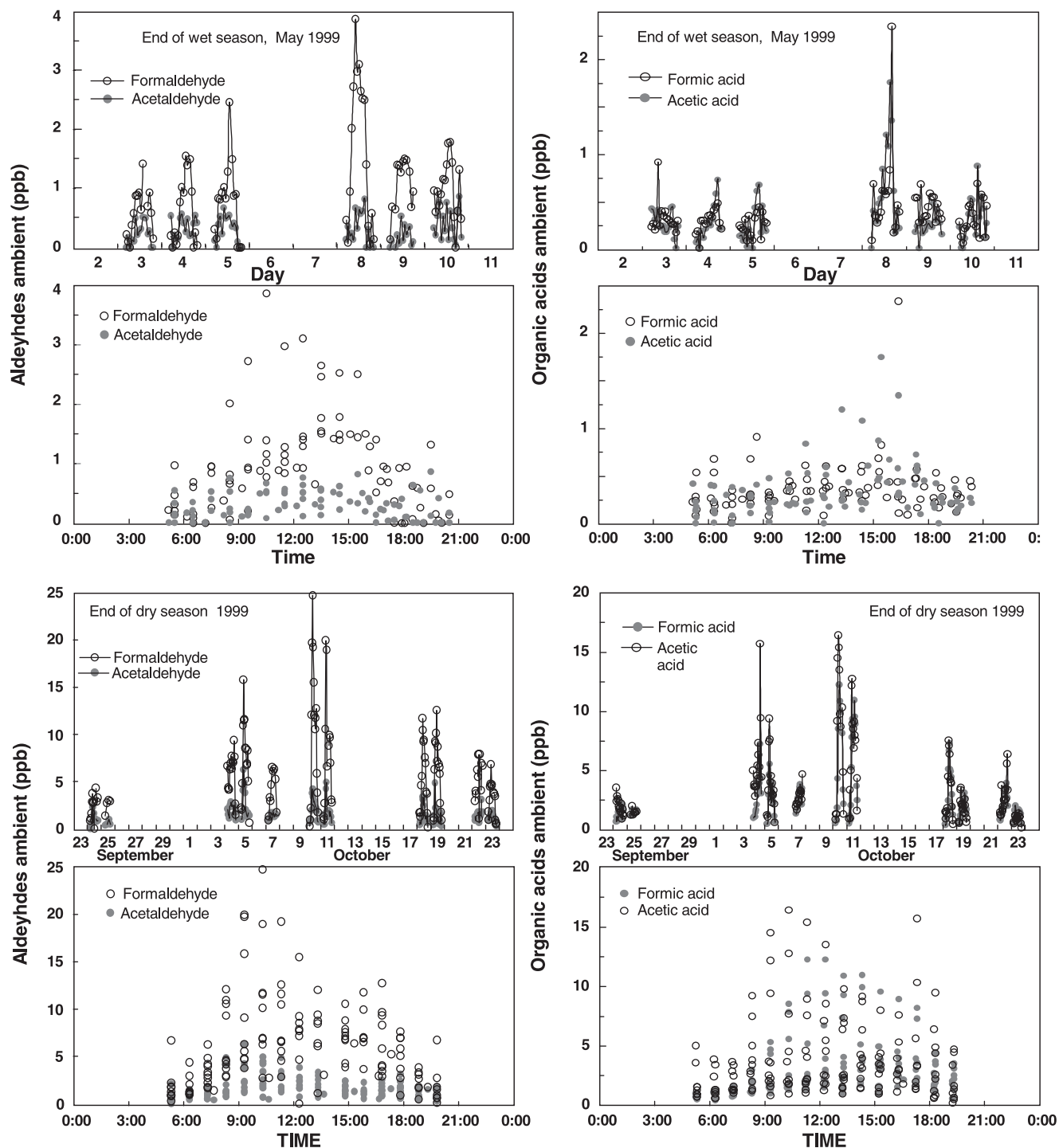


Figure 2. Daily and diurnal cycles of short chained oxygenated compounds as observed at the scaffold site in the Rebio Jaru at the edge of the canopy top (8–10 m) near the IBAMA camp during the wet and dry season. Note the different scales for the wet and dry season.

somewhat higher oxidation capacity under dry season conditions. This is also seen in the large increase of atmospheric ozone from maximum values below 20 ppb in the wet season up to 60 ppb in the dry season (Figure 1a).

3.3. C_1 – C_2 Oxygenated Compounds at the Canopy Top

[15] Atmospheric short-chain oxygenated compounds like acids, carbonyls and alcohols are known to have biogenic sources, both direct (through emission) and indirect (through

photochemical oxidation of biogenic emissions). Some of them are quite stable (acids, MeOH) and others are reactive (aldehydes). Furthermore, they can reflect a substantial part of the atmospheric carbon burden. Therefore, it is of high interest to track the daily and diurnal atmospheric concentrations of these compounds in relation to the isoprenoids. We found considerable amounts of C_1 – C_2 oxygenated VOCs. Figure 2 shows the organic acid and carbonyl data in daily and diurnal cycles. During the wet season, formaldehyde

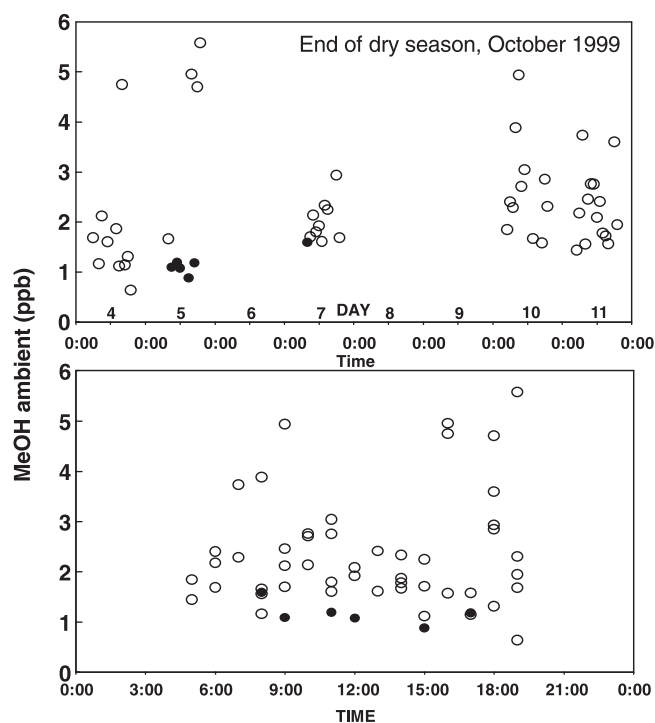


Figure 3. Daily and diurnal cycles of atmospheric methanol as observed at the scaffold site in the Rebio Jaru at the edge of the canopy top (8–10 m) near the IBAMA camp during the wet and dry season. Filled circles represent values obtained at the analytical detection limit.

shows clear diurnal cycles with maxima between 1.5 and 4 ppb. Acetaldehyde mixing ratios were below 1 ppb and did not exhibit a clear maximum. Formic and acetic acid also showed diel cycles with maxima in the late afternoon reaching atmospheric concentrations between 0.75 and 2.5 ppb. Measurements in the dry season show fundamental differences compared to those in the wet season. The diurnal behavior of both aldehydes was similar to that observed during the wet season, but both compounds were found at much higher mixing ratios. Formaldehyde peaked around noon between 5 and 25 ppb, while acetaldehyde maxima ranged up to 5 ppb. A similar increase was found for both organic acids. Again, both acids exhibited clear diurnal cycles, reaching maxima around noon or earlier between 4–17 ppb for formic acid and 2–12 ppb for acetic acid. Though the data set is of limited size, it is of interest to point out a possible shift of atmospheric maximal mixing ratios from noon to earlier morning hours (in the case of formaldehyde) and from early afternoon to noon or earlier morning hours in the case of the acids. In addition to the seasonal comparison of short chain acids and aldehydes, we measured the atmospheric concentrations of methanol, which may have direct biogenic as well as anthropogenic sources. Unfortunately, we are not able to present data for the wet season but for the dry season only (Figure 3). We found mixing ratios between 1 and 6 ppb without a clear daily maximum.

3.4. Isoprenoids at the Canopy Top

[16] As described in the previous sections, isoprene was a dominant compound of the VOC species as identified by

GC/MS, whereas the monoterpene species were generally one order of magnitude lower in concentration. Diurnal data sets obtained on the scaffold at the canopy top (8–10 m above ground level) near the IBAMA camp confirm the GC/MS snapshots. Figure 4 compiles the data on diurnal and daily cycles for the biogenic compounds. For the wet season we observed clear diurnal cycles for isoprene as well as for the sum of monoterpenes. Isoprene reached its maximum around 9 ppb in the early afternoon. Monoterpenes showed a similar behavior, peaking around 0.6–0.7 ppb. Isoprene oxidation leads to production of MVK and MACR, which reached maximal values near 1 ppb. In the wet season, neither of these compounds had a distinct daily maximum. In fact, the highest concentrations were often observed in the dark hours early in the morning and at early night. The situation changed substantially during the dry season. The most striking differences were found for isoprene mixing ratios which increased from end of September to end of October and reached maximal values up to 25–30 ppb. Although it must be kept in mind that these samples were obtained at the canopy top near the biogenic sources, it is nonetheless remarkable that the dry season isoprene concentrations were more than twice the wet season data observed at the same sites and heights. The isoprene oxidation products MVK and MACR were found with maxima around 1–2 ppb. Monoterpene concentrations did not increase from wet season to dry season as isoprene concentrations did. Interestingly, the monoterpene species composition also showed fluctuations between and as well within seasons (Table 2). This behavior is thought to derive from a mixture of influences such as the seasonal development of plant species and from different chemical reactivities of monoterpene species as well.

3.5. VOC Species During Wet and Dry Season: Mean Values at and Above the Canopy

[17] For a better comparison of wet and dry season results the diurnal data were sorted and compiled. Figure 5 shows an overview of the mean values observed under daylight (1000–1800) conditions. As shown in Figure 5a, isoprene, monoterpenes and the isoprene oxidation products MVK and MACR show different patterns comparing wet and dry season results. Isoprene dominates the composition with increasing concentrations from the beginning to the end of October. Especially during the dry season, its atmospheric concentration reaches enormous values, both at the canopy top (see also section 3.3) as well as above the canopy. In general accordance with mixing ratios found near the canopy, the values at 40–50 m also showed a significant increase up to 12 ppb compared to the wet season. Such high values are in close accordance with modeled isoprene surface concentrations up to 10 ppb for July [Granier *et al.*, 2000]. The concentrations are decreasing toward the end of October to values more typical to the wet season. The oxidation products MVK and MACR also had higher concentrations during the dry season. The ratios of their average concentrations were similar in both seasons. Monoterpene concentrations, typically below 0.5 ppb in the wet season, are only about 1/10 of those observed for isoprene. However, it has to be kept in mind that monoterpenes represent twice as much

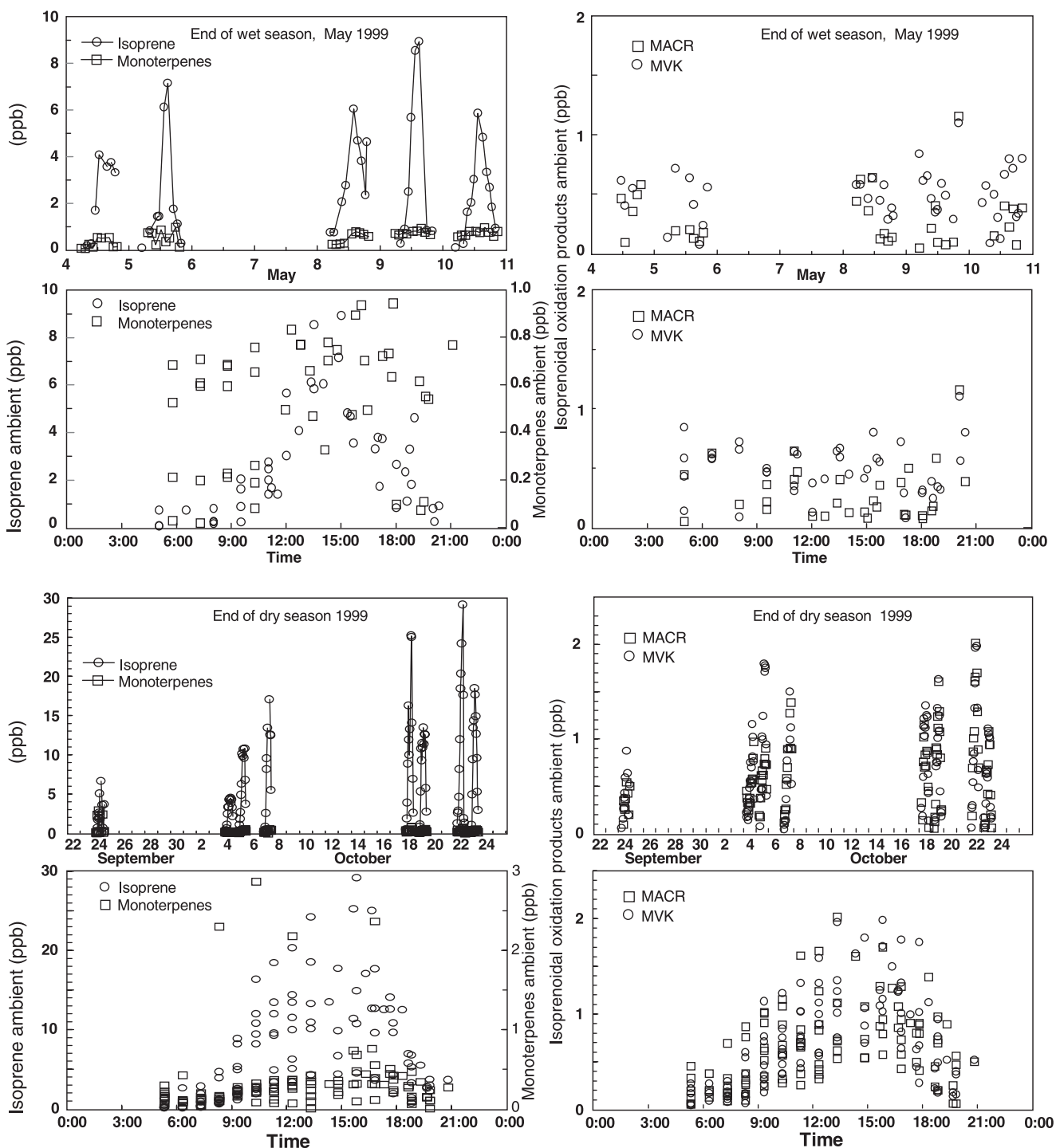


Figure 4. Compilation of daily and diurnal cycles for the biogenic isoprenoids and their oxidation products during the wet and dry season. MKV and MACR, methyl vinyl ketone and methacrolein, respectively. Note the different scales for the wet and dry season.

carbon as isoprene. Atmospheric monoterpene concentrations in the dry season cover similar ranges as in the wet season. C_1 and C_2 oxygenated compounds also showed significant differences between wet and dry seasons (Figures 5b and 5c). Both organic acids and aldehydes exhibit very high mixing ratios under dry season conditions. Aldehyde concentrations typically increased by a factor of 4–5 from wet to dry season, as did the concen-

trations of both organic acid species. Part of this increase can be ascribed to air pollution by vegetation fires. But this does not exclude an increase of secondary biogenic sources. Higher isoprene concentrations together with a higher oxidative capacity of the air may contribute to these oxygenated compounds. According to *Carter and Atkinson* [1996], isoprene oxidation by OH yields about 60% formaldehyde. Similarly, *Sanhueza et al.* [1996] provide evi-

Table 2. Monoterpene Species Composition (%) as Observed at the Two Sites and Different Heights During the End of the Wet and the End of the Dry Season^a

	End of Wet Season				End of Dry Season				
	Scaffold		Tower (25 m)	Tower (51 m)	Scaffold			Tower (25 m)	Tower (51 m)
	4–5 May	8–10 May	17–19 May	17–19 May	4–7 October	18–19 October	22–23 October	17–19 October	17–19 October
α-Pinene	19.94	12.56	8.55	10.36	36.5	48.3	42.8	8.55	10.36
Camphene	39.46	72.02	61.80	64.29	28.9	6.6	15.9	61.80	64.29
Sabinene	8.07	4.11	11.03	7.58	7.3	8.4	8.5	11.03	7.58
β-Pinene	14.55	4.72	3.58	5.29	13.9	17.9	13.5	3.58	5.29
Myrcene	10.39	0.83	4.12	3.72	2.9	4.9	3.4	4.12	3.72
α-Phellandrene	0.65	0.05	0.32	0.27	0.6	0.3	0.1	0.32	0.27
3-Carene	1.14	0.64	0.65	0.17	0.1	0.8	0.5	0.65	0.17
α-Terpinene	0.26	0.00	0.10	0.19	0.1	0.6	0.3	0.10	0.19
p-Cymene	3.00	4.37	6.14	4.59	1.5	2.1	3.1	6.14	4.59
Limonene	2.42	0.54	3.28	3.17	8.0	8.7	10.3	3.28	3.17
γ-Terpinene	0.14	0.17	0.43	0.37	0.3	1.4	1.6	0.43	0.37

^a Values represent the means as calculated from the 24-h values as observed during the given periods. Scaffold, 8 m sampling height.

dence that isoprene is a main precursor for formic acid, which is in accordance with *Jacob and Wofsy* [1988] and *Neeb et al.* [1997a, 1997b].

3.6. Isoprene and Its Oxidation Products

[18] In this remote environment, the only known source of MVK and MACR is isoprene oxidation. Under these

conditions, the ratio (MVK + MACR)/isoprene can provide an indication of the extent of oxidation. The average daytime values of this ratio found in this study are listed in Table 3 for the different sampling sites, heights, and seasons. In the wet season, the ratio was generally quite constant at different heights and sampling sites at around 0.2 (notwithstanding the limited samples collected at

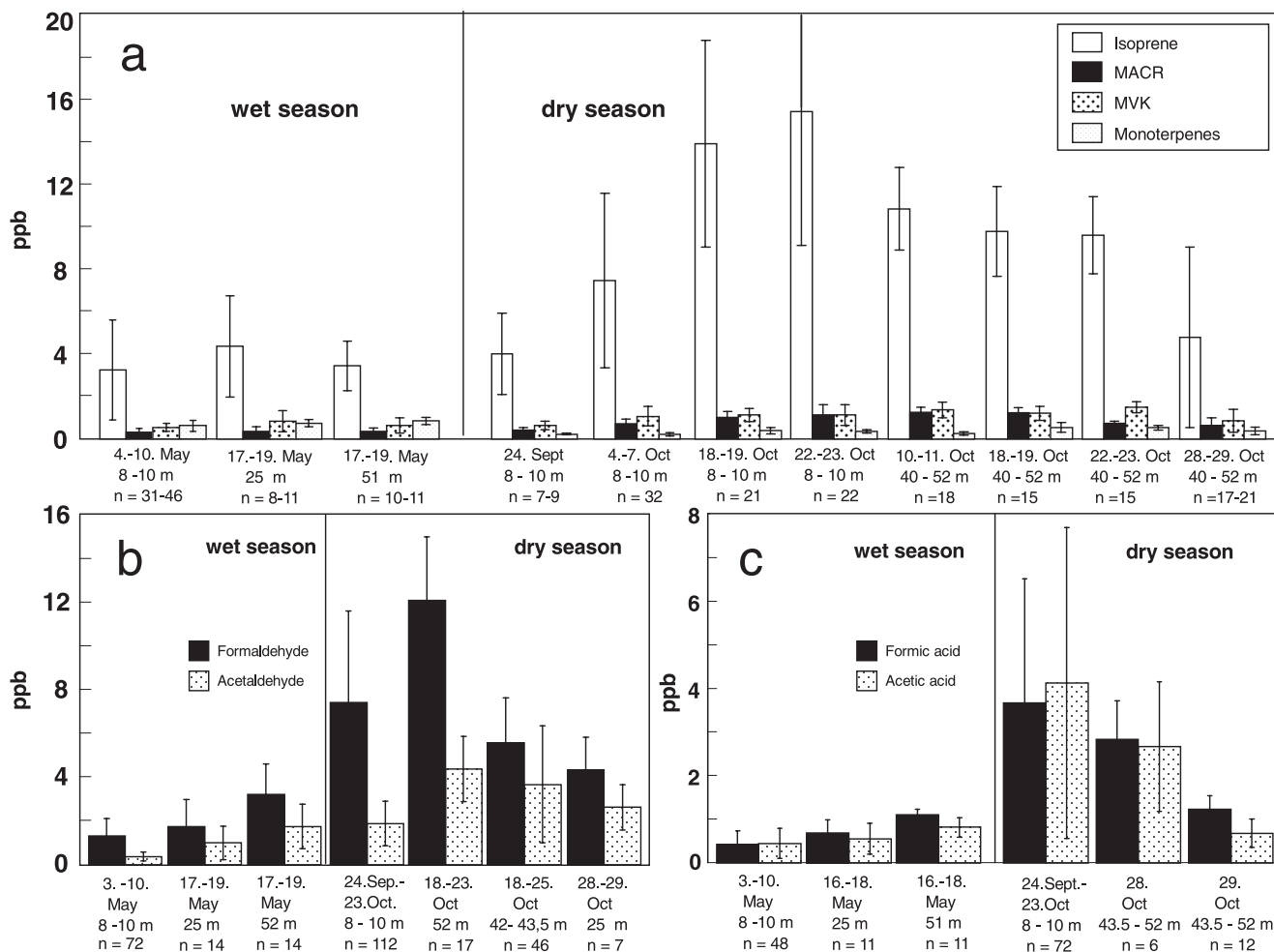


Figure 5. a–c. Overview of the mean values as observed under daylight (1000–1800) conditions for all VOC species investigated at different sites and heights; grouped as measured with different techniques.

Table 3. Ratios (ppb/ppb) Isoprene Oxidation Products Versus Isoprene ((MVK + MACR)/Isoprene) and Methyl Vinyl Ketone Versus Methacrolein (MVK/MACR) During the End of the Wet and the End of the Dry Seasons 1999 in Rondônia, Brazil^a

Site, Height	(MVK + MACR)/Isoprene		MVK/MACR	
	Wet Season	Dry Season	Wet Season	Dry Season
Camp tower, 8–10 m	0.22 ± 0.17 (18)	0.21 ± 0.12 (56)	2.76 ± 1.44 (18)	1.30 ± 0.44 (56)
Forest tower, 1 m	0.68 ± 0.49 (2)	2.87 (1)	4.22 ± 1.21 (2)	0.88 (1)
Forest tower, 25 m	0.20 ± 0.10 (5)	0.31 ± 0.10 (3)	2.16 ± 0.85 (5)	1.27 ± 0.49 (3)
Forest tower, 40–45 m	–	0.31 ± 0.30 (29)	–	1.28 ± 0.47 (29)
Forest tower, 50–52 m	0.23 ± 0.09 (7)	0.30 ± 0.16 (21)	2.09 ± 0.69 (7)	1.45 ± 0.66 (21)

^a All data are given as means ± S.D. (*n*) and reflect daytime conditions (1000–1800 LT).

the forest floor, where lower light levels and less mixing is expected). In the dry season at the forest site, the ratio was consistently higher at ~ 0.3 . This suggests that only a small increase in overall oxidation occurred in the transition between the wet and dry seasons in spite of the substantial increase of ozone during daytime hours (see Figure 1) [Andreae et al., 2002]. However, the ratio (MVK+MACR)/isoprene is not purely photochemically driven, as it is expected to be influenced by the isoprene emission rate and the proximity to emission sources as well as by atmospheric mixing [Montzka et al., 1995]. Considering this, the constancy of the ratio between completely different sites and between sampling locations both within the canopy (25 m) and above the canopy (>40 m), in both seasons, is remarkable. Perhaps of more significance to the ratio is the amount of available NO_x, which is nonlinearly related to OH concentrations and is a key variable in the efficient production of MVK and MACR from isoprene oxidation. Biesenthal et al. [1998] have described a logarithmic type of dependence of the (MVK + MACR)/isoprene ratio on the average mixing ratios of NO_x for several different campaigns spanning a wide range of NO_x regimes. In this work, daytime values of NO_x increased only slightly from ca. 0.2 ppb in the wet season to <0.5 ppb in the dry season [Andreae et al. 2002]. For these NO_x levels, the reported (MVK + MACR)/isoprene ratios agree extremely well with the relationship shown in the work of Biesenthal et al. [1998].

[19] The overall diurnal course of the (MVK + MACR)/isoprene ratio is shown in Figure 6. The trend is consistent between seasons, and is similar to other observations by Montzka et al. [1995] and Biesenthal et al. [1998] in temperate forest regions. The relatively higher ratios in the early morning hours are likely the manifestation of a variety of factors at work beneath the nocturnal inversion which serve to remove isoprene preferentially over its longer lived oxidation products (e.g. OH (from alkene ozonolysis), NO₃ chemistry, dynamic effects, ozonolysis [Hurst et al., 2001]).

[20] The ratio MVK/MACR is also useful in examining the oxidant conditions during the day. This ratio depends on the yields of MVK and MACR from isoprene oxidation and on the relative reaction rates of isoprene, MVK, and MACR with both OH and ozone. Oxidation of isoprene by OH in the presence of NO_x produces MVK and MACR with respective yields of 32 and 23% [Tuazon and Atkinson, 1990]. If MVK and MACR did not undergo further oxidation, the concentration ratio MVK/MACR would consequently be ~ 1.4 . However, MACR is removed through OH-oxidation more quickly than MVK, which serves to

drive up the ambient ratio MVK/MACR. For ozonolysis, relative yields and reaction rates are reversed in both cases: isoprene yields more MACR than MVK, and MVK reacts more quickly with O₃ than MACR, both of which result in a lower MVK/MACR ratio. The average daytime values of MVK/MACR for both seasons are shown in Table 3, and also on a diurnal basis in Figure 6. In the dry season, the daytime ratios were typically ~ 1.3 – 1.5 , which is quite close to the relative OH production yield of 1.4. Based on steady state calculations, these values suggest a relatively high [O₃]/[OH] ratio in the dry season [Starn et al., 1998], i.e., a relatively low oxidation capacity due to low OH concentrations. With low OH concentrations, subsequent

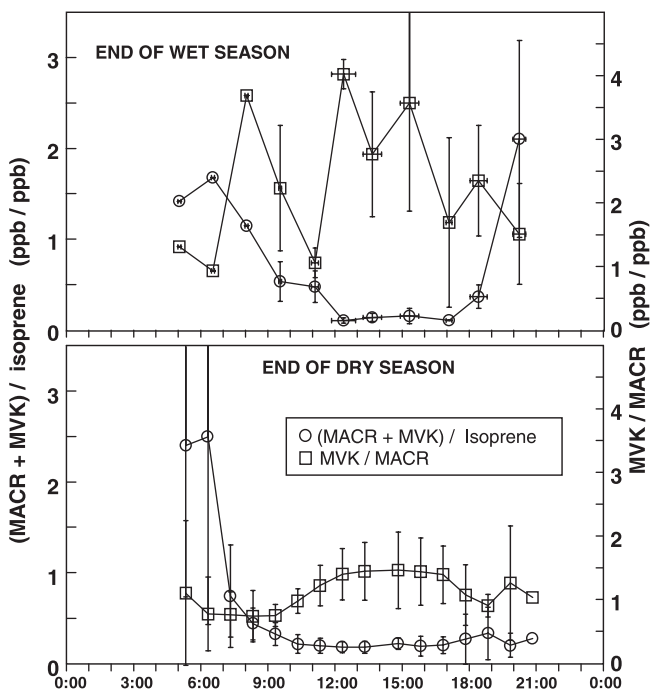


Figure 6. Diurnal courses of methyl vinyl ketone (MVK) and methacrolein (MACR) versus isoprene and MVK/MACR ratios indicating the oxidation capacity during the end of the wet and dry season 1999. Data for the wet season show the mean values (\pm S.D.) of data ($n = 1$ – 5) grouped for sampling intervals of 30–70 min (sampling times 8 min each). Dry season data, obtained from automatic measurements with a higher time resolution at always the same daytime, are given as means (\pm S.D.) of samples ($n = 3$ – 8 , except last data point; sampling times 40 min).

Table 4. Potential Pyrogenic Contributions to Atmospheric Mixing Ratios of Some Selected VOC Species Given in ppb^a

ppb CO	Tropical Rainforest			Savanna and Grassland			Extratropical Forest		
	250	500	2000	250	500	2000	250	500	2000
Isoprene	0	0	0.1	0	0.1	0.3	0.1	0.2	0.8
Monoterpenes	0.1	0.1	0.4	0	0	0.1	0.1	0.1	0.6
Formaldehyde	3.1	6.3	25	1.6	3.2	13	4.8	9.6	38
Acetaldehyde	1.0	2.0	8	1.2	2.4	9.8	0.8	1.5	6.2
Formic acid	1.6	3.2	13	1.6	3.3	13	4.1	8.2	33
Acetic acid	2.4	4.7	19	2.3	4.7	19	4.1	8.3	33
Methanol	4.2	8.4	34	4.4	8.7	35	4.1	8.2	33

^a The contribution was related to several CO mixing ratios, which were observed during the end of the dry season as minimum, mean, and maximum values (C. Amman and J. Beck, personal communication, 2000). Data were estimated according to emission factors for pyrogenic species emitted from various types of biomass burning in relation to CO according to *Andreae and Merlet* [2001].

oxidation of the longer-lived MVK and MACR is hindered, with the result that the observed ratio tends to be closer to the production yield ratio. In the wet season, one would expect MVK/MACR to be even lower with the lower ozone (and, presumably, OH) concentrations. However, the ratio MVK/MACR was on average somewhat higher in the wet season, but much more scattered (see Figure 6) due to the higher individual uncertainties on MVK and MACR (the result of lower sample volumes and lower MVK and MACR concentrations) which were amplified when examining their ratio. For this reason, it is difficult to draw any meaning from the wet season MVK/MACR data or to make any meaningful comparisons with the dry season MVK/MACR data. The trend of the diurnal course of MVK/MACR in the dry season (Figure 6) agrees well with that found in other studies [cf. *Montzka et al.*, 1995; *Starn et al.*, 1998].

4. Conclusions

[21] Isoprene is an important species in the tropical environment (and in fact likely dominates because of its high reactivity), but there are other VOCs which can reach atmospheric concentrations comparable to or even exceeding that of isoprene. These findings are in close accordance with a similar report about VOC species and concentrations at a tropical rainforest site north of Manaus [*Kesselmeier et al.*, 2000]. The data confirm the low amounts of atmospheric monoterpenes (<10% of isoprene mixing ratio) which was observed in the above study. This is a consequence of either low monoterpene emission rates or/and high reactivities of these compounds whose oxidation products may rapidly end up in aerosol particles [*Christoffersen et al.*, 1998; *Kavouras et al.*, 1998, 1999; *Calogirou et al.*, 1999]. Next to isoprene, formaldehyde was a predominant VOC species. In addition, short-chain organic acids are present in substantial amounts. In addition to biomass burning, which is a substantial source of these oxygenated compounds in the dry season, sources for the aldehydes and acids may be numerous. Direct and indirect emissions by vegetation coupled with a bi-directional exchange [*Kesselmeier*, 2001; *Kuhn et al.*, 2002a] complicate the discussions. Furthermore, soils are also proposed to be involved in the production and exchange of these compounds [*Sanhueza and Andreae*, 1991; *Trapp and Deserves*, 1995; *Sanhueza et al.*, 1996]. For formic acid in particular, it has been shown that 80 to 100% stems from biogenic sources [*Glasius et al.*, 2000]. The question is

whether such compounds derive from photochemical decomposition of other biogenic hydrocarbons (indirect emission) or are produced and released by the plants themselves (direct emission). Direct emission of oxygenated compounds from vegetation has been reported [cf. *Kesselmeier*, 2001], but the high reactivities of isoprene and monoterpenes imply that a significant secondary oxidation source from these compounds is likely [*Neeb et al.*, 1997a, 1997b]. Hence, both direct as well as indirect release occurs and we assume that during the wet season with low biomass burning activities direct and indirect biogenic emission may contribute to a similar extent. Furthermore, vegetation may serve as a sink for the oxygenated compounds and the direction and rate of the exchange between the vegetation and the atmosphere may be determined by a compensation point [*Kesselmeier*, 2001]. Within this context, it is of high interest that *Kuhn et al.* [2002a] report on the deposition of formic and acetic acid to vegetation during both seasons. Similarly, *Rottenberger et al.* [2002] also found a deposition of short-chain aldehydes at the same site.

[22] Dramatic changes are evident upon comparing the wet and dry season data. The oxygenates were an order of magnitude higher in concentration in the dry season. The dominant source for this enlargement may be emissions from vegetation fires [*Holzinger et al.*, 1999]. In a recent paper *Andreae and Merlet* [2001] compile the available data for emission factors and emission ratios for a large number of volatile compounds. According to their review, biomass burning contributes substantially to the atmospheric burden of the short chain oxygenated VOC species we identified within this rainforest study. Hence, the high mixing ratios of acids and aldehydes may in some part be derived from forest fires during the dry season. Interestingly, isoprene concentrations also increase greatly during the dry season, although forest fires are expected to contribute little. Taking into account isoprene/CO emission factors for biomass burning [*Andreae and Merlet*, 2001] and daytime CO mixing ratios with 250, 500 and 2000 ppb (minimum, mean value and maximum, respectively; C. Ammann and J. Beck, personal communication, 2002), we estimate a potential contribution to atmospheric concentrations by pyrogenic isoprene smaller than 0.1 ppb (Table 4). In contrast, the release of pyrogenic oxygenates such as formaldehyde, acetaldehyde, formic acid, acetic acid and methanol are substantial, suggesting that pyrogenic contributions to the high concentrations of these compounds at the end of the dry season are likely. Though fires would burn at night as

well the sharp diurnal changes are assumed to result from deposition at night when a stable boundary layer prevents further transport from above. In contrast to the other VOCs, monoterpene concentrations in the dry season were typically no larger than those observed during the wet season. The relative decrease of monoterpenes may have several reasons. Some monoterpene species exhibit higher reactivities, thus they might vanish faster than isoprene due to higher ozone concentrations. Another possible explanation for the low dry season concentrations relative to other compounds can be a decrease in the number of physiologically active monoterpene emitting tree species due to leaf dropping of a substantial number of trees during the dry season. Thus, in contrast to isoprene mixing ratios, monoterpene concentrations do not increase during the dry season, even though they might also be released in small amounts by fires (see Table 4). This question can only be adequately answered by the identification and quantification of monoterpene emitters within the forest [Kuhn et al., 2002b] and monoterpene fluxes above the forest [Rinne et al., 2002]. Overall, the question is whether seasonal development of the vegetation and climatological factors (light, temperature) exhibit a strong impact on biogenic isoprenoid emission rates. This data is currently under evaluation. First data exploration showed that calculating the emission capacity by a light and temperature involving algorithm [Guenther, 1997], the potential emission rates increased from 67–128% (mean 100) to 63–209% (mean 140) from the wet to the dry season. This is in accordance with a substantial increase of isoprene emissions on a branch level (J. Kesselmeier, et al., Volatile organic compound emissions account for a significant part of the residual net terrestrial carbon sink, submitted to *Global Biogeochemical Cycles*, 2002; Kuhn et al., in preparation). However, also other factors such as stress by ozone deposition may have caused increased emissions and higher wind speed during the dry season might have facilitated emission by decreasing diffusive resistance [Penuelas and Llusia, 2001]. Interestingly, the increase of atmospheric mixing ratios of isoprene from end of September to end of October matches with an increase of active biomass due to increased precipitation. This was in fact directly observed for some tree species which went from having no active leaves at the beginning of the dry season field measurements to being fully green at the end. VOC emission data obtained from enclosure studies within the forest are under investigation.

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