EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM TROPICAL SAVANNA VEGETATION AND BIOMASS BURNING

Dissertation

zur Erlangung des Grades

Doktor der Naturwissenschaften

am Fachbereich Chemie und Pharmazie

der Johannes Gutenberg-Universität in Mainz

vorgelegt von

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geboren in München

Mainz, 2004

Tag der mündlichen Prüfung: 21. Dezember 2004

D77 – Mainzer Dissertation

ABSTRACT

Emissions of volatile organic compounds from tropical savanna vegetation and biomass burning

This dissertation focuses on characterizing the emissions of volatile organic compounds (VOCs) from tropical savanna vegetation and biomass fires. The measurements were performed with a proton-transfer-reaction mass spectrometer (PTR-MS), which enabled the online detection of a large number of VOCs.

The biogenic emissions of tropical savanna vegetation were studied in a woodland savanna in Venezuela. Two field campaigns were carried out, the first during the wet season in September/October 1999, and the second in March/April 2000 during the dry season. Three of the most important grass and tree species of the Venezuelan savanna were studied, namely the grasses *Trachypogon plumosus, Hyparrhenia rufa* and *Axonopus canescens*, and the tree species *Byrsonima crassifolia, Curatella americana* and *Cochlospermum vitifolium*. The emission rates and the controlling variables were determined with a dynamic plant enclosure system. Most biogenic emissions showed a diurnal variation, with highest values at noon and early afternoon, and low or no emissions during the night. In general, the emissions increased exponentially with increasing temperature and solar radiation, but correlated better with temperature. The emission rates of VOCs showed high variability caused, primarily, by the natural fluctuations of meteorological conditions during field measurements. The emission data were therefore normalized to a standard temperature of 30°C, and *standard emission rates* thus determined allowed for interspecific and seasonal comparisons, as well as with data from the literature.

The range of average daytime (10:00-16:00) emission rates of total VOCs measured from green (mature and young) grasses was between 510-960 ngC/g/h. Methanol (detected at protonated mass 33) was the primary emission (140-360 ngC/g/h), followed by acetaldehyde (mass 45), butene and butanol (mass 57) and acetone (mass 59) with emission rates between 70-200 ngC/g/h. The emissions of propene (mass 43) and methyl ethyl ketone (MEK, mass 73) were <80 ngC/g/h, and the emission of isoprene and C_5-alcohols (mass 69) was between 10-130 ngC/g/h. The normalized average emissions at 30°C (standard emissions) of total

VOCs was in the range 200-400 ngC/g/h. The oxygenated species methanol, acetaldehyde, acetone and MEK, represented 70-75% of the total. The remaining 30% consisted of olefins (propene; butene) and other unidentified species. The total daytime VOC emissions from dry grasses were in the range 120-470 ngC/g/h, and the standard emissions were between 24-44 ngC/g/h. Methanol accounted for about half of the emissions from dry grasses. The emission of VOCs was found to vary by up to a factor of three between plants of the same species (for both, green and dry grasses), and by up to a factor of two between the different species. The annual source of methanol from savanna grasses worldwide estimated in this work was 3 to 4.4 TgC, which could represent up to 12% of the current estimated global emission from terrestrial vegetation. For acetone, acetaldehyde and MEK, the savannas may contribute up to ~10%, 4% and 30% of the biogenic source, respectively, but these numbers are very uncertain since particularly the biogenic sources of these species are poorly quantified.

Three of the most common tree species in the Venezuelan savanna were investigated. Two of these species, *Byrsonima* and *Cochlospermum,* were isoprene emitters, and isoprene was also their primary emission (which accounted for 70-94% of the total carbon emitted by these species) followed by methanol and butene + butanol. The daytime average emission rates of isoprene measured in the wet season were 27 µgC/g/h for *Byrsonima* and 123 µgC/g/h for *Cochlospermum*. The daytime emission of methanol and butene + butanol was between 0.3 and 2 µgC/g/h. The total sum of VOCs emission measured during the day in the wet season was between 30 and 130 µgC/g/h. In the dry season, in contrast, the methanol emission from *Cochlospermum* saplings –whose leaves were still developing– was an order of magnitude higher than in the wet season (15 µgC/g/h). The isoprene emission from *Byrsonima* in the dry season was comparable to the emission in the wet season, whereas isoprene emission from *Cochlospermum* was about a factor of three lower (~43 µgC/g/h). The total sum of daytime VOCs emission in the dry season was between 2 and 26 µgC/g/h. The ratio of carbon released as VOCs to the carbon assimilated by photosynthesis during daytime varied from 0.2 to 15%. The higher ratios were observed for the specimens with higher isoprene emission. The standard emission of total VOCs of all measured tree species ranged between 0.6 and 27 µgC/g/h in the wet season, and 0.2 and 5 µgC/g/h in the dry season. Biogenic emission inventories show that isoprenoids are the most prominent and best-studied compounds. The standard emission rates of isoprene and monoterpenes of the young savanna trees were in the lower end of the range found in the literature. The biogenic emission of other

VOCs has been sparsely investigated, but in general, the standard emissions reported here were within the range observed in previous investigations.

The biomass burning study comprised the measurement of VOCs and other trace-gas emissions of 44 fires from 15 different fuel types, primarily from Africa and Indonesia, in a combustion laboratory. The average sum of emissions (excluding CO_2, CO and NO) from African fuels was ~18 g(VOC)/kg. Six of the ten most important emissions were oxygenated VOCs. Acetic acid was the major emission, followed by methanol and formaldehyde. The emission of methane was of the same order as the methanol emission (~5 g/kg), and that of nitrogen-containing compounds was ~1 g/kg. An estimate of the VOC source from biomass burning of savannas and grasslands worldwide suggests that the sum of emissions is about 56 Tg/yr, of which 34 Tg correspond to oxygenated VOCs, 14 Tg to unsaturated and aromatic compounds, 5 Tg to methane and 3 Tg to N-compounds. The estimated emissions of CO, CO_2 and NO are 216, 5117 and 9.4 Tg/yr, respectively.

The emission factors reported here for Indonesian fuels are the first results of laboratory fires using Indonesian fuels. Acetic acid was the highest organic emission, followed by acetol (mass 75) a compound not previously reported in smoke, methane, mass 97 (tentatively identified as a mixture of furfural, dimethylfuran, ethylfuran), and methanol. The sum of total emissions of Indonesian fuels was 91 g/kg, which is 5 times higher than the total emissions from African fuels. This difference was because Indonesian fuels burned mostly by smoldering combustion, whereas African fuels were consumed primarily by flaming combustion, during which mostly oxidized compounds (e.g. CO_2, H_2O and NO) are produced.

The results of this study show that oxygenated compounds, especially methanol, dominate the emissions of VOC from savanna grasses. For the measured tree saplings, methanol was also an important emission, exceeded only by isoprene. The biomass burning experiments also demonstrate the importance of oxygenated VOCs, which represent about 60% of the total trace-gas emission measured from the burning of African and Indonesian fuels. Due to the vast area covered by tropical savannas worldwide, the biogenic and biomass burning emission of methanol and other oxygenated compounds may be important for the regional and even global tropospheric chemistry. This study represents a significant improvement to the current biogenic and biomass-burning emission inventories.

Contents

1. Introduction

The atmosphere is the thin (several hundred km) gaseous envelope that surrounds the Earth. Besides varying amounts of water vapor (up to a few percent), it otherwise consists primarily of the gases nitrogen (78%), oxygen (21%) and argon (0.9%) and thousands of chemical species, so-called trace gases, which comprise the remaining ~0.1%. Among the trace gases, volatile organic compounds (VOCs), play an important role in atmospheric chemistry and the global carbon cycle (Fehsenfeld *et al.*, 1992). The family of the VOCs includes all gaseous organics, excluding CO and CO_2, and, generally, methane (CH_4). Actually, methane is the most abundant VOC in the atmosphere (average mixing ratio 1.7 ppm[1]) (Seinfeld and Pandis, 1998), but due to its low reactivity (atmospheric lifetime ~8 years) and importance as a greenhouse gas, it is frequently treated separately from other VOCs, which have atmospheric lifetimes of few hours to months and small direct impact on radiative forcing (IPCC, 2001) (therefore also often termed non-methane VOCs, NMVOCs). VOCs are key species affecting atmospheric chemistry on a local to global scale (Seinfeld and Pandis, 1998). They influence the oxidation capacity of the troposphere by reacting with the radicals OH, NO_3 and HO_2, and thus influence the concentration and distribution of several other trace gases. Production and depletion of tropospheric ozone (O_3) depend on the concentration of VOCs and NO_x ($NO_x = NO + NO_2$) (Trainer *et al.*, 1987b; NRC, 1991; Atkinson, 2000). The oxidation of certain VOCs (e.g. monoterpenes (Hoffmann *et al.*, 1997),

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[1] ppm (parts per million) = 10^{-6} by volume = μmol/mol. Other units of concentration used throughout the text: ppb (parts per billion) = 10^{-9} by volume = nmol/mol; ppt (parts per trillion) = 10^{-12} by volume = pmol/mol.

isoprene (Claeys *et al.*, 2004)) can lead to the formation of secondary organic aerosols (SOA) through gas/particle partitioning of their tropospheric reaction products. SOA have an impact on climate because they affect the radiation budget directly by scattering and absorbing solar radiation and indirectly by acting as cloud condensation nuclei (Andreae and Crutzen, 1997; IPCC, 2001). Large quantities of VOCs are emitted into the troposphere from a variety of sources both anthropogenic and biogenic. Biogenic sources include the oceans and freshwaters, outgassing from soil, sediments and geological hydrocarbon reservoirs, plant foliage and decomposition of organic material (Guenther *et al.*, 1995). Since vegetation is the main biogenic source, it is referred to this source when discussing biogenic emissions in the preceding text. The global emission rate of biogenic VOCs is about 1150 TgC/yr (Guenther *et al.*, 1995), which represent approximately 90% of the global total of VOCs entering the atmosphere, and more than double the sum of biogenic and anthropogenic methane emissions (Table 1.1).

Table 1.1. Annual global VOC and methane emission estimates (Tg C/yr)[a]

Source	Isoprene	Monoterpenes	Other VOCs	Methane
Canopy foliage	460	115	500	<1
Terrestrial ground cover and soils	40	13	50	175
Flowers	0	2	2	0
Ocean and freshwater	1	<0.001	10	15
Animals, humans and	0.003	<0.001	0.003	100
Anthropogenic (including biomass burning)	0.01	1	93	220
Total	~500	~130	~650	~510

[a] From Guenther (1999) and references therein.

The most important anthropogenic sources are combustion processes (fossil fuel and biomass burning), fossil fuel storage and transport, solvent use, industrial production processes, biological processes (e.g. landfills, rice fields, livestock husbandry) (Friedrich and Obermeier, 1999). The estimated global anthropogenic non-methane hydrocarbon (NMHC) flux is ~100 TgC/yr (Singh and Zimmerman, 1992).

This work focuses on the study of biogenic and biomass burning VOC emissions. A summary of the present state of knowledge regarding the chemistry of VOCs and the atmospheric importance of the biogenic and biomass burning sources is presented in the following sections.

1.1. Tropospheric chemistry of VOCs

In the troposphere, VOCs can be removed by reaction with the hydroxyl (OH) radical, nitrate radical (NO_3) and ozone, and many VOCs are transformed by photolysis, whereas physical loss processes of dry and wet deposition are of minor importance for most biogenic VOCs (Atkinson, 2000; Fuentes *et al.*, 2000). A brief overview of the processes leading to the formation of O_3, OH and NO_3, and the most relevant oxidative processes involving VOCs are presented next.

1.1.1. Formation of ozone, hydroxyl radicals and nitrate radicals in the troposphere

The sources of ozone in the natural troposphere are downward transport from the stratosphere to the troposphere (Logan, 1985; Roelofs *et al.*, 1997), and production in situ by photolysis of NO_2, which is formed by a series of reactions that involve VOCs and NO_x. The photooxidation of VOCs leads to the formation of organic peroxy radicals ($RO_2^\bullet$) and HO_2 radicals, which react with NO[2], converting NO to NO_2.

$$RO_2^\bullet + NO \rightarrow RO^\bullet + NO_2 \qquad \text{(R1.1)}$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad \text{(R1.2)}$$

Photolysis of NO_2 yields NO and ground state oxygen, $O(^3P)$, which reacts with molecular oxygen to form O_3, without loss of the catalysts OH, HO_2, NO and NO_2 (Crutzen, 1973)

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad \text{(R1.3)}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad \text{(M=air)} \qquad \text{(R1.4)}$$

Only 10% of all atmospheric ozone is located in the troposphere. Nevertheless its presence is of fundamental importance to atmospheric chemistry, as the OH radical is formed by the photolysis of O_3 at wavelengths <319 nm (Levy, 1971), to form O_2 and electronically

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[2] Based on the rate constants of the reactions of $RO_2^\bullet$ and HO_2 radicals with NO (R1.1; R1.2), versus those of $RO_2^\bullet$ and HO_2 with HO_2 (forming RO_2H and H_2O_2), and HO_2 with O_3 (yielding OH + $2O_2$) and the tropospheric concentrations of HO_2 and NO, net photochemical O_3 formation occurs for NO mixing ratios >10-30 ppt, while net O_3 destruction occurs for NO mixing ratios <10-30 ppt (Logan, 1985).

excited singlet oxygen atoms, $O(^1D)$, (R1.5). $O(^1D)$ atoms are deactivated to $O(^3P)$, which will follow either R1.4 (and regenerate O_3) or react with water vapor to generate OH radicals (R1.6), which would be a net loss of O_3

$O_3 + h\nu \rightarrow O_2 + O(^1D)$ (R1.5)

$O(^1D) + H_2O \rightarrow 2OH$ (R1.6)

The nitrate radical is formed according

$NO + O_3 \rightarrow NO_2 + O_2$ (R1.7)

$NO_2 + O_3 \rightarrow NO_3 + O_2$ (R1.8)

Its daytime abundance is low because it is effectively photolyzed, but it can increase to measurable levels during nighttime (Atkinson, 2000).

1.1.2. Reaction mechanisms and products

The initial reactions of VOCs with OH, NO_3 and O_3 have been elucidated over the past two decades (for reviews see e.g. Seinfeld, 1999; Atkinson, 2000; Atkinson and Arey, 2003), and the overview given below is taken largely from those articles. For most VOCs there are two general reaction mechanisms: (1) H-atom abstraction from C–H bonds (and to a much lesser extent O–H bonds) by OH and NO_3 radicals (important for alkanes, ethers, alcohols, carbonyls and esters), and (2) addition of OH, NO_3 and O_3 to the carbon atoms >C=C< bonds (important for isoprene, monoterpenes and other oxygenated compounds containing >C=C< bonds).

1.1.2.1. Reactions with OH and NO_3 radicals

The reactions of H-atom abstraction from C–H bonds by OH radicals and NO_3 radicals (during nighttime), and addition of OH and NO_3 radicals to the carbon atoms of a double bond result in the formation of alkyl, substituted alkyl or hydroxyalkyl radicals. A general tropospheric degradation scheme applicable for most VOCs is presented in Fig 1.1, showing the intermediate radicals alkyl (or substituted alkyl) radicals ($R^\bullet$), alkyl peroxy radicals ($RO_2^\bullet$), and alkoxy radicals ($RO^\bullet$). The scheme will be explained considering the oxidation of alkanes as example. The reaction of H-abstraction in alkanes occurs principally with OH, but also with NO_3 and Cl atoms (R1.9) (for unsaturated compounds, the reactions proceed by addition of OH or NO_3 to the double bond). Under all tropospheric conditions, the alkyl radicals $R^\bullet$ (and also hydroxyalkyl radicals for unsaturated compounds) thus formed, react rapidly and exclusively with O_2 to form an alkyl peroxy ($RO_2^\bullet$) radical (R1.10). $RO_2^\bullet$ can react with NO_2, NO, HO_2 and $RO_2^\bullet$ (R1.11-R1.14). The reactions of $RO_2^\bullet$ radicals with NO and HO_2 are important, since the competition between these reactions determines whether net O_3 formation (see R1.1) or net O_3 destruction occurs. R1.11 is negligible in the lower troposphere, since it forms alkyl peroxynitrates, which rapidly decompose back to the reactants. R1.12 leads to the formation of an alkoxy radical $RO^\bullet$ (and alkyl nitrate, $RONO_2$, for $RO_2^\bullet$ radicals with more than 3 carbon atoms). R1.13 forms hydroperoxides, which undergo wet and dry deposition, photolysis and reaction with OH. The combination reactions of $RO_2^\bullet$ radicals (R1.14) can form the corresponding alkoxy radical or an alcohol plus a carbonyl. The alkoxy radicals $RO^\bullet$ can react with O_2 (R1.15) which leads to a carbonyl, but it can also decompose or isomerize.

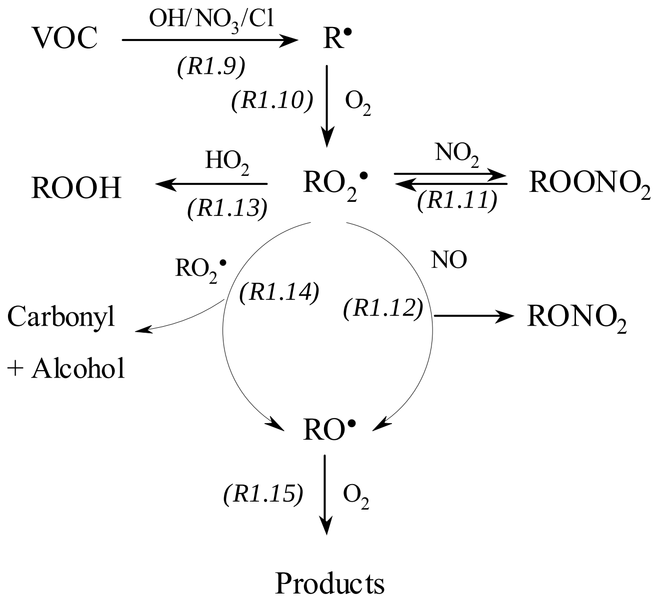


Figure 1.1. General oxidation reactions of VOCs in the troposphere. Reactions of alkyl radicals formed after H-atom abstraction from C–H bonds or after OH or NO_3 radical addition to >C=C< bonds (adapted from Atkinson, 2000).

1.1.2.2. Reaction with O_3

The reaction of O_3 with VOCs containing >C=C< bonds proceed by initial addition of O_3 to the double bond to form a primary ozonide, which rapidly decomposes via two pathways to form two sets of carbonyl plus a biradical species known as “Criegee intermediate” (mechanisms not shown). The biradicals can be collisionally stabilized or decompose by a number of routes which include reaction with water vapor to form α-hydroxyhydroperoxides which can decompose to a carboxylic acid plus H_2O or to a carbonyl plus H_2O_2 or they can rearrange to an energy-rich hydroperoxide with subsequent decomposition to an OH radical and a substituted alkyl radical. This formation of OH radicals may be an important source of OH radicals in the troposphere, especially in the late afternoon and during nighttime (Paulson and Orlando, 1996)

1.1.3. Lifetimes of VOCs in the troposphere

Table 1.2. Calculated tropospheric lifetimes for selected VOCs with respect to gas-phase reaction with OH radicals, and their tropospheric concentration range measured in rural/suburban areas

	Lifetime due to reaction with OH[a]	Concentration range Rural and Suburban areas[b] (nmol/mol)
Isoprene	1.4h	0.005-5.5
Monoterpenes	23 min – 2.6 h[c]	0.12-2[d]
Propene	5.3 h	0.02-2
1-Butene	4.4 h	0.01-0.04
Methanol	12 day	2-10[e]
2-Methyl-3-buten-2-ol (MBO)	2.4 h	0.6-7.9[f,g]
Acetaldehyde	8.7 h	0.1-4
Acetone	53 day	0.2-8
Acetic acid	14 day	0.5-2
Methyl ethyl ketone (MEK)	10 day	0.1-0.5
Methyl vinyl ketone (MVK)	7.3 h	0.01-1.7[b,g]
Methacrolein (MACR)	4.1 h	0.02-1.7

[a] Taken from Atkinson and Arey (2003), Atkinson (2000), or calculated from the room temperature rate constants for the reactions with OH (Finlayson-Pitts and Pitts, 2000). Assumed OH concentration: 2.0×10^6 molecule/cm^3, 12-h daytime average.

[b] Finlayson-Pitts and Pitts (2000) and references therein, unless noted otherwise.

[c] Lifetime (in polluted air) of monoterpenes due to the reaction with NO_3 is in the range of minutes (<30 min). But this loss reaction may be important only at night (Atkinson and Arey, 2003; for a 12-h nighttime average $[NO_3]= 2.5 \times 10^8$ molecule/cm^3)

[d] Rinne *et al.* (2002) ; Bonsang and Boissard (1999) and references therein.

[e] Heikes *et al.*, (2002) and references therein.

[f] ..Lamanna and Goldstein (1999) ; Schade and Goldstein (2001). Measured above a pine plantation.

[g] Spaulding *et al.* (2003). Measured above a pine plantation.

Rate constants for the gas-phase reactions of many VOCs with OH radicals, NO_3 radicals and O_3 have been measured (e.g. Atkinson and Arey, 1998; Finlayson-Pitts and Pitts, 2000, and references therein), and can be combined with assumed tropospheric concentrations of OH, NO_3 and O_3 to calculate the lifetimes of the VOCs with respect to each of these processes. As reaction with the OH radical is the dominant tropospheric loss process for a majority of VOCs, the lifetimes due to the reaction of selected compounds (that were measured in this work) with OH are presented in Table 1.2., together with their respective tropospheric mixing ratio range reported in the literature for rural and suburban areas (Finlayson-Pitts and Pitts, 2000).

1.2. Biogenic VOCs and atmospheric chemistry

The biosphere, especially vegetation, releases a mixture of several hundreds to thousands VOCs into the atmosphere (Fall, 1999; Kesselmeier and Staudt, 1999), and some of these compounds are emitted in large amounts and are reactive enough to significantly affect the chemistry of the troposphere (Chameides *et al.*, 1988; Fehsenfeld *et al.*, 1992; Fuentes *et al.*, 2000). Although there are large uncertainties associated with emission estimates of biogenic VOCs, it is currently estimated (Guenther, 1999) that the global budget (Table 1.1) is composed of 42% isoprene, 11% monoterpenes, and 46% other VOCs (including primarily C_1-C_3 oxygenated compounds, hexenal family of alcohols and aldehydes, and 2-methyl-3-buten-2-ol (MBO) (Fall, 1999)). From the tropospheric chemistry of VOCs outlined above can be understood that biogenic VOCs will have an influence on ozone production. Since there are a variety of competing reactions, ozone formation is a nonlinear process that depends mainly on the $[VOC]/[NO_x]$ ratio and the nature (reactivity) and concentration of the particular VOC (Fehsenfeld *et al.*, 1992). The only significant formation route of O_3 in the troposphere is the photolysis of NO_2 (R1.3 and R1.4) (NRC, 1991). The necessary NO_2 is produced by the reaction of organic peroxy ($RO_2^{\bullet}$) and HO_2 radicals (formed in R1.10) with NO (R1.1 and R1.2), when the ambient mixing ratio of NO is high enough. On the contrary, in NO-poor environments, the oxidation of VOCs leads to O_3 destruction, and furthermore suppressed OH concentration. Results of three-dimensional chemistry and transport models have shown that global VOC emissions, particularly isoprene, cause a 17-18% increase in the mean background tropospheric O_3 mixing ratios (Houweling *et al.*, 1998; Poisson *et al.*, 2000), and a 8-16% reduction in global OH concentrations (Roelofs and Lelieveld, 2000, Poisson, 2000 #194), and a 50% decrease in regional OH concentrations in the boundary layer of tropical rain forests, where isoprene emissions are especially high (Roelofs and Lelieveld, 2000). In field studies was also found out that biogenic VOCs dominate atmospheric chemistry in rural –mainly NO-poor areas– as their oxidation represents the major loss of OH radicals (Trainer *et al.*, 1987a; Lamanna and Goldstein, 1999). The concentration of carbon monoxide is a major factor in the control of OH radicals levels in the atmosphere, and the oxidation of biogenic VOCs appears to be a significant source of CO on a global level, accounting for 10-20% of the total (e.g. Hatakeyama *et al.*, 1991; Röckmann *et al.*, 1998).

Forest vegetation is the principal global source of atmospheric organic particles (Cachier *et al.*, 1985). Organic aerosols that are emitted directly in particulate form (e.g. pollen, spores, bacteria) are called primary organic aerosols, whereas the secondary organic aerosols (SOA) are products of VOCs oxidation. The volatility of the oxidation products is one of the most important parameters influencing aerosol formation. Those products having sufficiently low vapor pressures will exist primarily in the condensed phase, either forming new particles or condense onto pre-existing aerosol particles (Calogirou *et al.*, 1999; Finlayson-Pitts and Pitts, 2000). Natural SOA formation is believed to result mainly from oxidation of monoterpenes and sesquiterpenes (e.g. Hoffmann *et al.*, 1997). Additionally, recent field experiments have shown that photooxidation of isoprene could also generate an important fraction of the estimated global biogenic source of SOA (Claeys *et al.*, 2004).

1.2. Biomass burning and atmospheric chemistry

Biomass burning is a source of many trace gases (CO_2, CO, CH_4, NO, VOCs, HCN, CH_3CN, CH_3Cl among the most important) as well as particles, and therefore strongly influences the composition of the atmosphere (Crutzen *et al.*, 1979; Crutzen and Andreae, 1990; Fishman *et al.*, 1991). Between 2-5 × 10^{12} kg carbon are emitted from biomass burning in the tropics each year (Crutzen and Andreae, 1990), and savannas are the largest source, contributing to ~50% of all biomass burned in these areas (Hao and Liu, 1994; Andreae and Merlet, 2001). By comparison, the carbon mass released from global fossil fuel combustion is estimated at about 5.5 × 10^{12} kg/yr (Crutzen *et al.*, 1999). The atmospheric and, in general, environmental consequences of biomass burning are diverse. The oxidation of CO and VOCs in the presence of high levels of NO_x, as will be the case in the smoke plumes, leads to regional O_3 and photochemical smog production (Crutzen *et al.*, 1985; Delany *et al.*, 1985; Kirchhoff and Marinho, 1994). The impact of biomass burning on the global tropospheric ozone concentration has been investigated in several studies (e.g. Galanter *et al.*, 2000; Lelieveld and Dentener, 2000; Marufu *et al.*, 2000). All studies estimate the contribution of biomass burning to the global tropospheric ozone concentration to be in the order of 10%. Nevertheless, on a regional scale close to the source region, biomass burning contributes to a much larger extent to the ozone concentration (Marufu *et al.*, 2000). Ozone is also a key precursor of OH (i.e. photolysis of O_3 followed by reaction of O^1D with water vapor, see R1.5 and R1.6). Model results (Mason *et al.*, 2001) and estimates derived from the observed decrease rate for a number of chemical species (Hobbs *et al.*, 2003), have predicted that additional O_3 produced in the biomass burning plume will contribute to the formation of OH during the first hour or less of plume evolution. However, OH production reactions are constrained by the availability of NO_x (R1.3-R1.6), and after long-distance transport, the biomass burning air masses usually have low NO_x values (NO_x mixing ratios in the order of several hundred ppb close to the fire, which decreased with distance to the fire to values well below 10 ppb have been observed (Hobbs, 1996)).

Biomass fires are also an important source of particles. Smoke is a mixture of ash particles, soot, organic materials, and inorganic salts (Graham *et al.*, 2002; Mayol-Bracero *et al.*, 2002). Aerosols influence the radiative budget of the Earth directly (i.e. backscattering and absorption of solar radiation) and indirectly by modification of the cloud droplet size and the precipitation efficiency (Crutzen *et al.*, 1985; Penner, 2001; Ramanathan *et al.*, 2001). Recent studies have investigated the complex interactions of smoke from biomass burning with clouds in Amazonia (Andreae *et al.*, 2004; Koren *et al.*, 2004), describing additional effects that may have important consequences for regional climate. Andreae *et al.* (2004) report in situ measurements of aerosols, cloud drop size distribution and precipitation under different conditions, from very clean atmosphere to air masses heavily affected by biomass burning. According to their research, there are various cloud and precipitation regimes: (a) *Blue ocean* over clean maritime areas, and (b) *Green ocean*, over the unpolluted Amazon, where low concentrations of cloud condensation nuclei (CCN) –which produce water droplets, which coalesce rapidly into raindrops– result in an effective aerosol washout by precipitation. (c) *Smoky clouds* (i.e. clouds that grow out of the smoke haze produced by vegetation burning), showed considerably suppression and delayed onset of precipitation due to the high concentration of aerosols, which, in turn, results in high concentrations of small droplets that are slow to coalesce and precipitate. The delayed precipitation results in the constant presence of aerosols in the air, thus maintaining the rainless condition. Moreover, the water vapor is being transferred to greater heights, causing intense ice precipitation, from thunderclouds. (d) *Pyro-clouds*: an extreme form of smoky clouds that forms in the smoke plume over an active fire. There is a potential interaction of opposing effects in this case: on one hand, the high concentrations of the CCN stop the precipitation, and the heat of the fire invigorates the updrafts, hence there is a greater probability for overshooting cloud tops into the stratosphere. On the other hand, large ash particles may serve as giant CCN and initiate particles for precipitation.

The study of Koren *et al.* (2004) show that smoke aerosols have a “semi-direct” effect on climate, causing a reduction in cloud cover and warming the surface. The proposed mechanism can be summarized as follows: the direct effect of aerosols stabilizes the boundary layer by heating the smoke aerosol layer and cooling the surface. This process by itself reduces the convectivity and boundary layer cloud formation. This reduction of irradiance reaching the surface decreases the evaporation from vegetation and water bodies. With less moisture, a more stable boundary layer together with the competition for water vapor by the high concentrations of particles, there is less likelihood to form clouds. Additionally, the solar heating of the air by black carbon, leads to evaporation of the clouds. In the afternoon, since there is less cloud cover, sunlight passes through the atmosphere and warms the surface. They estimated a radiative forcing due to the semi-effect of the reduced cloud cover of +8 W/m^2 (i.e. warming effect), as opposed to the smoke negative forcing of –28 W/m^2.

1.3. Aim of this work

The main objectives of this work were to characterize the VOCs emitted to the atmosphere in tropical regions by savanna vegetation and biomass burning, and investigate their contribution to tropospheric budgets.

The qualitative and quantitative determination of the VOC emissions was made using proton-transfer-reaction mass spectrometry (PTR-MS), a chemical ionization technique for measurement of trace amounts of VOCs in air. A description of the technique and the instrument is given in Chapter 2.

The VOCs exchange between the vegetation and the atmosphere was investigated in field measurements carried out in a Venezuelan savanna. The dominant grass and tree species growing at this savanna were measured in both, the dry and the wet season. The grass tussocks could be studied at different developmental stages (i.e. young, mature and dry) in the different seasons, whereas the studied tree saplings were all very young, since they could not be taller than 1m, due to restrictions of the measurement system. Climatic factors such as solar radiation and temperature, as well as the CO_2 exchange of the plant were monitored. The effect of developmental, environmental and physiological factors on the VOC emission rates and emission composition should be examined and, if possible, quantified. Chapter 3 and 4 present the results of the grass and tree measurements, respectively.

The measurements of trace-gas emissions from biomass burning were carried out in the Fire Sciences Laboratory (Montana, USA). Fifteen different biomass types including savanna grass and litter, rice straw, peat and duff, mainly from Africa and Indonesia, were burned in the laboratory and the emissions were analyzed with PTR-MS and open-path Fourier transform infrared spectroscopy (OP-FTIR). The simultaneous measurement of both instruments has the potential to provide a broad characterization of VOCs. The environmental conditions during the experiments were controlled, the mass loss of the fuel during the fire was recorded, and the chemical and physical fuel properties of the biomass were analyzed. This information should allow for the calculation of trace-gas emission factors for the whole fire and also separated emission factors for the two main combustion phases, flaming and smoldering, as well as the relative proportion of VOC emissions integrated over both combustion stages. The results of these experiments will be discussed in Chapter 5.

2. Experimental

2.1. Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)

Proton-transfer-reaction mass spectrometry (PTR-MS) is a technique developed at the University of Innsbruck, which employs chemical ionization to measure traces of VOCs in real time. The technique has been described in detail by (Hansel *et al.*, 1995; Lindinger *et al.*, 1998); a summary of which is presented below.

2.1.1. Measurement principle

Trace-gas analysis based on chemical ionization (CI) has great advantages over conventional mass spectrometry using electron impact ionization (EI). The latter technique often suffers from strong fragmentation of molecular ionic species, which may result in such complex break-up patterns that the quantification of individual compounds, especially in complex gas mixtures, is not possible. CI techniques use ion-molecule reactions (IMR) rather than electron impact, thus ionizing molecules in a way that causes much less fragmentation. In the PTR-MS technique, the CI system is based on proton-transfer reactions, and uses hydronium ions H_3O^+ as proton donors (primary reactant ion). Most of the trace species analyzed produce only one product ion, which is measured at the molecular mass +1. Exceptions are the alcohols higher than methanol, and, to a lesser extent, heavier aldehydes (C > 3), which fragment by losing a water molecule (Spanel *et al.*, 1997; Spanel and Smith, 1997).

Hydronium ions are the most suitable primary reactant ions. They do not react with the most abundant chemical constituents of ambient air such as N_2, O_2, Ar and CO_2, as those species have proton affinities lower than that of H_2O molecules (166.5 kcal/mol i.e. 691 kJ/mol). Therefore, the air itself acts as the buffer gas containing the reactant substances. Most VOCs have proton affinities exceeding that of water, so proton transfer occurs on almost every collision with a H_3O^+ ion:

$$H_3O^+ + VOC \xrightarrow{k} VOC \bullet H^+ + H_2O \qquad \text{(R2.1)}$$

If the sum of product ions is less than ~5% of the primary ion signal (the H_3O^+ signal does not decline significantly due to reactions) the density of product ions $VOC{\bullet}H^+$ can be obtained from following relation:

$$[VOC{\bullet}H^+] = [H_3O^+]_0\,(1 - e^{-k[VOC]t}) \approx [H_3O^+]_0\,[VOC]\,k\,t \qquad (2.1)$$

where $[H_3O^+]_0$ is the density of H_3O^+ ions in the absence of neutral reactant molecules, k the reaction rate constant for the proton transfer from H_3O^+ to a specific VOC, and t is the average time the ions spend in the reaction region. The reaction rate of most exothermic proton-transfer processes is nearly equal to the collisional limiting value*;* k is therefore equal to either the Langevin rate constant, in the case of non-polar reactants (Su and Bowers, 1979), or the capture rate coefficient (Su and Chesnavich, 1982) or ADO (average dipole orientation) rate constant in the case of polar reactants (Su and Bowers, 1979). As [*VOC*] denotes small densities of organic trace compounds present in the atmosphere, the density of H_3O^+ ions, $[H_3O^+]$, is considered constant. The ion detection system measures the count rates $i(H_3O^+)$ and $i(VOC{\bullet}H^+)$, which are proportional to their respective ion concentrations. Since the reaction time and the respective reaction rate constants are known, the concentrations of the neutral organic compound [*VOC*] can be calculated.

2.1.2. The instrument

The PTR-MS instrument (Ionicon Analytik GmbH, Innsbruck, Austria) is essentially comprised of three parts: an ion source, a drift tube and the ion detection system (Figure 2.1).

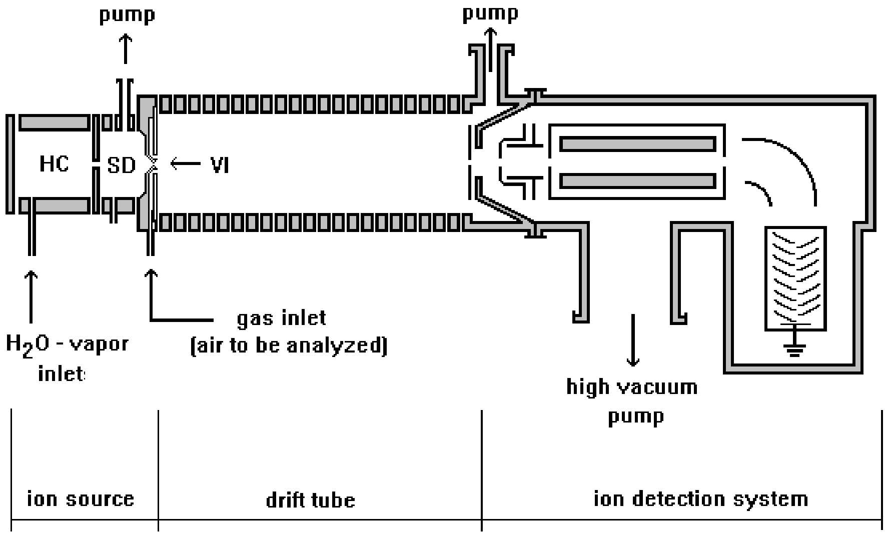


Figure 2.1. Schematic diagram of the Proton-Transfer Mass Spectrometer (Lindinger *et al.*, 1998). Abbreviations: HC, hollow cathode; SD, source drift region; VI, Venturi-type inlet.

A hollow-cathode (HC) ion source is used to produce H_3O^+ at high concentrations and purity from a plasma discharge. A stainless-steel reservoir filled with distilled water supplies a pure water vapor flow of 6-10 sccm (sccm = standard cubic centimeters per minute) to the HC. The higher the density of H_3O^+ ions produced, the higher the sensitivity of the instrument. The average count rates of primary H_3O^+ ions are 10^6 counts per second (cps), and the purity of the obtained primary ions is about 99.5%. No quadrupole system is needed to pre-select these ions before they enter the reaction region. When H_2O is used as a discharge gas in the hollow cathode, most of the ions emerging from the negative glow are already H_3O^+ ions. As showing in Table 2.1, all the ions produced by electron impact from H_2O, such as O^+, H^+, H_2^+, OH^+ and H_2O^+ react with H_2O at approximately the collisionally limited rate and finally end up as H_3O^+ ions.

Table 2.1. The reactions of ions produced by electron impact with H_2O (Ikezoe, 1987).

Reaction	Rate constant *k* (cm³/s)
$O^+ + H_2O \rightarrow H_2O^+ + O$	2.6×10^{-9}
$H^+ + H_2O \rightarrow H_2O^+ + H$	8.2×10^{-9}
$H_2^+ + H_2O \rightarrow H_3O^+ + H$	3.4×10^{-9}
$\rightarrow H_2O^+ + H_2$	3.7×10^{-9}
$OH^+ + H_2O \rightarrow H_3O^+ + O$	1.3×10^{-9}
$\rightarrow H_2O^+ + OH$	1.8×10^{-9}
$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	1.8×10^{-9}

In order to allow enough time for the ions to follow the reaction chains up to H_3O^+, a "source drift region" (SD) filled mainly with water vapor, is located adjacent to the hollow cathode. The only significant impurity ions observed are O_2^+ ions, which are produced within the source drift region due to the charge transfer from H_2O^+ ions to O_2. These O_2 molecules diffuse from the drift tube toward the ion source system (SD and HC), where they are ionized. O_2^+ ions do not react with H_2O, they are not converted into another ionic species, and are therefore capable of undergoing charge transfer reactions with neutral species in the drift region. Such processes would generate product ions other than those produced by reaction with H_3O^+, and therefore cause contamination in the spectra. Nevertheless, this source of error is small, as long as the density of O_2^+ ions is kept below 2% of the primary ion signal density.

After passing the SD region, the hydronium ions enter the drift tube via a Venturi-type inlet (VI). The drift tube has a length of ~9.2 cm and an inner diameter of 5 cm, and consists of a set of stainless steel rings isolated from each other, that sets up a homogeneous electric field of 65.2 V/cm, when a voltage of 600V is applied (see the standard operating conditions in Table 2.2). The drift tube is held at a pressure of ~2 mbar, and flushed continuously with the sample air (at a rate of ~16 sccm). The reaction time (*t* in Eq. 2.1), which is the time the H_3O^+ ions take to traverse the drift tube, can be determined either by direct measurement or calculation. Reaction time is measured by pulsing the ions at the entrance and at the exit of the drift tube and monitoring the arrival time spectrum, and calculated from the mobility values (μ) of H_3O^+ in air (Ellis *et al.*, 1976). As a result of the electric field *E* in the drift tube, the ions are accelerated to the so-called drift velocity v_d, which is given by the relation (Mason and McDaniel, 1988):

$$v_d = \mu E \tag{2.2}$$

The electric field experienced by the ions is proportional to the voltage (*U*) applied over the length of the drift tube (L_d):

$$E = \frac{U}{L_d} \tag{2.3}$$

Ion mobilities (μ) have been determined for numerous ions in a range of buffer gases, including H_3O^+ ions in nitrogen (Dotan *et al.*, 1976). Generally, μ is converted to the *reduced* mobility, μ_0, using standard temperature and pressure (STP) values of 1 atm for P_0 and 273.15 K for T_0.:

$$\mu_0 = \left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)\mu \tag{2.4}$$

In this equation, *P* is the pressure and *T* the temperature of the gas in the drift tube.

The reaction time is given by the equation given below, where *Lr* is the length of the reaction chamber:

$$t = \frac{L_r}{v_d} \tag{2.5}$$

Substituting Eqs. (2.2) – (2.4) into Eq. (2.5) gives:

$$t = \frac{L_r L_d}{\mu_0 U}\left(\frac{P}{P_0}\frac{T_0}{T}\right) \tag{2.6}$$

The H_3O^+ and product ions are focused at the end of the drift tube into the entrance of the detection system. The ion peaks of interest are selected by a mass analyzer (quadrupole mass spectrometer, Balzers QMG 421), and detected by an electron multiplier detector capable of single particle detection efficiency (i.e. measures hydronium and product ion count rates). To calculate the concentration of the neutral trace gases according to Eq. 2.1 the transmission of ions in the quadrupole has to be measured. The transmission is mass dependent; each mass has a specific efficiency for passing through the quadrupole to the detector, which also depends on the age and efficiency of the secondary electron multiplier (SEM). It is important, therefore that the transmission is measured on a regular basis for different substances which cover a suitable range of masses. In this work, the compounds used were methanol (mass 33), butanol (mass 57), acetone (mass 59), and toluene (mass 93). The headspace of the substances was measured one after another. The transmission was calculated from the reduction of the H_3O^+ signal and the increase of the specific signal of a product ion, i.e. $\Delta VOC^+/\Delta H_3O^+$. Using values obtained for selected masses, the transmission curve can be calculated with a fit function. To calculate concentrations (Eq.2.1), the measured signals have to be corrected by the specific transmission factor to get the "real" ion count signal. A typical transmission curve is shown in Figure 2.2.

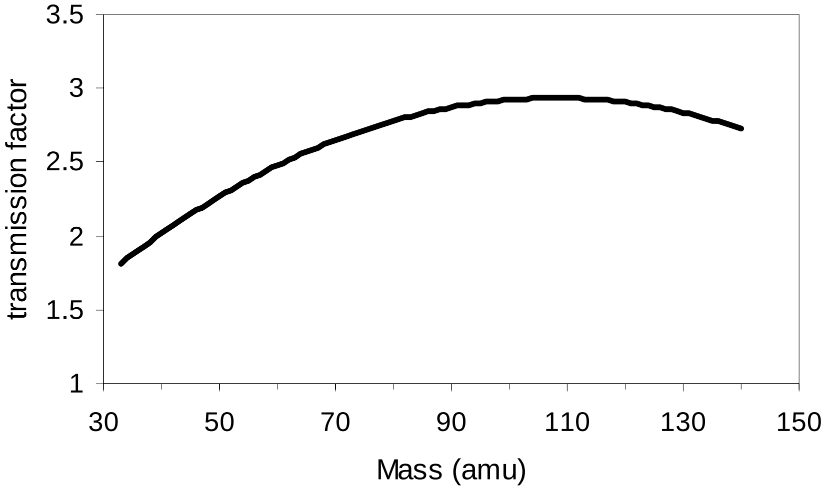


Figure 2.2. Mass-dependent transmission factor of the quadrupole mass spectrometer (as measured during the wet season field campaign in Calabozo, chapters 3 and 4)

Table 2.2. Main features and parameters of the PTR-MS system working under typical operating conditions

Length of the drift tube	$L_d = 9.2$ cm
Length of the reaction chamber	$L_r = 9.7$ cm
Pressure in the drift tube	P = 2 mbar
Pressure in the detection system	$P_{qms} < 4\times10^{-5}$ mbar
Flow rate of the air to be analyzed	$Flow_{air}$ 16 sccm
Flow rate of H_2O vapor into ion source	$Flow_{H2O}$ 6-10 sccm
Voltage applied to the drift tube	U = 600 V
Electric field to number density (E/N)	E/N = 136 Td
Drift velocity	$v_d = 980$ m/s
Reaction time	t = 98 μs
Reduced mobility of H_3O^+ ions in N2	$\mu_o = 2.7$ cm^2/sV

2.1.3. Possible sources of error

2.1.3.1. Reaction rate constants

Uncertainties in the values of the reaction rate constants for the proton transfer reaction (k), and the background signal of the instrument (see below) are the main sources of systematic error. The overall accuracy of the concentration determined by PTR-MS is estimated to be better than ±30%. As mentioned in section 2.1.1, the rate constants can be calculated theoretically (Su and Bowers, 1979) and empirically by measurements in the laboratory, using gas standards. The values of k are typically 1-3× 10^{-9} cm^3/s. The agreement between the calculated and the measured rate constants is usually between 15 – 20%. In this work, an average reaction rate of 2×10^{-9} cm^3/s was used to calculate the concentrations of most of the VOCs. For methanol (m33), acetonitrile (m42), acetalehyde (m45), acetone (m59), and methyl ethyl ketone (m73) the constants were experimentally determined in the lab to be 2.2, 3, 3.6, 3.4, and 4×10^{-9} cm^3/s, respectively.

2.1.3.2. Detection limits and precision

The detection limit of the PTR-MS instrument is predominantly determined by the background signal (noise) of the mass spectrometer/detector at a given mass. The background signal is measured regularly by directing the sample flow through a catalytic converter (filter). The converter consisted of a stainless steel tube filled with Platinum-coated quartz wool (Shimadzu) heated to 350°C, which efficiently removes the VOCs from the sampled air. As was shown by Hayward *et al.* (2002), the standard deviation (σ) of the background signal (precision) is described by the square root of the mean count rate of the product ions (v):

$$\sigma = \sqrt{v} \qquad (2.7)$$

The precision can be improved with longer integration (dwell) times. i.e. the fractional uncertainty (defined as σ/v) decreases as v increases (Taylor, 1997; Hayward *et al.*, 2002) according to:

$$\textit{Fractional uncertainty} = \frac{\sqrt{v}}{v} = \frac{1}{\sqrt{v}} \qquad (2.8)$$

Consequently, the precision of PTR-MS measurements can be determined by the noise statistics of the product ions, and so the error (1σ) of any mean ion signal (v, in cps) at a given dwell time (τ, s) is defined as (Hayward *et al.*, 2002):

$$NS = \frac{v}{\sqrt{v \times \tau}} \qquad (2.9)$$

In this work, τ was typically 10 s. Usually 10 filter measurement cycles of 1 s for each mass were averaged; details and exceptions are explained in sections 3 to 5. The detection limit was defined as the minimum mixing ratio that can be detected with a signal-to-noise ratio of 3 (S/N = 3). The determination of the detection limit for methanol is given as an example: the average background signal for methanol is around 80 cps, and therefore, the instrument noise is 2.8 cps at 10 s integration time, which corresponds to a detection limit of 280 ppt (ppt = 10^{-12} mol/mol). The detection limits for all masses measured by PTR-MS were calculated using the measured background signals at an average H_3O^+ signal of 1.25×10^6 cps. The results for the most important compounds are given in Table 2.3.

Table 2.3. Detection limits for some important compounds measured with PTR-MS

mass		DL (ppt)
33	Methanol	285
42	Acetonitrile	26
43	Propene, Cyclopropane; Propanol	503
45	Acetaldehyde	149
47	Ethanol, Formic acid, Dimethylether	611
57	Butenes; 2-Methyl-1-propene; Acrolein	205
59	Acetone, Methyl vinyl ether	85
61	Acetic acid, Hydroxyacetaldehyde	505
69	Furan; Isoprene	59
71	Methyl vinyl ketone; Methacrolein; C_5H_{10}	70
73	2-butanone (Methyl ethyl ketone); Butanal	141
75	Acetol	82
79	Benzene	67
81	Fragment of monoterpenes, $C_4H_4N_2$ (Pyrazine; Diazine; Pyridazine); Cyclohexadiene	63
83	Methylfuran	46
85	C_6-Alkenes	62
87	2,3-butanedione; Pentanone	89
93	Toluene; 1,3,5-cycloheptatriene	33
95	Phenol; $C_5H_6N_2$	83
97	Furfural; Dimethylfuran; Ethylfuran	46
101	Hexanone	72
107	Ethylbenzene; Xylenes; Benzaldehyde	55
121	Ethylmethylbenzenes, Trimethylbenzenes	89

2.1.3.3. Water clusters

In addition to reaction (R2.1), the H_3O^+ ions can cluster with water molecules in the sampled air:

$$H_3O^+ + nH_2O \rightarrow H_3O^+ \bullet (H_2O)n \qquad \text{(R2.2)}$$

The switching reactions of these cluster ions with the VOCs are a potential problem, since they complicate the interpretation of the mass spectra. However, the use of a sufficiently high electric field in the drift tube keeps the velocity of the ions sufficiently high to strongly suppress clustering of hydronium ions with water molecules. Rewriting Eq. (2.4) in terms of the number density of the buffer gas (air) in the drift tube (*N*) and at STP (*N_0*)

$$\mu_0 = \left(\frac{N}{N_0} \right) \times \mu \qquad (2.10)$$

and substituting Eq. (2.7) into (2.2) gives

$$v_d = \mu_0 \times N_0 \times \left(\frac{E}{N} \right) \qquad (2.11)$$

This shows that the drift velocity, v_d, is a function of the parameter E/N, the ratio of the electric field to the buffer gas number density. During this work E/N was usually kept at values >130 Td (1 Td = 1 Townsend = 10^{-17} V cm^2), resulting in a relative kinetic energy (KE_{cm}) of about 0.25 eV. This value is high enough to prevent significant formation of cluster ions of the type $H_3O^+(H_2O)n$ (*n* = 1, 2, 3 etc.), but also low enough to keep the fragmentation of protonated VOCs at a very low level.

Nevertheless, as the relative humidity of the air in the tropics can be very high, especially in the rainy season and inside the grass/tree chambers used for measuring the VOC emissions (see section 2.2), the fraction of cluster ions (primarily with n = 1) could be as high as 50% of the H_3O^+ signal. Since most compounds detectable with PTR-MS react with both H_3O^+ and $H_3O^+(H_2O)n$ ions, this set of reactions cannot be neglected. Therefore, clusters with n = 1 and 2 (detected at protonated masses 37 and 55, respectively) were also regarded as "primary ions" when calculating trace gas concentrations (Eq. 2.1).

2.1.3.4. Identification of VOCs by PTR-MS

In the PTR-MS technique, only the mass of the product ion is determined, which means that several compounds can contribute to the same mass. However, there are a number of methods that have been employed in the laboratory to distinguish between compounds of the same nominal mass (Lindinger *et al.*, 1998): different isobaric ions may be identified due to their different mobilities or drift velocities in the buffer gas. Isotopic abundances can also help to deduce the molecular formula of a compound. Another method is the collision-induced dissociation of ions. This technique uses the differences in binding energies of ions of the same mass (e.g. protonated acetone and propanal, mass 59), which show different break-up patterns or energy dependencies of their break-up coefficient when the mean collision energy in the drift tube (i.e. E/N) is increased. However, it is not always possible to apply these methods, especially during field measurements. In these situations, the number of potential candidates may be reduced significantly by considering the origin of the air to be analyzed, and so the major contributors to a specific mass can be elucidated by comparisons with previous measurements, with simultaneously measured species by means of other techniques or using model studies.

a) Biomass burning emissions

In this work, for the particularly challenging identification of VOCs present in smoke arising from biomass burning, simultaneous measurements with an open-path Fourier transform infrared spectrometer (OP-FTIR) instrument improved the specificity of mass identification by helping to identify and quantify the principal compound or compounds contributing to several PTR-MS masses. The results from the instruments intercomparison are discussed in detail in Chapter 5, section 5.4.2.

b) Biogenic emissions

In contrast to biomass burning emissions, the composition of the rural air and the biogenic emissions from vegetation are relatively simple, which facilitates the mass identification. The corresponding masses at which the various VOCs described here were detected have been discussed previously (e.g. Holzinger *et al.*, 2001a; Williams *et al.*, 2001; Warneke *et al.*, 2003; de Gouw *et al.*, 2003a).

There are a number of masses whose signal is more than 90-95% due to only one compound: Mass 33 (methanol, CH_3OH); mass 42 (acetonitrile, CH_3CN); mass 45 (acetaldehyde, CH_3CHO) and mass 59 (acetone, C_3H_6O). Propanal (CH_3CH_2CHO) could be potential contributor to m59, but the emission of propanal was found to be less than 10% of the acetone emission from a grassland site in USA (Fukui and Doskey, 1998).

The determination of isoprene (2-methyl-1,3-butadiene, $CH_2C(CH_3)CHCH_2$, mass 69) in clean air has practically no interference from other compounds (Crutzen *et al.*, 2000; Williams *et al.*, 2001). Pentenols (1-penten-3-ol and cis-2-penten-1-ol) –which are expected to fragment to $C_5H_9^+$ after protonation– were detected as result of leaf wounding at mass 69 (Karl, 2000). Also 2-methyl-3-buten-2-ol (MBO), can eventually contribute to this mass. Its emission appears to be restricted taxonomically to the genus *Pinus*, and has not be detected in any angiosperm or related gymnosperms (e.g. spruce, fir, cedar, juniper) (Harley *et al.*, 1998; Lerdau and Gray, 2003).In fact, MBO was found to be the most important biogenic emission in a North American pine forest (Goldan *et al.*, 1993), whereas no MBO was detected in measurements over a tropical rain forest (no coniferous trees) (Warneke *et al.*, 2001).

Acetic acid is detected at mass 61. Hydroxyacetaldehyde (glycolaldehyde, $CH_2(OH)CHO$), which is also detected at this mass, is a product of biomass burning (chapter 5), and has also been measured in the boundary layer at rural sites in the USA (Lee *et al.*, 1995; Lee *et al.*, 1998). Hydroxyacetaldehyde is formed in the oxidation of ethene and isoprene in the troposphere (Bacher *et al.*, 2001), but it has not been reported as a biogenic emission. The measurement of acetic acid with PTR-MS is somewhat problematic: approximately 30% of this acid fragments upon protonation to yield a water molecule and CH_3CO^+, which is detected at mass 43. The concentration of masses 61 and 43 were corrected by taking this fragmentation into account (see also section 5.4.2). Long response times caused by interactions of the acid with the inlet surfaces as well as loss of acetic acid, either in a long sampling line or in the drift tube, have been observed in previous studies (Holzinger *et al.*, 1999; Williams *et al.*, 2001a; de Gouw *et al.*, 2003b). The sampling line in this study was both relatively long (~ 7 m) and unheated, which increases the probability of water condensation on the inlet surface, and consequently additional loss of acetic acid in the aqueous phase. The sampling line and the cuvettes were checked repeatedly each day, and dried if necessary, in order to minimize this particular problem, but nevertheless the quantification of mass 61 is limited by the abovementioned factors.

Propene (C_3H_6), cyclopropane, 2- and 1-propanol (C_3H_6OH), are detected at mass 43. Propanol emissions have been measured from grasses and trees (König *et al.*, 1995; Kirstine *et al.*, 1998). Propene is a product of biomass burning (chapter 5), and has also been measured in the urbal and rural atmosphere over a large range of concentrations, mainly due to its short atmospheric lifetime and to its multiple of sources (Bonsang and Boissard, 1999; Karl *et al.*, 2003b).

Mass 57 could not be assigned to a particular compound: species with the molecular formula C_4H_8 (e.g. 1- and 2-butene), 2-propenal (acrolein, C_3H_4O), as well as butanol (C_4H_9OH) are all potential contributors.

Methacrolein (MACR, 2-methyl-2-propen-1-al) and methyl vinyl ketone (MVK, 1-buten-3-ol), C_4H_6O, are two important products of isoprene oxidation, and both compounds have the same protonated mass 71. To our knowledge, no other contributor to this mass has been reported for remote areas (Holzinger *et al.*, 2002).

Methyl ethyl ketone (MEK, butanone, $CH_3CH_2C(O)CH_3$) and butanal ($CH_3CH_3CH_2CHO$) both of which have been measured previously as biogenic emissions (Fehsenfeld *et al.*, 1992; König *et al.*, 1995; Kirstine *et al.*, 1998) are detected at mass 73. Laboratory studies have shown that ~80% of the butanal fragments and is detected at mass 55, at which mass the $H_3O^+(H_2O)_2$ cluster ion is also detected, and no quantification was possible. Therefore, mass 73 may be attributable largely to MEK.

Monoterpenes (general formula $C_{10}H_{16}$) are detected at mass 81 (67%) and nonfragmented at mass 137 (33%) (e.g. Holzinger *et al.*, 2000). Therefore, the sum of masses 81 and 137 is used for calculating the total monoterpene concentration in the present study.

There are also several compounds that cannot be accurately quantified by PTR-MS, which are reported to be of biogenic nature, like ethanol and formaldehyde (Kesselmeier *et al.*, 1997; Kirstine *et al.*, 1998), or hydrogen cyanide (HCN) which was recently found to be emitted in significant amounts from wounded clover (de Gouw *et al.*, 2000; Custer *et al.*, 2003). The proton affinity of HCN (m28), and formaldehyde (m31) is close to that of water, and therefore the back-reaction of protonated HCN and formaldehyde to neutral molecules –by collisions with water molecules present in the drift tube– is relevant. Ethanol is detected at mass 47, but under standard measuring conditions only 10-20% is expected not to fragment upon protonation.

3. Fluxes of VOCs from tropical savanna grasses

3.1. Introduction

Tropical and semi-tropical grassland and savannas cover up to one fifth of the global land surface, with total area estimates varying from 16 to 27×10^6 km^2 (House and Hall, 2001). The high temperatures and solar radiation that prevail in tropical savannas make these regions large potential sources of biogenic VOCs (Guenther *et al.*, 1999a), and important for photochemistry on a global scale. However, high uncertainties are associated with the emission inventories of biogenic VOCs –especially the oxygenated species– from savanna vegetation.

Recent studies have provided information on isoprene and monoterpene emissions from the vegetation of African tropical savannas and shrublands (Guenther *et al.*, 1996a; Klinger *et al.*, 1998; Greenberg *et al.*, 1999; Guenther *et al.*, 1999b; Otter *et al.*, 2002; Harley *et al.*, 2003), and vegetative species representative of the Kalahari and Miombo woodlands (Otter *et al.*, 2002; Greenberg *et al.*, 2003). Very few studies have been made to characterize emissions of other VOC (e.g. alcohols, carbonyls, acids and aromatics) from grasses in temperate regions (Hewitt and Street, 1992; Winer *et al.*, 1992; König *et al.*, 1995; Fukui and Doskey, 1998; Kirstine *et al.*, 1998), and there is no information available about emissions from tropical savanna grasses.

This study reports on the exchange of VOCs between three different tropical grass species and the atmosphere. The factors influencing the exchange process, like temperature, solar radiation and developmental differences of the measured plants were studied. Emission rates were normalized to a standard temperature of 30°C to facilitate intra and interspecies comparison as well as with data reported in the literature.

3.1.1. VOCs emission from plants to the atmosphere: biological background

3.1.1.1. Resistance mechanisms in the leaf

It is well known that vegetation releases a large number of VOCs that can affect atmospheric chemistry. On the other hand, dry and wet deposition to plants provides an important sink for gases or particulate matter. A free exchange of gases between the plant and the atmosphere is hindered by different leaf compartments (Kesselmeier and Bode, 1997) (Figure 3.1). *Cell membranes* – mainly consisting of lipids and proteins – provide a resistance that depends on the molecular size and the lipophilic character of the specific compound. Additionally, all cells are surrounded by a solid *cell wall*, which provides a porous medium for the circulation of water, minerals and nutrients. The acidity of the *apoplast* (pH 5–6.5) –which is the extracellular part including the cell walls– might influence the exchange of volatile compounds. Finally, the *cuticle*, a lipophilic and strongly water-resistant layer, which forms the interface between plants and their environment, acts as a barrier for water and most of the trace gases. The necessary exchange of CO_2 for photosynthesis is made through the *stomata* (Fig. 3.1), which are microscopic pores found in the epidermis of leaves. The stomata allow the uptake of CO_2 but also the loss of water, which means that plants have to control this exchange very efficiently. The measure of the maximum rate of passage of either water vapor or CO_2 through the stomata is known as *stomatal conductance*, g_s. The opening of the stomata is regulated by light, internal CO_2 level and leaf water potential.

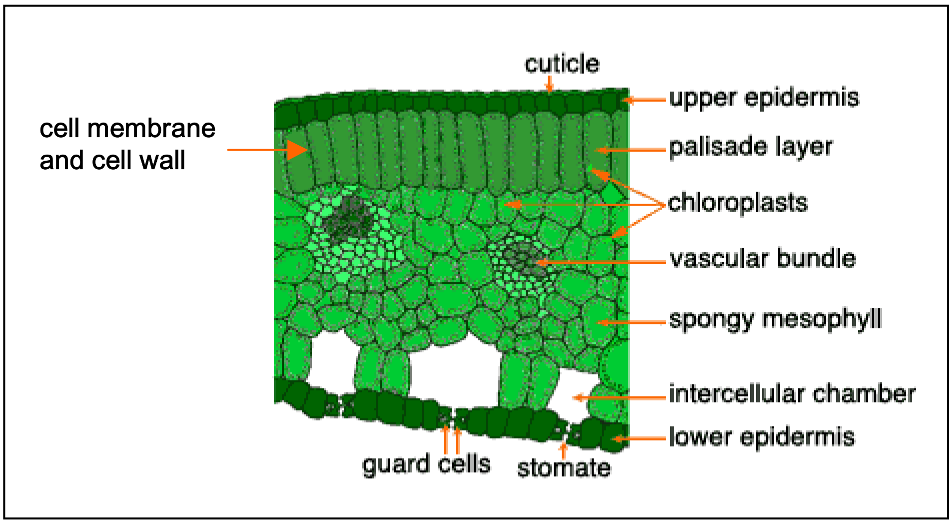


Figure 3.1. Cross section of a broad leaf showing the main cell compartments (reprinted with permission from the online Master Gardener Botany Module, Oregon State University, Copyright 1999).

3.1.1.2. Mechanisms involved in the synthesis and regulation of biogenic VOC emissions

The production and emission behavior of trace gases can be production dependent or storage dependent. In the first case, synthesis and emission are closely connected, and in the second case, the compounds are stored after synthesis in special cells and organs and thus released from storage pools (Kesselmeier and Staudt, 1999). The trace gas produced in the leaves has to pass through the stomata or diffuse through the hydrophobic cuticle to reach the atmosphere. The VOCs flux through the stomata is the product of stomatal conductance (g_s) and the difference in VOC partial pressure *(P)* between the leaf intercellular air space and the ambient atmosphere (Niinemets and Reichstein, 2003b). Despite the importance of stomata, the influence of stomatal conductance on the VOC fluxes is different for various compounds. While stomata affect the emission rates of methanol (Nemecek-Marshall *et al.*, 1995), acetic acid (Gabriel *et al.*, 1999), acetaldehyde (Kreuzwieser *et al.*, 2000), and linalool (Niinemets *et al.*, 2002), they do not control the isoprene (Monson and Fall, 1989; Fall and Monson, 1992; Sharkey and Loreto, 1993) and monoterpene (Guenther *et al.*, 1991; Loreto *et al.*, 1996) emission. The lack of stomatal control over the emission rates of isoprene and monoterpenes has been explained by the increase of VOC air-phase partial pressures, in response to the reduction in stomatal conductance. After the steady state has been reached, the increase in P balances the decrease in g_s and the VOC flux out of the leaf equals that before the stomatal closure (e.g. Monson and Fall, 1989; Fall and Monson, 1992). The compounds Henry´s law constant *(H)* determines its partitioning between air and liquid phases, and accordingly, the intercellular partial pressure. Compounds as alcohols, aldehydes, ketones and carboxylic acids have low H values, indicating preferential partitioning to aqueous phase, thus gas-phase concentrations (i.e. P) of these substances rise more slowly than stomata closes, resulting in a more or less temporal limitation of the diffusion flux through the stomata. In contrast, alkanes, alkenes and unsubstituted aromatics are preferentially partitioned to gas-phase, and their gas- and liquid-phase pools are generally in a steady state, which leads to immediate increases in ΔP and allowing the diffusion flux to be maintained at an unaltered level (Niinemets and Reichstein, 2003a).

The best-studied VOCs are isoprene and the monoterpenes (known collectively as isoprenoids). The biosynthesis of the isoprenoids has been worked out in detail (McGarvey and Croteau, 1995; Fall, 1999), whereas the mechanisms of formation of C_1 to C_3 oxygenated VOCs are not well known (Fall, 1999), except in the cases of ethanol and acetaldehyde (Kreuzwieser *et al.*, 1999b). A short overview of known or likely biochemical mechanisms responsible for the production of the most relevant VOCs measured in this work is presented next.

The isoprenoids are synthesized via a common C_5 precursor, isopentenyl pyrophosphate (IPP). IPP can be isomerized to dimethylallyl pyrophosphate (DMAPP), which is the substrate for isoprene synthase, a chloroplastic enzyme, which produces isoprene by cleaving pyrophosphate (Silver and Fall, 1991; Silver and Fall, 1995). In the biosynthesis of monoterpenes, the acyclic C_{10}-diphosphate, geranyl diphosphate (GPP, derived from condensation of IPP and DMAPP) serves as the precursor. Most monoterpenes are cyclic structures, and monoterpene cyclases catalyze their formation from GPP. Leaf isoprene emission occurs essentially without a leaf reservoir, while monoterpene-producing plants usually accumulate pools of these compounds within specialized structures, such as resin ducts or leaf storage cavities (Fall, 1999, and references therein).

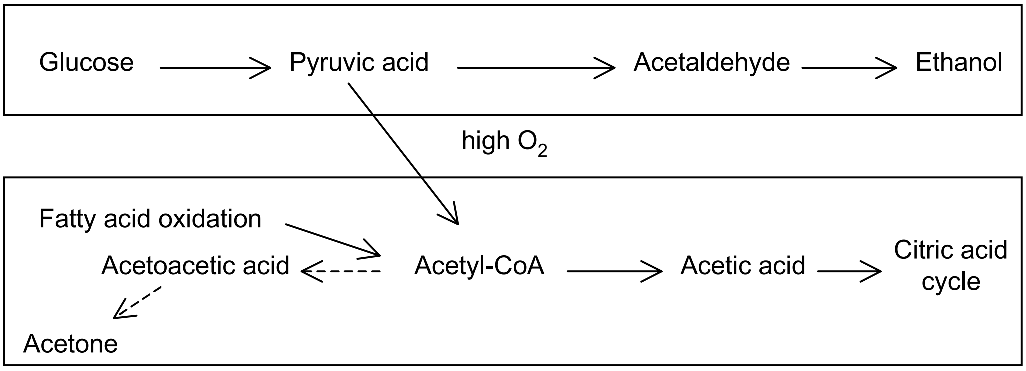
Methanol is produced by the demethylation of the pectin in plant cell walls (Macdonald and Fall, 1993b). As cell-wall expansion occurs (while the leaves are growing) the primary cell wall is formed in a very complex process, including the secretion of highly methylated pectins into the cell wall. Methanol is probably produced as a by-product during this process, and a fraction of this pool is then emitted through the stomata during transpiration (Fall and Benson, 1996). An unknown fraction of the produced methanol can partition back into the cell and be metabolized, likely in the following sequence:

$$\boxed{\text{Methanol} \longrightarrow \text{formaldehyde} \longrightarrow \text{formic acid} \longrightarrow CO_2 + H_2O}$$

Scheme 1

Acetaldehyde and ethanol are related by redox reactions that are controlled by cellular anaerobiosis in the cytosol (internal fluid of the cell), and acetic acid is a by-product of mitochondrial metabolism. (Fall, 1999), (schemes 2 and 3).

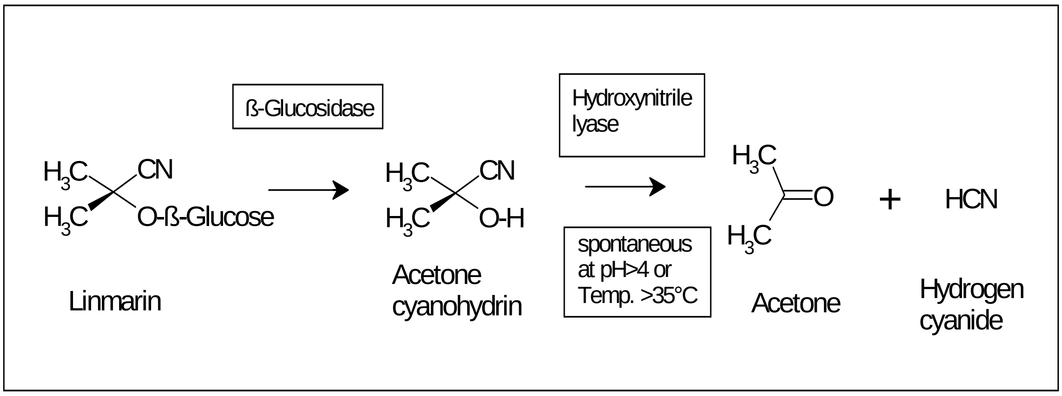
The biochemistry of acetic acid formation in plants has not been investigated. It is known that acetic acid can be incorporated into plant products via activation to acetyl-Coenzyme A (CoA), but whether its formation occurs by oxidation of acetaldehyde or hydrolysis of acetyl-CoA is unknown (Bode *et al.*, 1997).



Scheme 2

Scheme 3

Acetone can arise in biological systems by several pathways. Well-characterized mechanisms include the cyanogenesis (formation and release of hydrogen cyanide, HCN, to deter herbivores), which is a metabolic process and occurs in more than 2500 plant species (Vetter, 2000). For instance, the cyanogenesis in cassava (*Manihot esculenta*), an important food crop in tropical regions, converts the amino acid valine into the cyanogenic glycoside linamarin, which is stored in the cell vacuole. Upon rupture of the cell by feeding herbivores or physical damage, linamarin comes in contact with a β-Glucosidase (present in the cell wall). The resultant acetone cyanohydrin (Scheme 4) may enzymatically as well as spontaneously decompose to form acetone and HCN (McMahon *et al.*, 1995; Fall, 2003).



Scheme 4

By similar pathways, a variety of other cyanogenic glycosides give rise to different carbonyl products, such as butanone, methacrolein (MACR) and benzaldehyde. In non-cyanogenic plants, such as pines, acetone arises in both light-dependent and independent processes (Janson and de Serves, 2001), which may be related to the decarboxylation of acetoacetate (Scheme 3) which occurs in soil microorganisms and animals or, may be as a result of as yet uncharacterized mechanisms (Fall, 2003).

3.2. Experimental

3.2.1. Field Site

3.2.1.1. Geographical and meteorological characteristics

Field experiments were carried out in a woodland savanna at the *Estación Biológica de los Llanos,* during the wet season from 24 September to 17 October 1999, and in the dry season from 18 March to 9 April 2000. The site is located near Calabozo (Fig. 3.2) in the central part of Venezuela (8°53'N; 67°19'W, 86 m a.s.l.). It is typical of the Central Eastern Orinoco *llanos* of Venezuela, which occupy more than a quarter of the country (approximately 22×10^4 km^2).

In this region the climate is driven by seasonal movements of the equatorial trough (Inter-tropical Convergence Zone) (Riehl, 1979). The changing position of the trough influences seasonal rain patterns. During the winter, when the trough is in the Southern Hemisphere, a five-month dry season occurs (December to April), while a seven-month wet season occurs when the trough is over Venezuela (May to November). The rainfall at the site shows a 22-year average of 1315 mm. Around 98% of the rainfall occurs between April and November. The annual mean temperature is 27.6°C.

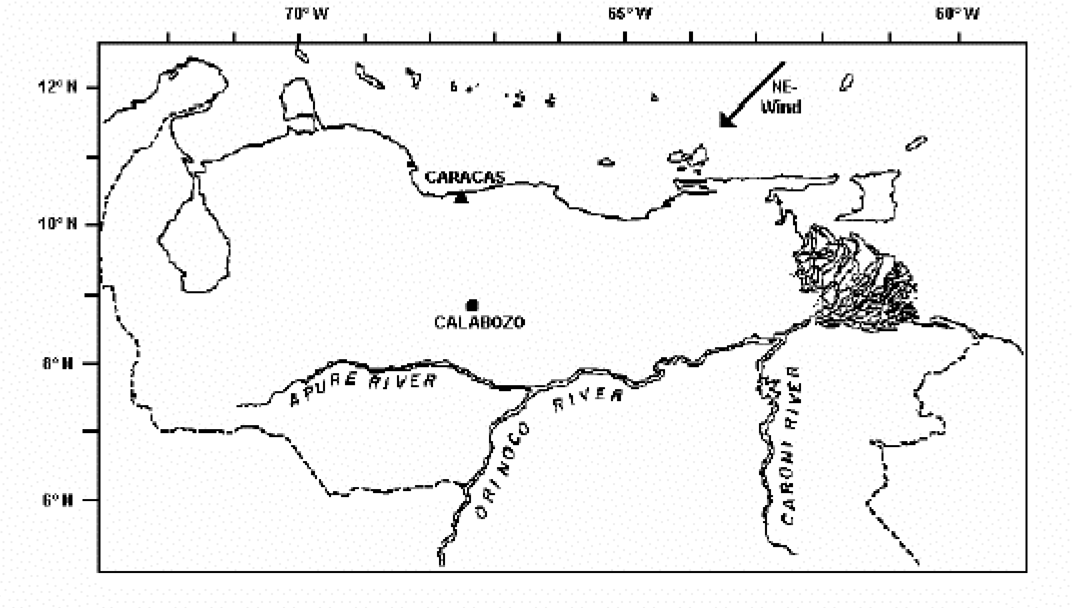


Figure 3.2. Map of Venezuela showing the location of the sampling site.

A region of trade winds lies between the equatorial trough and the sub-tropical highs. These wind systems are steadiest at the surface and are weaker in the wet season than in the dry season. Northeast and east-northeast trades are the most frequent winds for the area north of 5^o N, indicating that a large amount of surface air reaching the savanna region comes from the ocean. Fire frequency is about once every two years, typical of moist savannas (Scholes and Walker, 1993). Soils are acidic, have a low rate of mineralization, and are poor in nutrients, such as phosphorous and nitrogen (San José and García-Miragaya, 1979). The vegetation is diverse; the more abundant grasses are from the genera *Trachypogon, Axonopus, Adropogon, Paspalum, Leptocoryphium, Sporobolus* and *Elyonurus*. The dominant tree species are *Curatella americana, Byrsonima crassifolia, Bowdichia virgilioides*, and *Casearia sylvestris* (Silva and Moreno, 1992). Tree/grass ratios mainly depend on the water availability during the dry season, with higher tree densities in areas where the water table is high. Frequent burning produces a low diversity of tree species and maintains a vigorous grass layer (Medina and Silva, 1990). In the Calabozo woodland savanna, the production of grass is about 430 g of aboveground biomass per m^2 and year (San Jose and Medina, 1976; Medina and Silva, 1990).

3.2.1.2. Ambient air mixing ratios

With the exception of periodic emissions from biomass burning during the dry season (Sanhueza *et al.*, 1991), the study region is little affected by air pollution. The mean diel mixing ratio cycles of ozone, carbon monoxide, isoprene, acetone and methanol during both field campaigns, 1999 and 2000, are given in Figure 3.3. Daytime mixing ratios between 10:00 and 16:00 local time (LT, local time is UTC - 4 Hours) are considered representative of boundary layer concentrations (Sanhueza *et al.*, 2000). The average daytime mixing ratios of the VOCs measured in Calabozo are shown in Table 3.1.

The diurnal variation and mixing ratios of CO is similar in both seasons (Fig. 3.3; Table 3.1). The influence of biomass burning plumes was noted during daytime only at few days and for short time in the dry season campaign. The daytime mixing ratios are comparable to the levels measured previously at this site (Donoso *et al.*, 1996), and lie in the lower end of the range (~50-150 nmol/mol) measured in remote areas (Finlayson-Pitts and Pitts, 2000). Stable conditions near the surface were produced at night, which restricted the exchange of gases between the nocturnal mixing layer and the boundary layer, and trapped local emissions caused CO levels to increase. Especially in the dry season when emissions from biomass burning were trapped, a peak around 20:00 LT was observed. But also in the wet season highest mixing ratios were recorded at night, and concentration levels slowly decreased during the night. This feature can be explained by the fact that the steady Northeasterly wind flow collapsed occasionally during the evening and traffic emissions were advected from Calabozo, a nearby town with a population of about one hundred thousand people. Plumes of other anthropogenic tracers like benzene and toluene have been detected occasionally (Holzinger *et al.*, 2001b). Furthermore, CO emissions from degrading dry grass have been observed during the night at the Calabozo site and a South-African savanna (Sanhueza *et al.*, 1994; Schade *et al.*, 1999).

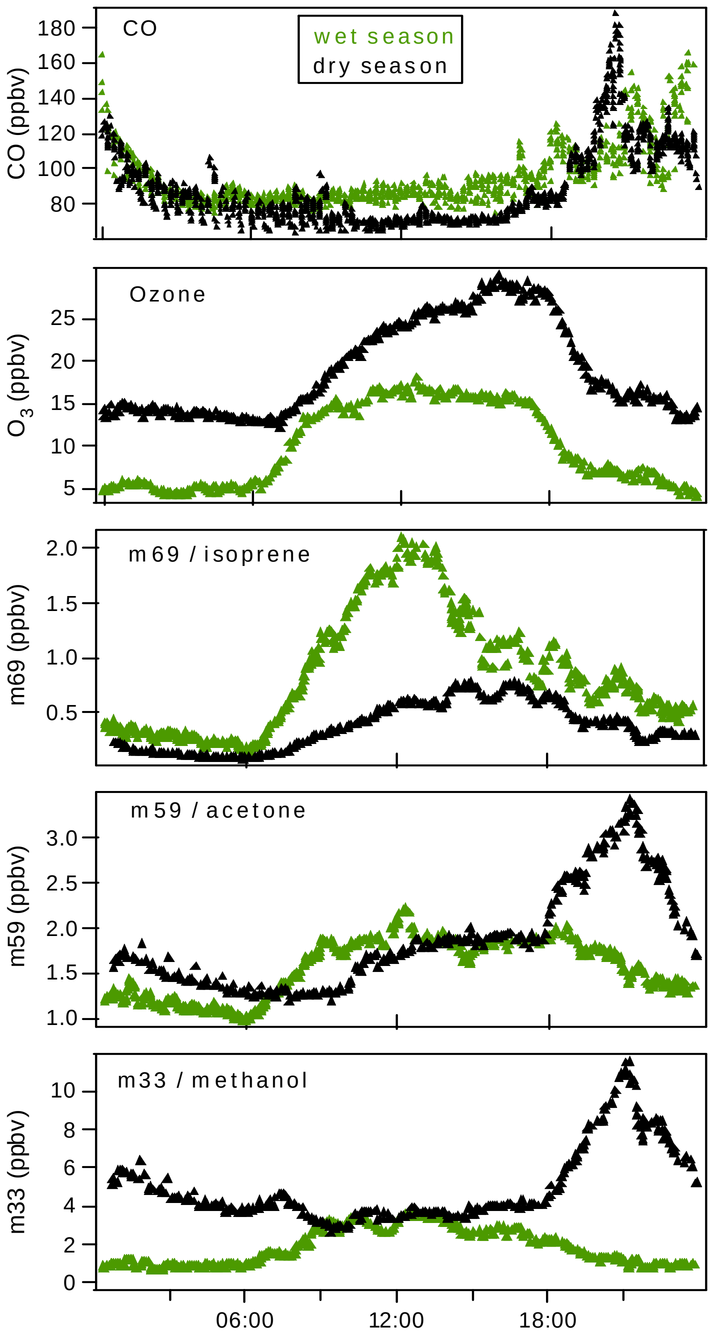


Figure 3.3. Diurnal cycles of selected VOC mixing ratios at Calabozo during the 1999 wet season and 2000 dry season.

Table 3.1. Daytime atmospheric mixing ratios of ozone, CO and several important VOCs, measured in Calabozo in the wet and dry season.

	Wet season		Dry season	
	Average	(SD)	Average	(SD)
O_3	16.01	(4.85)	25.25	(7.04)
CO	84.10	(24.8)	80.0	(9.60)
m33 / methanol	3.03	(0.35)	3.60	(1.08)
m42 / acetonitrile[b]	0.12	(0.04)	0.25	(0.07)
m43 / propene + others	0.62	(0.10)	0.49	(0.38)
m45 / acetaldehyde	0.65	(0.10)	0.77	(0.54)
m57 / butene + others	0.32	(0.03)	0.31	(0.20)
m59 / acetone	1.86	(0.12)	1.75	(0.36)
m61 / acetic acid	1.26	(0.24)	0.56	(0.22)
m69 / isoprene[a]	1.62	(0.68)	0.81	(0.24)
m71 / MVK + MACR[a]	0.98	(0.46)	0.40	(0.20)
m 73 / MEK	0.27	(0.04)	0.20	(0.05)
m81+m137 / monoterpenes	0.12	(0.06)	0.06	(0.02)

Mixing ratios in nmol/mol. Data are averages from measurements between 10:00 h and 16:00 h during 22 days in the wet season (1999), and 15 days in the dry season (2000) Unpublished results, except [a] (Holzinger *et al.*, 2002); [b](Sanhueza *et al.*, 2004)

Diurnal variations in O_3, with lower concentrations during nighttime, were observed in both seasons (Fig. 3.3). The ozone trapped in the nocturnal boundary layer is depleted mainly due to surface deposition, and the morning increase is mostly due to the down mixing of ozone-rich air from the "remnant" boundary layer. The ozone increase after noon in the dry season has been observed before at this an other sites in the central part of the Venezuelan savanna region (Sanhueza *et al.*, 1985; Johansson and Sanhueza, 1988; Sanhueza *et al.*, 2000), and also in a Brazilian savanna during biomass burning periods (Kirchhoff *et al.*, 1996). It is likely that photochemical production of ozone occurs in the savanna region during the dry season, which explains the increase of ozone during the day, as well as the higher boundary layer concentrations in this season.

Methanol (m33) daytime mixing ratios were similar in both seasons with mean values of 3 nmol/mol in the wet season (range 2.4-3.6 nmol/mol) and 3.6 nmol/mol (range 3.2-8 nmol/mol) in the dry season (Table 3.1). The diel cycle of methanol correlates well with solar radiation in the wet season. The concentration increased from less than 1 nmol/mol before dawn up to maximum 3.6 nmol/mol during the day and rapidly decreased after sunset. During the dry season, the diel cycle looked completely different, showing highest concentrations up to 12 nmol/mol during the evening, which was also observed for CO (Fig. 3.3) and acetonitrile (mass 42, not shown) (Sanhueza *et al.*, 2004). CO is a tracer for combustion in general and acetonitrile is a biomass burning tracer (Lobert *et al.*, 1990; Holzinger *et al.*, 1999). The concentration of other compounds, e.g. acetone (m59; Fig. 3.3), acetaldehyde (m45; not shown), butene and butanol (m57; not shown) which are emitted in high concentrations from biomass burning (Chapter 5) also peaked at night during the dry season, indicating that the increase is due to biomass burning emissions trapped in the nocturnal mixing layer. The mostly larger standard deviations observed in the dry season (Table 3.1) are probably caused by the influence of biomass burning emissions.

Mass 43, as already mentioned, cannot be assigned to a single compound, but due to the little anthropogenic influence at the measuring site, its signal is postulated to be mainly due to propene and propanol. Donoso *et al.* (1996) measured C_2-C_6 hydrocarbons, including propene, at pristine sites and rural locations affected by hydrocarbon emissions from oil and gas producing fields in Venezuela. The mean daytime concentration of propene measured in their work in Calabozo (wet season) was 0.25 nmol/mol, significantly lower than the concentration measured at mass 43 (0.62 ± 0.08 nmol/mol) during the 1999/2000 campaigns, which suggests that other compounds may have contributed to this mass.

Acetaldehyde (m45) showed a diurnal cycle in the wet season that correlates well with solar radiation (not shown), with maximum values around midday (~0.8 nmol/mol) and minimum during the night. During the dry season the diel variation is comparable to that of methanol (Fig. 3.3) with maximum values up to 2 nmol/mol around 21:00 LT. The daytime averages were similar in both wet and dry seasons (Table 3.1), and comparable to the levels found at two rural sites in Canada (~0.5 nmol/mol) (Shepson *et al.*, 1991), and at a forested site in Alabama (1.3 nmol/mol) (Goldan *et al.*, 1995a).

Mass 57, which signal is attributed to butene and butanol, showed similar mixing ratios in the wet and the dry season. Maximum concentrations were observed during the night in both seasons.

There was little seasonal difference observed in the daytime mixing ratio of acetone (m59, Table 3.1). The values are well within the ranges measured at rural sites (Riemer *et al.*, 1998, and references therein). In the wet season, the acetone concentrations increased during the morning and remained constant after midday (Fig. 3.3). The levels decreased very slowly after 18:00 and reached the lowest values just before sunrise. During the dry season, the increase in the morning was shifted later by about 3 hours.

The seasonal pattern observed for ambient acetic acid (m61, not shown) is very similar to the described by Sanhueza *et al.* (1996), who measured this acid in 1990 and 1993 at the same site. During the wet season, acetic acid shows a diurnal cycle with lower concentrations during the night and highest levels in the early afternoon, while during the dry season an important increase was observed late in the afternoon. Besides the diurnal variation, strong seasonal differences were found. The average daytime values in the dry season were lower than in the wet season (Table 3.1). The mixing ratios measured at Calabozo in 1990 were also lower in the dry than in the wet season, and comparable to the abovementioned levels, whereas in 1993 the relation was the opposite, with average levels of 0.67 (wet season) and 1.64 (dry season) nmol/mol (Sanhueza *et al.*, 1996). Higher mixing ratios in the dry season than in the wet season were measured as well at other sites in Venezuela and Amazonia (Andreae *et al.*, 1988; Talbot *et al.*, 1990; Sanhueza *et al.*, 1996; Kuhn *et al.*, 2002). This variability may be caused by a greater or lesser influence of biomass burning during different field campaigns, which directly emits acetic acid (see chapter 5) or its precursors (e.g. alkenes) (Jacob and Wofsy, 1988). The repeated rainfall events that occurred during the first three days of measurements in the 2000 dry season campaign (rather not representative for typical weather conditions of this season), probably removed the acetic acid very efficiently and, likely more significant, suppressed biomass burning activity for some days, originating the relatively low daytime mixing ratio during the 2000 dry season campaign.

A very clear diurnal pattern for isoprene (m69) was observed in the wet season. Morning isoprene mixing ratios increased rapidly along with increasing solar radiation, indicating pronounced release from the vegetation. The variability is small before 10:00 LT compared with values later in the day. This might indicate that the increase of isoprene is not entirely due to emission but also due to mixing with the air above the nocturnal mixing layer containing higher concentrations of isoprene (Holzinger *et al.*, 2002). During the night, when no emissions occur, but the loss processes were also active, the concentration was reduced to very low levels. Compared to the wet season, during the dry season a much smaller day to night variation was observed. This is likely due to both lower daytime concentrations and higher nighttime levels. Furthermore, during the night a good correlation of protonated mass 69 with acetonitrile was observed (Holzinger *et al.*, 2002), showing some influence of biomass burning on the nighttime levels measured.

3.2.2. Enclosure (chamber) system

There are several measurement techniques to determine the exchange rate of VOCs between vegetation and the atmosphere (for a review see Fuentes *et al.*, 2000). Enclosure systems are best suited if the scale of the measurement ranges from individual leaves and branches to whole plants, whilst micrometeorological systems may be used to derive emissions at an ecosystem level. There are two types of enclosure system: static enclosures, in which the air is not exchanged between the chamber and the outside (e.g. Zimmerman *et al.*, 1978; Fukui and Doskey, 1996), and dynamic (flow-through) enclosures, which are continuously flushed with air (e.g. Winer *et al.*, 1992; Macdonald and Fall, 1993b; König *et al.*, 1995).

VOC flux measurements from grasses and small trees presented in this work were performed using dynamic chambers. A schematic diagram of the chamber system used is presented in Figure 3.4. The experimental setup consisted basically of the pump system, which provided the airflow through the chamber system (~20-50 L/min), the chambers, and the analyzing section. The trace gas flux measurements were carried out differentially, with one empty chamber serving as reference, and one or more sampling chambers enclosing the plant. All the surfaces in contact with the air to be analyzed were made of Teflon (including the inner chamber surfaces, valves, tubings, fittings and ferrules) or of teflonized material (the ventilators). Teflon materials (FEP-, PFA- and PTFE Teflon types, DuPont, Germany) provide chemically inert surfaces, which minimize outgassing or memory effects.

The grass chambers were designed and used previously for measurements of CO emissions from degrading grasses (Schade *et al.*, 1999). A stainless steel cylinder measuring 33 cm in diameter and 30 cm in height was slightly inserted (1-2 cm) into the soil around the grass tuft or small tree to be studied. Care was taken not to damage or disturb any part of the plant. Two steel bars (3 cm in diameter, 70 cm high), were fixed outside the cylinder. If necessary, the system could be extended to max. 1 m by additional bars, which enabled the adjustment of the chamber depending on the height of the enclosed plant (see also Fig 3.5). Each chamber consisted of a 1.2 m high bag made of 50 μm FEP-Teflon foil. The bag was wrapped around outside the cylinder with a rubber band before it was placed on the soil, and then pulled up from inside the cylinder around the grass tuft. At the top it was tightened around a Plexiglas ring, which could be varied in height along the outside steel bars. In the middle the bag was held in position by means of two teflonized ventilators, which ensured that the air inside the chamber was well mixed. These ventilators were fixed to the outside steel bars by strong magnets, which could also be varied in height. The top of the chamber was a Teflon-film circle, which was also attached to the Plexiglas-ring. The top had a ~10 cm diameter hole in the center, through which the ambient air was drawn. In addition, a windbreaker of Teflon film was put on top of it in order to keep ambient air from mixing with the air from the chamber when strong wind produced turbulence outside the chamber.

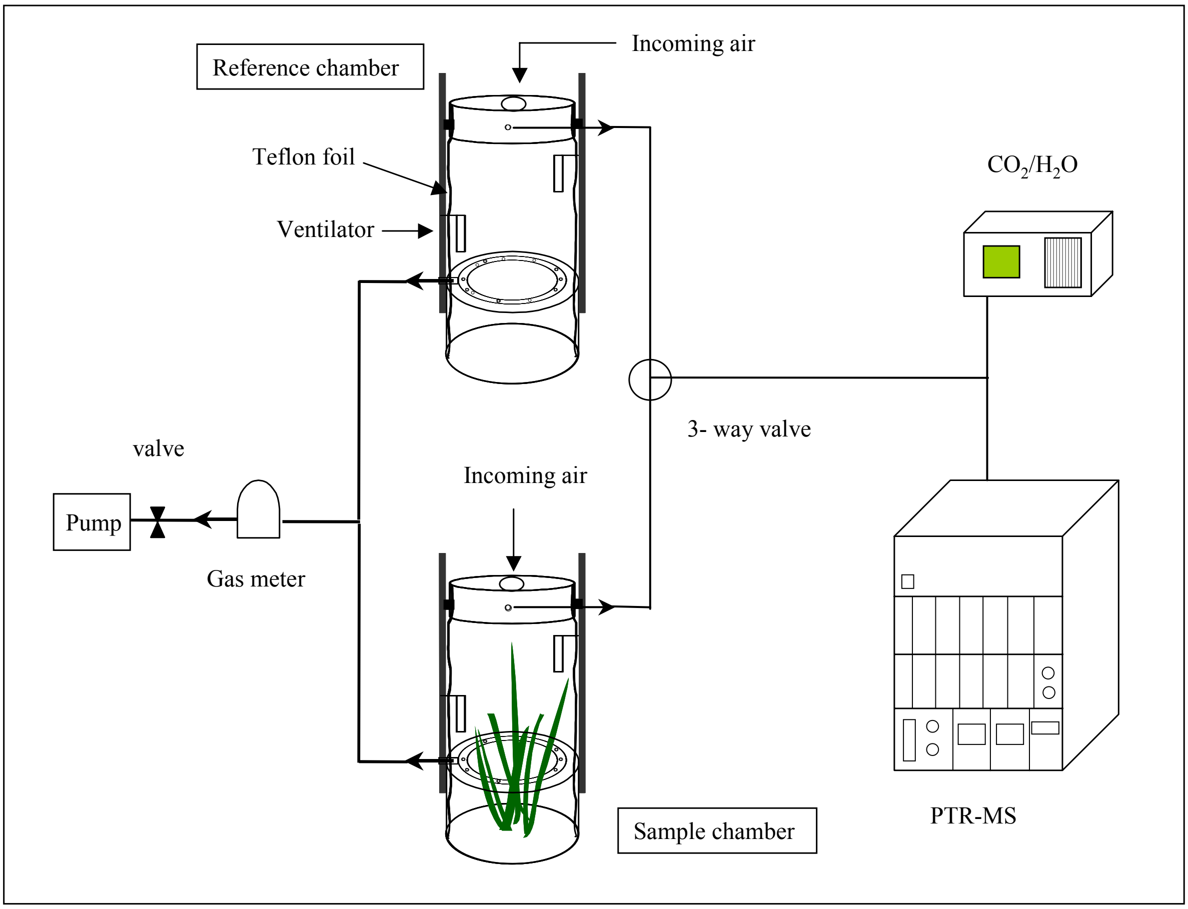


Figure 3.4. Schematic illustration of the experimental setup for plant enclosure measurements

A membrane pump (Vacuubrand MD4) was used to draw the ambient air through the chambers, providing a continuous flow that resulted in a residence time of about 2 min. The air was sucked into the chamber from the top and exited it via a 1/2” OD PFA-Teflon tube ring at the bottom. This ring – which had nearly the diameter of the steel cylinder – was punctured at regular intervals by a number of 1-2 mm holes in order to ensure that the air-flow through the chamber was as even as possible. The sampling air was pumped to the instruments through a 1/8” OD PFA-Teflon tube.

The temperature inside the chambers was monitored continuously with fine wire thermocouples (Omega, USA) during all experiments. Ambient temperature and relative humidity were measured with a Rotronic MP408A-T4 W4W sensor, and global radiation (400-1100 nm) was measured with a pyranometer (Skye). Other meteorological parameters such as wind direction and wind velocity (Thies Clima sensors) and precipitation (Campbell Scientific Raingauge) were also measured.

3.2.3. Trace gases analytical methods

All analytical instrumentation was housed in a mobile laboratory ~5-7 meters from the chambers. The inlet for ambient air measurements, and the sensors for wind velocity and direction, were fixed at a height of 5 m to a pole placed on top of the mobile laboratory.

a) VOCs

A detailed description of the measurement principle and functioning of the PTR-MS is given in Chapter 2. The PTR-MS was operated in the selected-ion mass mode and measured a selection of 15-40 masses; with a sampling time of 1 s. Time resolution for one dataset was <50 s.

b) CO_2 and H_2O

The CO_2 and H_2O exchange behavior of the enclosed grasses/trees were monitored with a dual-channel infrared gas analyzer (LI-6262, LI-COR Inc., USA) operating in differential mode. The instrument was calibrated regularly using a calibration gas (CO_2 in nitrogen, 310 μmol/mol).

c) O_3 and CO

Ozone measurements were made using a photometric ozone analyzer (Dasibi, model 1008 PC). This instrument measures the absorption of ultraviolet radiation at 254 nm in ambient air relative to that of air scrubbed of ozone, and has an estimated precision of ±2 nmol/mol and a detection limit of 2 nmol/mol.

Carbon monoxide concentrations were measured using a reduction gas-detector (Trace Analytical) in combination with a molecular sieve 5A column for CO separation.

Every 15 min, gas samples were automatically supplied to the injection valve by a Metal Bellow pump (model MB-21). High-pressure mixtures of CO in synthetic air (258 nmol/mol) were used for calibration in the field. These calibration mixtures were prepared at the MPI-Mainz, by static dilution from a commercial mixture supplied by Deuste-Steininger (Muhlhausen, Germany).

3.2.4. Calculation of exchange rates

Exchange rates or fluxes (E) of VOCs and CO_2/H_2O are usually expressed in units of either unit mass or number of moles of the emitted compound per unit time and normalized to the dry weight or leaf surface area of the investigated plant. Exchange *rates* are given in terms of the dry weight and *fluxes* refer to leaf area. In this work, the exchange of VOCs was calculated from the concentration difference between the sampling and the reference chamber ($\Delta c = c_{sample} - c_{reference}$, in ppb or ppm), taking into account the airflow through the chamber (Q, in L/min), the molar volume of ideal gas at STP (V_m = 22.414 L/mol), and the dry weight (dw, in g) or the leaf area (A, in m^2) according to the following equations:

$$E = \frac{\Delta c \times Q}{V_m \times dw} \qquad \text{or} \qquad E = \frac{\Delta c \times Q}{V_m \times A} \tag{2.12}$$

The dry weight was determined by weighting the plant material after drying it at 90°C for ~48 h. For trees, leaf area was measured after photocopying the leaves by using a calibrated scanner system (ScanJET IIXC, HP, USA) and calculated using the software SIZE 1.10 (Müller, Germany). In the case of grasses, the leaf area was estimated from the dry weight measurements and specific leaf weight values estimated in a previous study for two of the three species (Baruch and Bilbao, 1999).

3.2.5. Measurement procedure and plant species

During each set of measurements, reference and sample chambers had the same height, which was adapted to the chosen grass tussock. The reference chamber was placed near the sample chambers on a spot of bare soil, which in our judgement appeared to have the same characteristics as the soil around the grass being studied. In the wet-season campaign, a set of measurement comprised *one* sample and *one* reference chamber, while in the dry season campaign, two 3-way valves were added to the sampling system, and it was possible to analyze *three* sample chambers at the same time (Fig. 3.5). Due to this improvement, more grasses and trees were studied in the dry season, and also the total measurement period for each plant species was extended.

Figure 3.5. Chamber setup during measurements and investigated grass species: (a) young *Trachypogon* grasses in the chambers the dry season (mobile laboratory in the background); (b) *Axonopus canescens*; (c) *Trachypogon plumosus;* (d) *Hyparrhenia rufa*.

Each measurement series consisted of a sequence of 10 min measurement cycles of: (1) ambient air, (2) PTR-MS background, (3) reference chamber, and (4) sample chamber (or chambers). An automatic valve system switched sequentially between the various measurements. Each measurement series took 40-60 min (depending on the number of sample chambers); each chamber was measured at least once every hour. Therefore, volatile organic compound mixing-ratios or exchange-rate values were obtained as 10 min average ± standard deviation. Since measurements were made successively and not simultaneously, the background signal was interpolated between two consecutive measurement cycles and then subtracted from the samples (i.e. ambient and chamber air) to derive a mass signal corrected for the noise and impurities of the PTR-MS. Similarly, in order to determine the actual concentration difference between the sample and reference chambers, reference chamber concentrations were interpolated to account for the time difference between measurements.

Due to the capacity of burned *Trachypogon* to shoot up few days after the fire, the presence of young grasses is common in the dry season. Studies on the biomass production and allocation of this species, have shown that burned *Trachypogon* individuals grow as fast as unburned plants when the wet season begins (approximately in April-May), reaching a similar maximal biomass by August and October (Baruch and Bilbao, 1999). At the start of the wet season, about 80% of the total mass of unburned plants is standing necromass. As the growing season advances, the dead material abscises gradually with the simultaneous production of new biomass, which peaks during August and October. *Hyparrhenia* and *Axonopus* display a greater mortality following fire. Especially the large standing dead biomass of *Hyparrhenia* grasses at the end of the dry season facilitates the combustion and increases the fire intensity and consequently its damage (Williams and Baruch, 2000).

The savanna area where the measurements were made did not undergo any burning in the dry season previous to the wet-season measurements in 1999, so that, green grasses were mixed with senescent and dead standing grasses. These *mature* grass tussocks were studied as they were found. However, after the measurements, dry and green grasses were separated and dry-weighted separately. The net emissions of VOCs from mature grasses were calculated considering only the fraction of green grasses within the chamber, since as we discuss later, dry grasses exhibited negligible emissions of most VOCs compared to the emission of green grasses. Inversely, for the calculation of emission rates from dry grasses (in the dry season) the dry weight from dry and green grasses (where present) was taken into account.

The date of each set of measurements and the dry weights of the studied grass tussocks are given in Table 3.2. In the dry season, *dry* grasses and also *young* green grasses that regrew from a previously burned plot were measured; they will be henceforth marked as ../d and ../y respectively, in order to distinguish them from the grasses measured in the wet season (Table 3.2).

Table 3.2. Dry weight and estimated leaf area of grasses measured during the wet (September-October 1999) and the dry season (March-April 2000)

Species	Short name	Date of measurement	Dry weight[a] (g) green	dry	Estimated Leaf area[b] (m^2)
Wet season (1999)					
Trachypogon plumosus	Tp 1	29-30 Sept	23.4	28.2	0.39
	Tp 2	01 Oct	23.0	20.4	0.38
	Tp 3	02 Oct	60.6	58.0	1.00
	Tp 4	03-04 Oct	32.3	22.6	0.53
	Tp 5	04-05 Oct	51.3	33.9	0.85
Hyparrhenia rufa	Hr 1	13-14 Oct	25.2	n.p.	0.39
	Hr 2	14 Oct	36.9	n.p.	0.58
	Hr 3	15 Oct	18.9	n.p.	0.30
Axonopus cansescens	Ac 1	15 Oct	58.3	25.8	0.94
	Ac 2	15 Oct	34.1	49.7	0.55
Dry season (2000)					
Trachypogon plumosus	Tp 1/y	25-29 Mar	17.3	n.p.	0.29
	Tp 2/y	25-29 Mar	28.7	n.p.	0.48
	Tp 3/y	25-29 Mar	29.7	n.p.	0.49
	Tp 4/y	29-31 Mar	13.1	n.p.	0.22
	Tp 5/y	03-05 Apr	30.3	n.p.	0.50
	Tp 1/d	29-31 Mar	n.p.	74.4	1.23
	Tp 2/d	02-03 Apr	7.9	26.1	0.56
Hyparrhenia rufa	Hr 1/d	06-08 Apr	n.p.	63.3	0.99
	Hr 2/d	06-08 Apr	n.p.	36.0	0.56
	Hr 3/d	06-08 Apr	n.p.	23.0	0.36
Axonopus cansescens	Ac 1/d	29-31 Mar	11.2	73.6	1.36
	Ac 2/d	02-03 Apr	5.6	22.4	9.45
	Ac 3/d	02-03 Apr	5.7	31.5	0.60

[a] Wet season *Trachypogon* and *Axonopus* grass tussocks consisted of green grasses mixed with dry grasses, which were dry-weighted separately. Only the dry weight from the green part was considered for the calculation of emission rates. In the dry season, there were some green blades of grass among the dry grasses; both, green and dry parts were included in the calculation of emission rates.

[b] Leaf areas were estimated using the specific leaf weight values for *Trachypogon* and *Hyparrhenia* grasses determined by Baruch and Bilbao, (1999). Specific leaf weights were in the range 60-64 g/m^2, both for grasses regrown after burning and unburned grasses. No specific leaf weight was available for *Axonopus*, therefore an average value of 62.2 g/m^2 was used.

n.p., not present, some grass tussocks had either only green or only dry grasses.

The leaf area was not determined for the grasses measured in this study, but *Baruch and Bilbao* (1999) studied biomass production and net photosynthesis of *Trachypogon* and *Hyparrhenia* grasses in Calabozo, and report specific leaf weights for grasses regrown after burning as well as unburned grasses. The leaf areas presented in Table 3.2 were estimated from those results.

3.3. Results

3.3.1. Meteorological conditions

A summary of the daytime (10:00-16:00 LT) meteorological conditions during the field campaigns is given in Table 3.3. The average total radiation during daytime was around 675 W/m^2 in both wet (WS) and dry season (DS)[3]. In the wet season, radiation was highly variable, since it rained almost every day, particularly in the afternoon and during the night. It is important to mention that the first three days of chamber measurements in the dry season (25-27 March) were unusually rainy and cloudy. Therefore, lower radiation and temperature, and higher relative humidity values were observed during the measurements of the three first young *Trachypogon* grasses (Tp1/y-Tp3/y). After that, there were no more precipitation events during the dry-season campaign.

The prevalent wind direction was Northeasterly. The average daytime wind speed was 1.6 ± 0.4 and 3.1 ± 1.3 m/s in the wet and dry season campaign, respectively. The ambient temperature was higher and the relative humidity lower in the dry season than in the wet season. The air temperature measured inside the chambers was on average 6 and 7.8°C higher than the ambient temperature in the wet and the dry season, respectively. A high correlation between radiation and the ambient temperature as well as the temperature inside the chambers was observed (Figure 3.6).

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[3] The photosynthetically active radiation (PAR, 400-700 nm) was not measured in this work, but a mean factor of 2.11 (Ting, K.C. and G.A. Giacomelli, 1987) may be used to convert radiation (W/m^2) into PAR (μmol/s/m^2), since the fraction of PAR in total radiation is on average 45-50%.

Table 3.3. Meteorological conditions and temperature inside the chamber during grass enclosure measurements. Values are daytime means (10:00-16:00 LT); SD in parentheses.

	Radiation ($W m^{-2}$)	Temp. ambient (°C)	Temp. Chamber (°C)	Amb. Relat. Humidity (%)
	Wet season			
	Trachypogon plumosus (mature grass)			
Tp 1	602.6 (240.6)	29.7 (1.3)	37.8 (3.4)	68.6 (6.6)
Tp 2	845.2 (316.2)	32.0 (2.0)	39.7 (3.5)	64.7 (7.7)
Tp 3	762.4 (271.0)	29.6 (4.3)	38.7 (11.2)	71.5 (8.6)
Tp 4	816.1 (132.0)	29.5 (0.7)	37.5 (2.0)	74.6 (5.1)
Tp 5	742.4 (224.5)	29.4 (1.0)	37.5 (2.6)	71.0 (5.3)
	Axonopus canescens (mature grass)			
Ac 1[a]	771.9 (316.7)	34.6 (1.2)	39.8 (1.4)	59.9 (1.1)
	Hyparrhenia rufa (mature grass)			
Hr 1	60.6 (57.7)	23.1 (1.4)	23.7 (1.6)	97.1 (5.1)
Hr 2	198.6 (44.6)	24.0 (0.8)	26.4 (1.0)	99.1 (2.4)
Hr 3	796.5 (179.2)	34.0 (0.7)	39.3 (2.5)	66.3 (5.5)
WS*	**677.3 (183.3)**	**30.6 (1.2)**	**34.8 (2.1)**	**67.3 (4.1)**
	Dry season			
	Trachypogon plumosus (young grass)			
Tp 1/y	360.5 (258.2)	29.1 (3.2)	31.5 (3.4)	73.7 (17.0)
Tp 2/y	415.6 (305.8)	29.6 (3.4)	32.1 (3.4)	72.1 (17.8)
Tp 3/y	399.0 (292.0)	29.5 (3.3)	32.0 (3.5)	71.8 (17.9)
Tp 4/y	779.1 (300.2)	34.4 (1.7)	44.4 (3.9)	41.1 (7.5)
Tp 5/y	601.0 (272.3)	35.0 (1.6)	40.8 (2.7)	40.3 (4.9)
	Trachypogon plumosus (dry grass)			
Tp 1/d	702.0 (300.6)	34.4 (1.4)	44.1 (2.4)	40.9 (7.0)
Tp 2/d	775.8 (316.1)	35.3 (1.4)	46.6 (4.7)	39.1 (4.9)
	Axonopus canescens (dry grass)			
Ac 1/d	685.8 (297.8)	34.5 (1.5)	44.7 (2.8)	40.5 (7.0)
Ac 2/d	854.7 (290.0)	35.9 (1.1)	48.1 (4.2)	37.6 (4.1)
Ac 3/d	804.3 (301.5)	35.4 (1.2)	46.1 (2.9)	39.4 (4.5)
	Hyparrhenia rufa (dry grass)			
Hr 1/d	752.8 (414.0)	35.6 (1.8)	44.1 (5.8)	39.5 (7.2)
Hr 2/d	706.6 (267.0)	35.3 (2.0)	43.2 (3.7)	41.4 (8.6)
Hr 3/d	666.3 (304.4)	35.1 (1.3)	42.9 (4.5)	40.7 (7.0)
DS*	**674.4 (125.5)**	**34.7 (3.1)**	**42.4 (6.6)**	**42.7 (4.3)**

* Wet (WS) and dry season (DS) daytime averages (10:00 –16:00 LT), were calculated from all data collected during the measurement campaigns: ws, 24 September to 17 October 1999; ds, 18 March to 9 April 2000

[a] Ac2 was not measured during daytime, only after 16:00 h and during the night

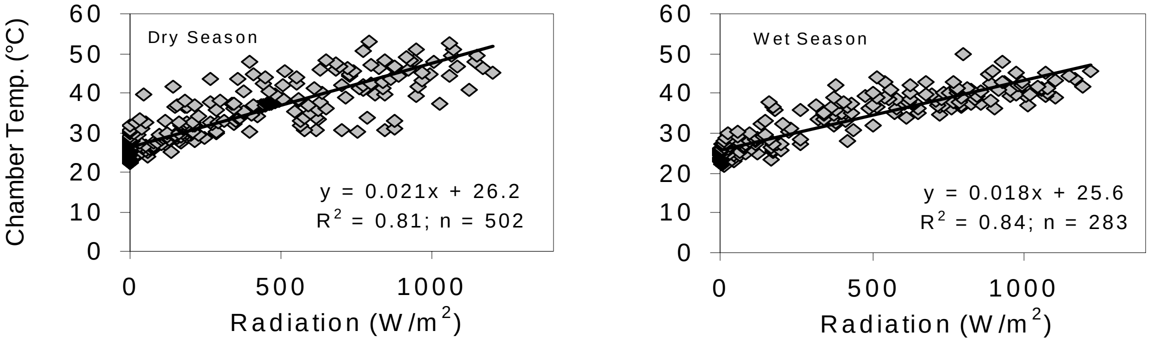

Figure 3.6. Correlation of the solar radiation and chamber temperature in the dry and wet season. Data are 10-min averages.

3.3.2. Exchange of VOCs

The daytime (10:00-16:00 LT) mean exchange rates of VOCs for the three studied grass species in both seasons, are presented in Tables 3.4-3.6. The nighttime emission rates are included in the appendices (Table 8.1). Deposition (as well as CO_2 assimilation) is indicated as negative values. Analysis of variance (ANOVA), a statistic method that compares the amount of systematic variance in the data to the amount of unsystematic variance, was applied in all cases in which the difference between the concentration in the sample and reference chambers was less than 2 times the detection limit of the analyzed VOC. ANOVA enabled to test whether the mean of the reference and the sample chamber were actually different, or if the observed differences were due to the variability of the measurements during the sampling time (caused by the instrument noise and natural fluctuations of the emissions). The results showed in some cases that there was no exchange between the grasses and the atmosphere, and were quoted as not detected (n.d.).

The CO_2 assimilation of mature *Trachypogon* during daytime ranged from 68 to 129 µmol/g/h, at average radiation values between 600-845 W/m^2 (Table 3.4). The assimilation of young *Trachypogon* grasses was between 61-170 µmol/g/h at radiation values that ranged from 360 to 780 W/m^2. The three young grass tussocks (Tp1/y-Tp3/y) measured at the days during which the rainfall events occurred at the beginning of the dry season campaign, showed the lowest assimilation (see also the low average radiation, Table 3.4), whereas Tp4/y and Tp5/y, the two individuals measured few days after the rain, exhibited the highest assimilation of all grasses measured (~160 μmol/g/h), at average radiation values >600 W/m^2, comparable to the average radiation measured in the wet season. This suggests that the CO_2 assimilation may be up to 60% higher in the young than in the mature grasses. This agrees with previous studies which showed higher net photosynthesis from recently burned *Trachypogon* tussocks than from unburned ones (Baruch and Bilbao, 1999). The green *Axonopus* tussock showed a relatively low CO_2 uptake of 65 μmol/g/h (Table 3.5). The high variability in assimilation of the mature *Hyparrhenia* grass is explained by the also high variability of the solar radiation during the measurements (Table 3.6).

Methanol (m33) was the most abundant emission of all green grasses. The average methanol daytime emission ranged from 12-47 nmol/g/h. The average emission rates of acetaldehyde (m45) butene + butanol (m57) and acetone (m59) were lower than 10 nmol/g/h. An emission rate lower than 3 nmol/g/h was measured for propene (m43), isoprene + C_5-alcohol (m69) and MEK (m73). Acetic acid (m61) was deposited on mature *Trachypogon* grass, whereas the mature *Axonopus* and *Hyparrhenia* showed no exchange.

Most VOCs emission rates from dry grasses were lower than those from green grasses. Methanol was emitted in substantial amounts, as was also mass 57. Emission and also deposition of acetaldehyde (m45) and acetone (m59) was observed. It is noticeable that –as opposed to green grasses– acetic acid was mostly emitted by dry grasses.

The emission rates exhibited a high variability within grasses of the same species as well as among the different species. The different factors that influence the emission of VOCs will be analyzed in the following sections.

Table 3.4. VOC exchange rates and CO_2 assimilation from *Trachypogon plumosus* in the wet and dry season. Data are 10-min averages ± SD of daytime (10:00-16:00) measurements. n.d. means not detected. Also shown are n = number of measurements, Rad = average radiation, T = average temperature inside the chamber.

	n	**Rad**	**T**	**CO_2**	**m33**	**m43**	**m45**	**m57**	**m59**	**m61**	**m69**	**m73**
		($W\,m^{-2}$)	**(°C)**	**($\mu mol\,g^{-1}\,h^{-1}$)**	**($nmol\,g^{-1}\,h^{-1}$)**							
Wet Season / *Trachypogon plumosus* (mature grass)												
Tp 1	24	602	38	-93.38 ± 60.2	47.72 ± 16.5	1.23 ± 5.8	16.32 ± 21	13.31 ± 7.8	3.92 ± 9.0	-2.76 ± 8.4	3.17 ± 5.4	4.44 ± 3.3
Tp 2	7	845	40	-91.94 ± 16.2	23.10 ± 4.2	0.38 ± 1.5	1.38 ± 2.6±	0.60 ± 1.1	n.d.	-3.22 ± 3.5	n.d.	n.d.
Tp 3	10	762	39	-67.56 ± 40.7	32.56 ± 13.1	0.59 ± 1.6	5.44± 2.6	6.33 ± 3.8	3.32± 1.8	-3.0 ± 5.5	1.09 ± 1.1	1.71 ± 1.4
Tp 4	6	816	38	-129.41 ± 21.8	24.15 ± 3.9	0.20 ± 1.0	5.68 ± 4.1	0.13 ± 1.6	2.58 ± 0.7	-4.64 ± 6.3	n.d.	0.10 ± 0.4
Tp 5	7	742	38	-119.20 ± 41.1	23.80 ± 13.5	n.d.	5.28 ± 6.6	1.59 ± 2.1	3.07 ± 2.3	-4.12 ± 6.8	n.d.	0.39 ± 0.6
Average mature Tp				**-100.30**	**30.27**	**0.59**	**6.82**	**4.39**	**3.23**	**-3.55**	**2.13**	**1.66**
Dry Season / *Trachypogon plumosus* (young grass)												
Tp 1/y	22	361	32	-129.09 ± 32.3	11.92 ± 2.2	0.88 ± 0.5	2.07 ± 3.5	0.19 ± 0.7	8.79 ± 2.8	n.d.	n.d.	0.81 ± 0.2
Tp 2/y	22	416	32	-94.51 ± 17.6	15.09 ± 1.9	n.d.	0.42 ± 1.3	0.24± 0.6	0.99 ± 0.6	n.d.	n.d.	0.97 ± 0.3
Tp 3/y	22	399	32	-61.95 ± 20.1	12.90 ± 2.6	0.73 ± 0.4	2.24 ± 1.9	0.27 ± 0.4	6.64 ± 2.2	n.d.	0.10 ± 0.1	0.49 ± 0.1
Tp 4/y	13	779	44	-158.68 ± 56.7	27.16 ± 5.0	3.84 ± 1.2	15.06 ± 9.9	9.09± 3.2	8.07 ± 2.4	n.d.	n.d.	4.02 ± 2.5
Tp 5/y	14	601	41	-166.75 ± 40.9	12.64 ± 4.1	2.94 ± 1.3	2.18 ± 2.7	2.88± 1.5	2.27 ± 1.7	n.d.	0.22 ± 0.5	1.59 ± 0.6
Average young Tp				**-122.20**	**15.94**	**2.10**	**4.39**	**2.53**	**5.35**	**n.d.**	**0.16**	**1.57**
Dry Season / *Trachypogon plumosus* (dry grass)												
Tp 1/d	13	702	44	-4.23 ± 0.7	7.26 ± 1.1	0.64 ± 0.1	0.72 ± 0.2	0.90 ± 0.3	0.54 ± 0.2	0.91 ± 0.7	n.d.	0.34 ± 0.1
Tp 2/d	7	776	47	-25.41 ± 2.9	0.61 ± 2.0	-0.75 ± 0.4	n.d.	n.d.	-3.78 ± 1.3	n.d.	n.d.	n.d.
Average dry Tp				**-14.82**	**3.93**	**-0.06**	**0.72**	**0.90**	**-1.62**	**0.91**	**n.d.**	**0.34**

Table 3.5. VOC exchange rates and CO_2 assimilation from *Axonopus canescens* in the wet and dry season. Data are 10-min averages ± SD of daytime (10:00-16:00) measurements. n.d. means not detected. Also shown are n = number of measurements, Rad = average radiation, T = average temperature inside the chamber.

	n	**Rad**	**T**	**CO_2**	**m33**	**m43**	**m45**	**m57**	**m59**	**m61**	**m69**	**m73**
		($W\,m^{-2}$)	**(°C)**	**($\mu mol\,g^{-1}\,h^{-1}$)**	**($nmol\,g^{-1}\,h^{-1}$)**							
Wet Season / *Axonopus canescens* (mature grass)												
Ac 1	5	772	35	-65.27 ± 28.5	36.61 ± 1.7	-1.91 ± 2.7	8.72±4.4	3.80 ± 1.6	5.00 ± 3.0	n.d.	1.74 ± 1.3	0.94 ± 0.5
Dry Season / *Axonopus canescens* (dry grass)												
Ac 1/d	13	686	35	3.99 ± 0.7	10.76 ± 0.9	1.27 ± 0.3	1.40 ± 0.1	1.99 ± 0.4	2.25 ± 0.3	0.57 ± 0.3	n.d.	0.50 ± 0.1
Ac 2/d	7	855	36	-20.05 ± 3.5	9.72 ± 3.2	0.19 ± 0.7	-2.03 ± 0.7	n.d.	-2.55 ± 0.8	0.79± 1.0	n.d.	n.d
Ac 3/d	7	804	35	-15.07 ± 5.2	19.22 ± 3.8	1.39 ± 0.5	n.d.	1.46 ± 0.9	n.d.	2.77 ± 1.0	n.d.	n.d
Average dry Ac				**-10.38**	**13.23**	**0.95**	**-0.32**	**1.72**	**-0.15**	**1.38**	**n.d.**	**0.50**

Table 3.6. VOC exchange rates and CO_2 assimilation from *Hyparrhenia rufa* in the wet and dry season. Data are 10-min averages ± SD of daytime (10:00-16:00) measurements. n.d. means not detected. Also shown are n = number of measurements, Rad = average radiation, T = average temperature inside the chamber.

	n	**Rad**	**T**	**CO_2**	**m33**	**m43**	**m45**	**m57**	**m59**	**m61**	**m69**	**m73**
		(W m^{-2})	**(°C)**	**(μmol g^{-1} h^{-1})**				**(nmol g^{-1} h^{-1})**				
					Wet Season / *Hyparrhenia rufa* (mature grass)							
Hr 1	7	61	23	-0.93± 15.0	5.55 ± 5.1	n.d.	0.66 ± 2.0	0.38 ± 3.1	1.16 ± 1.5	n.d.	n.d.	0.63 ± 0.3
Hr 2	5	199	24	-12.71 ± 3.7	2.75 ± 2.2	n.d.	2.85 ± 0.9	1.17 ± 0.8	3.24 ± 2.5	n.d.	0.57 ± 0.5	0.67± 0.4
Hr 3	5	797	34	-127.78 ± 1.8	27.62 ± 4.9	n.d.	8.86 ± 4.0	2.62 ± 1.9	5.73 ± 2.9	n.d.	1.60 ± 0.2	1.02± 1.1
Average mature Hr				**-47.14**	**11.97**	**n.d.**	**4.13**	**1.39**	**3.38**	**n.d.**	**1.08**	**0.77**
					Dry Season / *Hyparrhenia rufa* (dry grass)							
Hr 1/d	8	753	36	-11.73 ± 2.5	5.82 ± 2.7	0.43 ± 0.5	0.29 ± 0.7	0.39 ± 0.6	n.d.	1.11 ± 0.7	n.d.	0.18± 0.2
Hr 2/d	8	707	35	-26.00 ± 6.8	18.63 ± 4.6	5.11 ± 2.9	3.15 ± 1.3	4.07 ± 1.9	3.83 ± 1.8	7.51 ± 3.7	0.86 ± 0.5	1.71 ± 0.6
Hr 3/d	8	666	35	-41.87 ± 7.9	2.68 ± 4.7	0.68 ± 0.8	-1.3 ± 2.0	0.43 ± 0.9	n.d.	1.08 ± 0.9	n.d.	0.55 ± 0.6
Average dry Hr				**-26.53**	**9.04**	**2.07**	**0.72**	**1.63**	**3.83**	**3.23**	**0.86**	**0.81**

3.3.2.1. Relation of VOCs emission to assimilated CO_2

For a plant, the emission of VOCs represents a loss of carbon and energy that were both previously gained by photosynthesis. The relation between the carbon emitted as VOC and the carbon assimilated by photosynthesis during daytime was determined and is shown in Table 3.7. On average, 0.09% and 0.05% of the assimilated carbon by *mature and young Trachypogon* respectively, was emitted as VOCs. Growing new leaves demands a lot of energy in form of carbohydrates that are supplied by photosynthesis, thus it may be speculated that less carbon is available to be reemitted as VOCs from young plants. For the single green *Axonopus* the relation was 0.15%. The average for *Hyparrhenia* (0.6%) is rather high, but more realistic seems to be the value from Hr3, 0.07%. The other two *Hyparrhenia* specimens were measured under low radiation conditions (Table 3.6), and therefore exhibited a very low photosynthesis rate. As VOCs emissions are controlled by both radiation and temperature, but as will be shown later on, especially by temperature, it is possible that the emissions of Hr1 and Hr2 were disproportionately high. This suggests that the emissions of VOCs are more closely linked to temperature than to photosynthetic activity.

Table 3.7. Average total carbon gained by photosynthesis during daytime (10:00-16:00) and percentage emitted as VOCs

		Carbon gain by CO_2 assimilation (μgC g^{-1} h^{-1})	Total VOC-C emitted (ngC g^{-1} h^{-1})	Percentage of C emitted as VOCs
Wet season				
Trachypogon plumosus (mature grass)	Tp 1	-1120.6	2192.9	0.20
	Tp 2	-1103.3	352.9	0.03
	Tp 3	-810.5	1113.5	0.14
	Tp 4	-1553.0	536.2	0.04
	Tp 5	-1430.4	618.2	0.04
Axonopus canescens (mature grass)	Ac 1	-783.2	1160.2	0.15
Hyparrhenia rufa (mature grass)	Hr 1	-11.2	173.0	1.54
	Hr 2	-152.5	341.2	0.22
	Hr 3	-1533.4	1021.2	0.07
Dry season				
Trachypogon plumosus (young grass)	Tp 1/y	-1549.1	589.0	0.04
	Tp 2/y	-1134.2	284.9	0.03
	Tp 3/y	-743.4	515.7	0.07
	Tp 4/y	-1904.2	1745.4	0.09
	Tp 5/y	-2001.0	619.1	0.03

For one of the dry *Trachypogon* and all *Axonopus* grass tussocks, a fraction of the total grass blades were still green (Table 3.2), whereas the rest of the “dry grasses” appeared to be only “dead standing grass”. Nevertheless, most of the dry grasses still exhibited some photosynthetic activity (Tables 3.4-3.6), but it was not possible to quantitatively establish the contribution of the green grasses to the total VOCs emissions.

The loss of assimilated carbon reported in the literature was found to range between a few thousandths and some percent (e.g. Fehsenfeld *et al.*, 1992; Street *et al.*, 1996; Kesselmeier *et al.*, 1997), and in some cases, 10, 20 and even more than 50% (Sharkey and Loreto, 1993; Staudt and Bertin, 1998). The high losses were observed from trees (see also chapter 4) that were high isoprene and monoterpene emitters, which was not the case of the grasses.

3.3.2.2. Diurnal cycle of emissions

A typical diurnal variation of emission of selected VOCs, along with assimilation, solar radiation and chamber temperature is shown in Figure 3.7. The data represent hourly averages ± SD of methanol (m33), acetone (m59) and m57 (probably mostly butene and butanol) from the dry season measurements of a young *Trachypogon* (Tp4/y) and a dry *Trachypogon* tussock (Tp1/d) measured during two consecutive days.

The CO_2 data illustrates the substantially different physiological activity of the green and dry grasses. Green grasses exhibited a pronounced diurnal variation, the highest photosynthetic activity was reached around midday, and release of CO_2 (respiration) occurred during the night. In contrast, for dry grasses, no respiration was detected during the night, and they showed a minimal CO_2 uptake during the day, which was less than one tenth of the mean CO_2 uptake of green grasses. This suggests that some parts of the dry *Trachypogon* were still active, albeit there were no green grass blades found in this particular grass tussock (Tp1/d, see Table 3.2).

The H_2O exchange (transpiration) was also monitored in both the reference and the sample chamber, but data are not shown since they were not meaningful, i.e. transpiration should have occurred during the day, but the H_2O values of the sample chamber were negative in the majority of cases, which means that there was more water vapor in the reference than in the sample chamber. A possible cause for this problem may be the influence of the soil moisture and evaporation. The evaporation of water from the soil probably occurred at a different rate in the reference than in the sample chamber. In the former, the soil was exposed to direct sunlight, while in the latter the grass mostly shaded the soil. Especially during the wet season, the soil was exposed alternatively to intense rainfall and high solar radiation and temperatures, and the transpiration of the grasses was completely masked by the evaporating water.

The observed emission rates clearly show that the young *Trachypogon* emits VOCs during the day, with emission maxima around midday, and very little emission at night. Similar diurnal cycles were observed with mature grasses of all measured species during the wet season. The deposition (negative rates) observed in the second night (30 March, between 20:00-22:00 LT; Fig. 3.7) was probably an artifact, likely due to the fast increase of the atmospheric concentrations of these trace gases in the nighttime boundary layer in the dry season (see Fig. 3.3). The ambient concentration at the time of measurement may have been lower than the subtracted interpolation.

Within a chamber temperature range of 23-50°C and a radiation range of 0-1200 W/m^2, the methanol emission rate of Tp4/y varied by a factor of 20 between 2 and 40 nmol/g/h. The nighttime emissions between 21:00 and 5:00, with an average of 5 nmol/g/h represents approximately one fifth of the mean daytime emission (27 nmol/g/h, Table 3.4). The emission of butene and butanol (m57) ranged between 1-25 nmol/g/h, and the emission of acetone (m59) between 0.6-15 nmol/g/h. The nighttime emission of these compounds was about a factor of 10 lower than the emissions during the day.

The dry *Trachypogon* showed a significant diel cycle only for methanol (Fig. 3.7). The emission of methanol from the dry grasses was less than 25% of the emission from the green grasses, whereas the emissions of m59 and m57 were negligible compared to those of green grasses. The methanol emission from the dry *Axonopus* and *Hyparrhenia* also showed a diurnal cycle which correlated with temperature and radiation (not shown). The average methanol emission of these dry grasses was ~30% of the emitted by the green grasses (Tables 3.5, 3.7, excluding Hr1 and Hr2 because of the bad weather conditions during measurements)

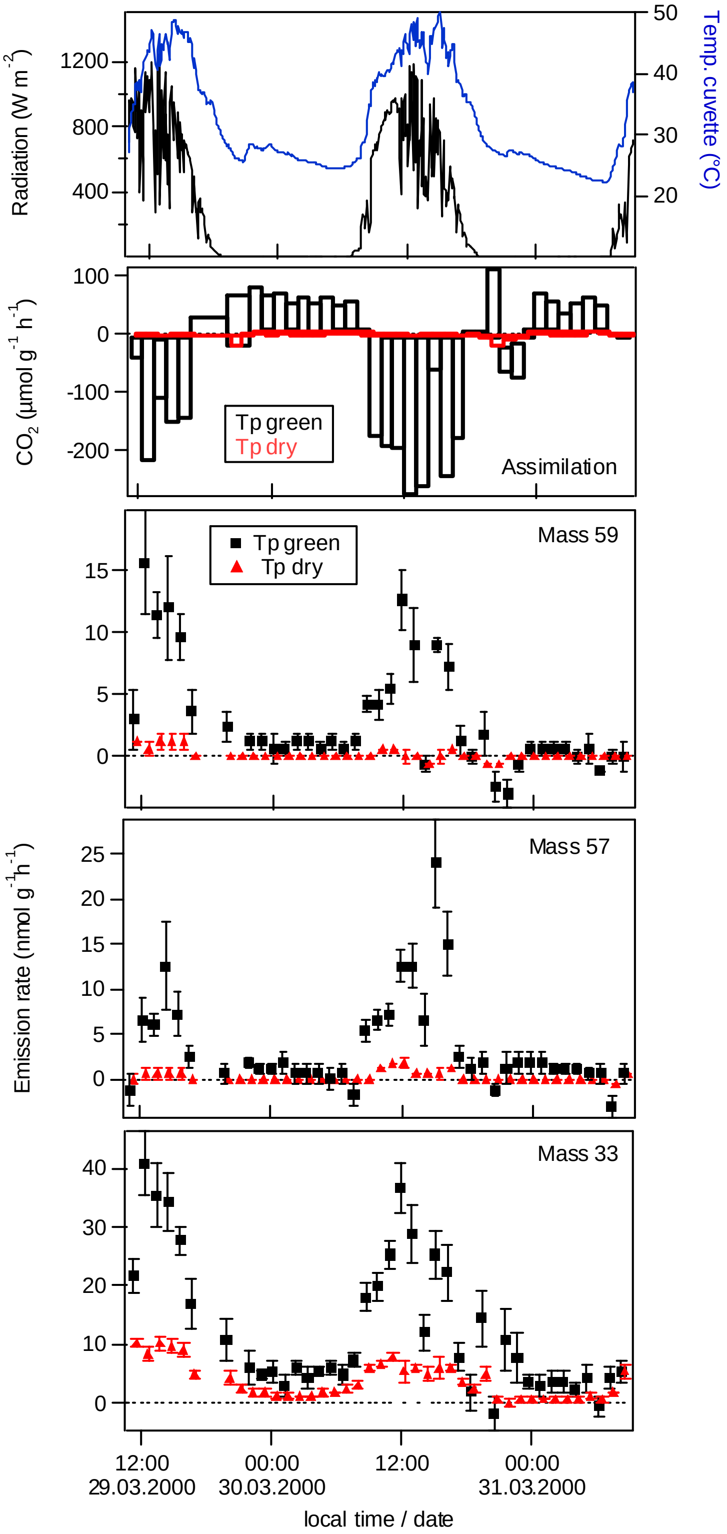

Figure 3.7. Diurnal cycle of VOC emission rates from young green and dry *Trachypogon* measured in the dry season campaign (Tp4/y and Tp1/d), together with global radiation, chamber temperature and CO$_2$ assimilation.

3.3.2.3. Temperature and light dependence of VOCs emissions

Based on the diurnal cycle (Fig. 3.7) and the interdependence of the solar radiation and chamber temperature (Fig. 3.6), good correlation of both parameters with VOC emissions is expected. For the temperature dependence analysis, all emission data for a particular grass species in the wet or dry season were aggregated into 1°C intervals. Chamber temperature was preferred over ambient temperature, because these values are closer to the actual leaf temperature, which was not measured. For the light dependence analysis, the data were aggregated into radiation intervals of ~50 W/m^2. Figures 3.8 and 3.9 show these correlations for the young *Trachypogon* grass, measured in the dry season. The temperature and light dependence of the other grass species emissions behave in a similar way. The results for the other studied species can be found in the appendices (Figures 8.1-8.3).

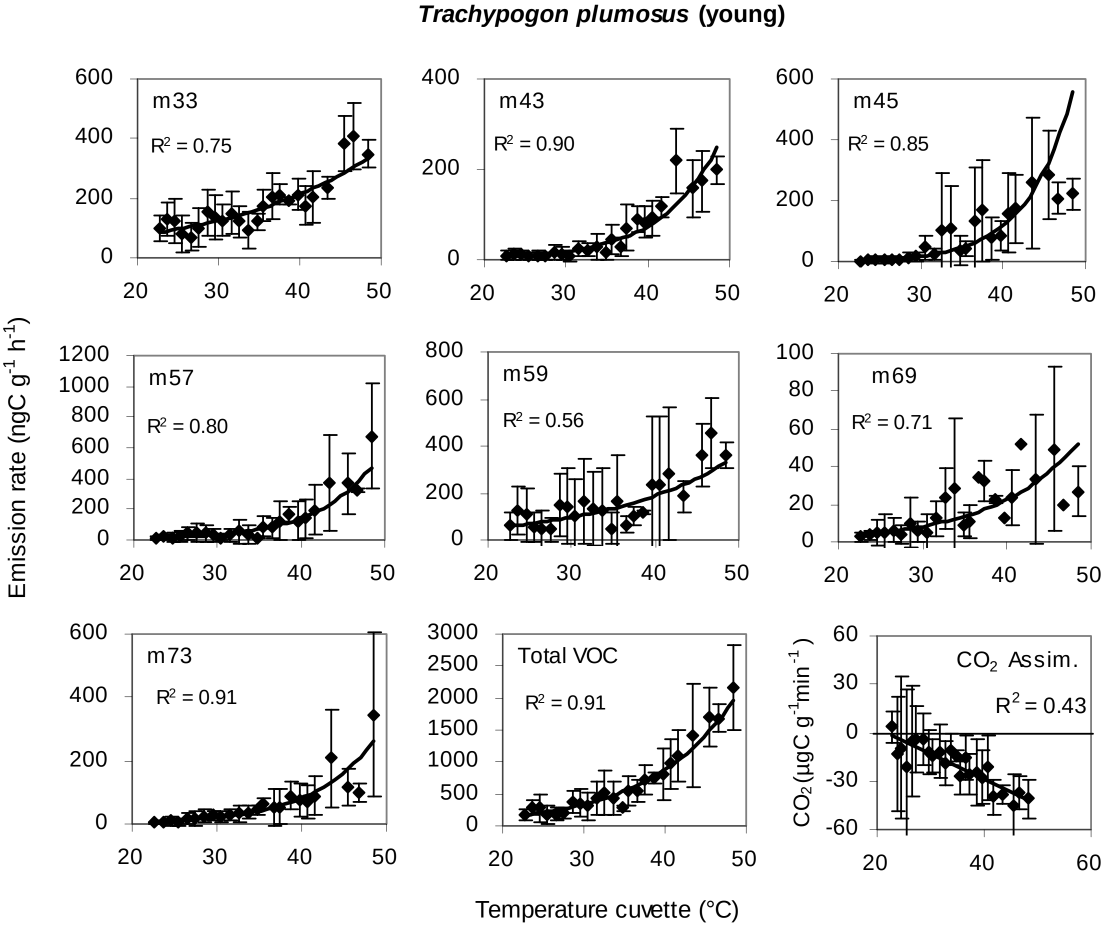

Figure 3.8. Chamber temperature dependence of VOC emissions from young *Trachypogon* grasses in the dry season. Emission rates data from all measured grass tussocks were aggregated into 1°C intervals; error bars represent standard deviation. R^2 refers to exponential fit, except for CO$_2$ (linear).

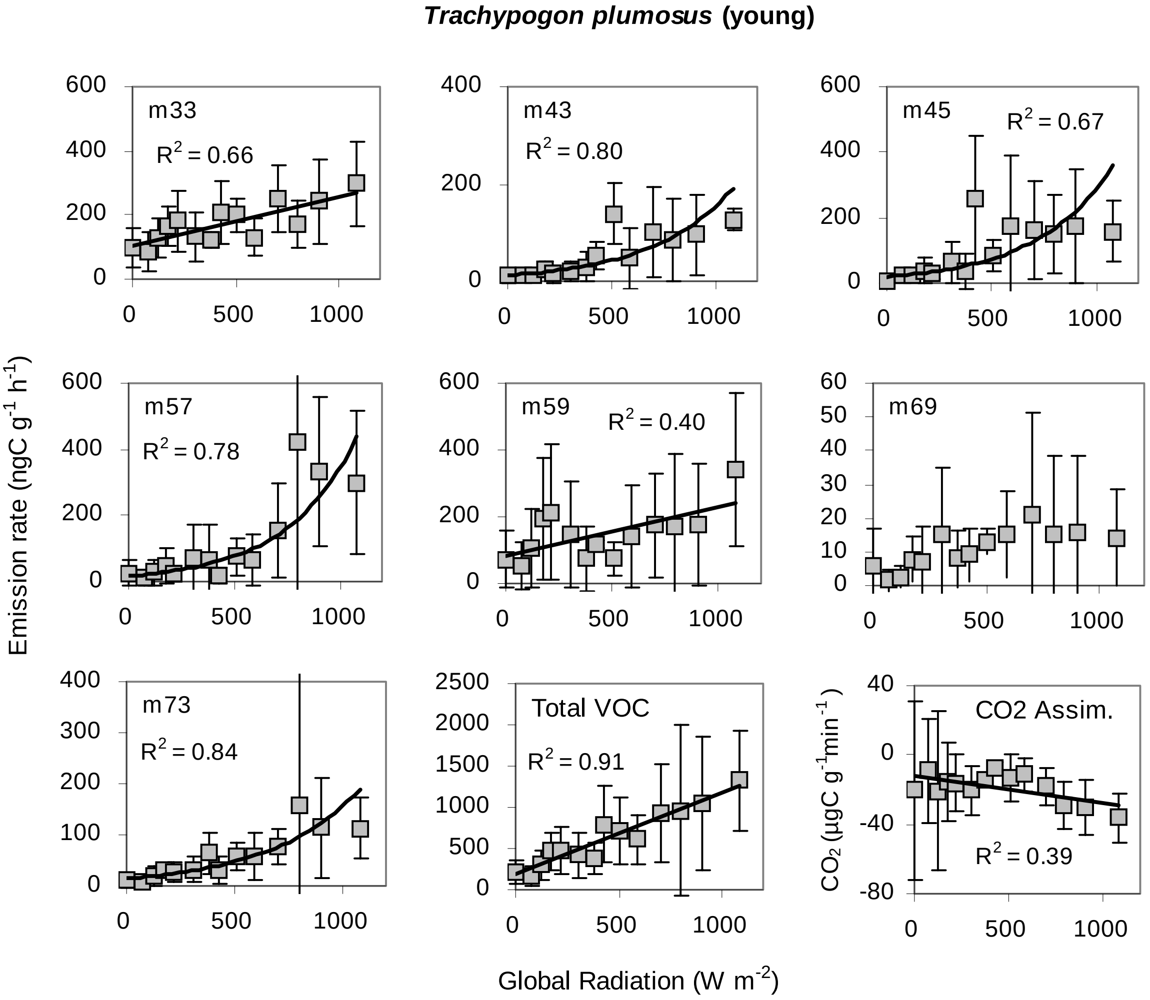

Figure 3.9. Solar radiation dependence of VOC emissions from young *Trachypogon* grasses in the dry season. Emission rates data from all measured grass tussocks were aggregated into 50-100 W/m^2 intervals; error bars represent standard deviation. R^2 refers to exponential fit for masses 43, 45, 57 and 73, and linear fit for masses 33, 59, total VOCs and CO_2.

The emission of VOCs increased exponentially with the temperature in the chamber (Fig 3.8). The temperature inside the chamber was between 5-10°C higher that the actual ambient temperature (Table 3.3), therefore the highest emissions observed at temperatures higher than 40°C probably will not occur frequently in the savanna. Nevertheless, for most VOCs there was generally no saturation or emission decrease observed at high temperatures, and therefore all data were included in the correlation analyses. The discontinuity of the temperature response of acetaldehyde (m45) and isoprene and/or C_5-alcohol (m69) emissions at the highest temperatures (Fig. 3.8) may be due to the few measurements points averaged (n=4), but since it was also observed in mature *Trachypogon* (Appendix, Table 8.1) for m45, m57, m69 and m73, it may be also an indicative of an optimum or saturation curve at temperatures higher than ~45°C. The temperature response of isoprene (and MBO) emission is well known and is represented by an optimum curve, with maximal emission between temperatures of 40-45°C, when the enzymatic activity is at its maximum, followed by a rapid decline at higher temperatures owing to enzyme deactivation (e.g. Monson *et al.*, 1992; Fall, 1999).

The correlation with radiation was also exponential for most VOCs (Fig. 3.9). Exceptions, for which the best fit was linear, were methanol (m33), acetone (m59) and the sum of all VOCs. The emission of m69, and m45 exhibited a light response that has been previously observed for isoprene and MBO emissions from a variety of trees (e.g. Guenther *et al.*, 1993; Schade and Goldstein, 2001); the emission increased linearly up to a radiation of ~700 W/m^2 and saturated at higher light intensities.

All VOCs exhibited a better correlation with temperature than with light. Also in previous studies it has been found that temperature is the most important driver of oxygenated VOC emissions (Schade and Goldstein, 2001; Karl *et al.*, 2003a). A strong temperature dependence has been reported for emissions of acetone (Macdonald and Fall, 1993a), methanol (Macdonald and Fall, 1993b), formaldehyde, acetaldehyde, formic acid and acetic acid (Kesselmeier *et al.*, 1997). But temperature is obviously not the only factor influencing the emissions. There are also studies that indicate that some of these compounds are correlated with stomatal conductance (which gives a relative description of the stomatal opening) (Nemecek-Marshall *et al.*, 1995; Kesselmeier *et al.*, 1997), possibly because these compounds are transported out of the plant through the transpiration stream. In this work, stomatal conductance could not be derived for the grass measurements, since the transpiration rate is needed for the calculation, and, as mentioned earlier, transpiration data could not be used. Nevertheless, there is usually a close relation of stomatal conductance and CO_2 exchange. CO_2 assimilation was linearly well correlated with temperature and radiation –and therefore with VOCs emission– for young *Trachypogon* (Fig 3.8 and 3.9), as well as for all mature grasses (Tables 8.1-8.3 in Appendix 8.4).

Since the plants were studied in the field, where it is impossible to do the measurements under controlled meteorological conditions, the most probable causes of the high variability observed in the VOC emission rates (Tables 3.4-3.6) are the different light and especially temperature conditions during the measurements. Therefore, in order to study plant-to-plant, interspecies and seasonal variabilities of VOCs exchange, the emission data were normalized based on the observed relationship with temperature.

The VOCs emission dependencies on temperature were analyzed on the basis of the following algorithm,

$$E = E_{St} \exp[\beta \times (T - T_{St})] \qquad (3.1)$$

where E is the emission rate at temperature T, E_{St} is the emission rate at a standard temperature T_{St} (usually 303 K), and β is an empirical temperature coefficient. This algorithm has been used to simulate the temperature dependence of monoterpene emissions (e.g. Guenther *et al.*, 1993), and more recently the emission of oxygenated VOCs (Schade and Goldstein, 2001; Karl *et al.*, 2003a). The algorithm used to model isoprene emissions (Guenther *et al.*, 1993), which includes light and temperature dependency, was also tested, but it underestimates the VOC emissions during both day and night.

The β-coefficient establishes the temperature dependence of the emission rate in equation 3.1. For monoterpenes an average value of 0.09 K^{-1} is commonly used (Guenther *et al.*, 1993), and for methanol, acetaldehyde and acetone values that vary from 0.04 to 0.13 K^{-1} have been calculated from field measurements at a pine forest in California (Schade and Goldstein, 2001) and a hardwood forest in Michigan (Karl *et al.*, 2003a). Tables 3.8-3.10 summarize the values for the β-coefficients for the present grass measurements.

It should be noted that for some measurements the emission rates had only a low correlation with temperature, and a few had negative correlations. The range of β-coefficients (given for each species in both seasons) only includes the values for positive correlations. The β-values were between a minimum of 0.01 and a maximum of 0.47 K^{-1}. On average, the valaues of β varied by a factor of 2.5 (between 0.08 and 0.23 K^{-1}) for all grass species. Among the green grasses, the highest values were found for methanol (β=0.4) and acetaldehyde (β=0.47) emissions from *Hyparrheni*a. The range of β-factors for the emission of methanol and mass 57 from mature *Trachypogon* was larger than for the young *Trachypogon* (Table 3.8). All other compounds emitted by *Trachypogon* grasses (including dry grasses) had similar values of temperature dependence. For *Axonopus* also both, the mature and dry grasses, exhibited similar β-factors ranges for all VOCs (Table 3.9), as opposed to the mature *Hyparrhenia*, for which all compounds, except MEK (m73), had larger temperature dependencies than those from dry grasses. The variations in the estimates of β can be attributed to leaf-to-leaf and seasonal variations, different vapor pressures and solubilities of VOCs, diverse storage and emission pathways in different plants (Guenther *et al.*, 1993), stress and insect attack.

The temperature-dependence data for the emission of acetic acid (m61) were not included in the tables because it was only emitted by dry grasses (Tables 3.4-3.6). Similar temperature dependencies were found for all grass species. The average β-factor for *Trachypogon* was 0.10 ± 0.02 (n=18; R^2=0.53), for dry *Axonopus* 0.13 ± 0.01 (n>8; R^2 = 0.7), and for dry Hyparrhenia 0.10 ± 0.06 (n>11, R^2 = 0.30-0.47).

Table 3.8. Values for the temperature dependence, β [K^{-1}], of VOC emissions from *Trachypogon plumosus*. Errors are SD from fits to the data. Numbers in parentheses give *n*, number of measurements, and the correlations coefficients (R^2) for fits of *lnE* versus $(T-T_{ref})$.

	m33	m43	m45	m57	m59	m69	m73
Wet Season / *Trachypogon plumosus* (mature green grass)							
Tp 1	0.25 ± 0.03 (34, 0.73)	0.19 ± 0.10 (20, 0.17)	0.27 ± 0.05 (19, 0.60)	0.32 ± 0.03 (31, 0.76)	0.09 ± 0.03 (24, 0.37)	0.18 ± 0.06 (24, 0.29)	0.23 ± 0.04 (27, 0.53)
Tp 2	0.05 ± 0.02 (9, 0.57)	-0.00 ± 0.16 (6, 0.0)	-0.20 ± 0.24 (5, 0.18)	-0.06 ± 0.10 (4, 0.15)	n.d.	n.d.	n.d.
Tp 3	0.12 ± 0.03 (18, 0.46)	0.14 ± 0.03 (13, 0.66)	0.17 ± 0.04 (17, 0.51)	0.20 ± 0.02 (23, 0.79)	0.11 ± 0.02 (28, 0.55)	0.18 ± 0.03 (23, 0.61)	0.19 ± 0.03 (22, 0.70)
Tp 4	0.22 ± 0.04 (24, 0.63)	0.09 ± 0.06 (12, 0.17)	0.11 ± 0.05 (10, 0.37)	0.10 ± 0.08 (13, 0.13)	0.12 ± 0.03 (28, 0.36)	n.d	0.14 ± 0.07 (14, 0.25)
Tp 5	0.18 ± 0.04 (14, 0.57)	n.d.	0.21 ± 0.07 (10, 0.54)	0.20 ± 0.07 (11, 0.45)	0.09 ± 0.03 (14, 0.51)	n.d.	-0.05 ± 0.19 (10, 0.01))
range	**0.05-0.25**	**0.09-0.19**	**0.11-0.27**	**0.1-0.32**	**0.09-0.12**	**0.18**	**0.14-0.23**
Dry Season / *Trachypogon plumosus* (young grass)							
Tp 1 /y	0.06 ± 0.02 (30, 0.20)	0.12 ± 0.04 (22, 0.27)	0.28 ± 0.06 (19, 0.56)	0.11 ± 0.06 (31, 0.11)	0.01 ± 0.00 (33, 0.62)	n.d.	0.19 ± 0.04 (26, 0.51)
Tp 2 /y	0.10 ± 0.03 (34, 0.31)	n.d.	0.27 ± 0.07 (13, 0.58)	0.08 ± 0.04 (24, 0.14)	0.04 ± 0.02 (30, 0.07)	n.d.	0.25 ± 0.03 (29, 0.72)
Tp 3 /y	0.06 ± 0.01 (36, 0.37)	0.19 ± 0.04 (21, 0.60)	0.30 ± 0.05 (19, 0.47)	0.14 ± 0.04 (27, 0.33)	0.13 ± 0.06 (32, 0.16)	0.16 ± 0.03 (18, 0.60)	0.25 ± 0.05 (15, 0.65)
Tp 4 /y	0.08 ± 0.01 (39, 0.67)	0.14 ± 0.02 (28, 0.71)	0.19 ± 0.02 (28, 0.75)	0.12 ± 0.01 (37, 0.75)	0.12 ± 0.01 (32, 0.75)	n.d.	0.13 ± 0.02 (37, 0.62)
Tp 5 /y	0.14 ± 0.02 (27, 0.69)	0.22 ± 0.03 (22, 0.72)	0.21 ± 0.02 (22, 0.81)	0.08 ± 0.01 (29, 0.55)	0.14 ± 0.04 (30, 0.33)	0.12 ± 0.02 (24, 0.56)	0.08 ± 0.01 (31, 0.48)
range	**0.06-0.14**	**0.12-0.22**	**0.19-0.3**	**0.08-0.14**	**0.01-0.14**	**0.12-0.16**	**0.08-0.25**
Dry Season / *Trachypogon plumosus* (dry grass)							
Tp 1 /d	0.10 ± 0.01 (40, 0.72)	0.11 ± 0.02 (21, 0.62)	0.14 ± 0.02 (22, 0.64)	0.12 ± 0.02 (25, 0.62)	0.10 ± 0.02 (31, 0.60)	n.d.	0.12 ± 0.02 (24, 0.72)
Tp 2 /d	-0.03 ± 0.02 (15, 0.12)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 3.9. Values for the temperature dependence, β [K^{-1}], of VOC emissions from *Axonopus canescens*. Errors are SD from fits to the data. Numbers in parentheses give *n*, number of measurements, and the correlations coefficients (R^2) for fits of *lnE* versus *$(T-T_{ref})$*.

	m33	**m43**	**m45**	**m57**	**m59**	**m69**	**m73**
			Wet Season / *Axonopus canescens* (mature green grass)				
Ac 1	0.25 ± 0.07	n.d.	0.44 ± 0.15	0.16 ± 0.24	0.06 ± 0.33	-0.57 ± 0.08	0.24 ± 0.24
	(4, 0.86)		(4, 0.81)	(3, 0.28)	(3, 0.002)	(4, 0.74)	(4, 0.10)
Ac 2	0.09 ± 0.01	n.d.	0.16 ± 0.04	0.16 ± 0.02	0.15 ± 0.06	0.14 ± 0.02	0.06 ± 0.04
	(5, 0.94)		(6, 0.83)	(6, 0.91)	(3, 0.83)	(6, 0.90)	(6, 0.34)
range	**0.09-0.25**		**0.16-0.44**	**0.16**	**0.15**	**0.14**	**0.06-0.24**
			Dry Season / *Axonopus canescens* (dry grass)				
Ac 1	0.12 ± 0.01	0.15 ± 0.01	0.14 ± 0.01	0.14 ± 0.01	0.16 ± 0.01	n.d.	0.15 ± 0.02
/d	(40, 0.71)	(30, 0.86)	(24, 0.82)	(32, 0.81)	(34, 0.79)		(32, 0.74)
Ac 2	0.09 ± 0.01	0.06 ± 0.07	0.12 ± 0.06	n.d.	n.d.	n.d.	n.d.
/d	(19, 0.77)	(7, 0.13)	(7, 0.43)				
Ac 3	0.05 ± 0.01	0.07 ± 0.04	n.d.	0.06 ± 0.02	n.d.	n.d.	n.d.
/d	(21, 0.59)	(10, 0.29)		(20, 0.41)			
range	**0.05-0.12**	**0.06-0.15**	**0.12-0.14**	**0.06-0.14**	**0.16**		**0.15**

Table 3.10. Values for the temperature dependence, β [K^{-1}], of VOC emissions from *Hyparrhenia rufa*. Errors are SD from fits to the data. Numbers in parentheses give *n*, number of measurements, and the correlations coefficients (R^2) for fits of *lnE* versus *$(T-T_{ref})$*.

	m33	**m43**	**m45**	**m57**	**m59**	**m69**	**m73**
			Wet Season / *Hyparrhenia rufa* (mature green grass)				
Hr 1	0.29 ± 0.11	n.d.	0.47 ± 0.09	0.28 ± 0.08	0.31 ± 0.07	n.d.	0.20 ± 0.11
	(29, 0.20)		(26, 0.53)	(19, 0.42)	(27, 0.41)		(31, 0.11)
Hr 2	0.40 ± 0.13	n.d.	0.34 ± 0.13	-0.03 ± 0.22	0.18 ± 0.43	0.18 ± 0.18	-0.05 ± 0.13
	(9, 0.55)		(9, 0.48)	(7, 0.00)	(9, 0.02)	(7, 0.17)	(8, 0.03)
Hr 3	0.13 ± 0.03	n.d.	-0.05 ± 0.06	0.11 ± 0.05	-0.09 ± 0.07	-0.01 ± 0.01	0.04 ± 0.04
	(7, 0.82)		(6, 0.14)	(5, 0.68)	(7, 0.27)	(6, 0.04)	(6, 0.19)
range	**0.13-0.40**		**0.34-0.47**	**0.11-0.28**	**0.06-0.31**	**0.18**	**0.04-0.2**
			Dry Season / *Hyparrhenia rufa* (dry grass)				
Hr 1	0.06 ± 0.01	0.08 ± 0.04	0.08 ± 0.08	0.08 ± 0.03	n.d.	n.d.	0.10 ± 0.03
/d	(28, 0.63)	(9, 0.41)	(7, 0.20)	(11, 0.36)			(8, 0.63)
Hr 2	0.09 ± 0.01	0.24 ± 0.04	0.16 ± 0.03	0.16 ± 0.01	0.18 ± 0.02	0.13 ± 0.02	0.16 ± 0.02
/d	(27, 0.81)	(9, 0.85)	(13, 0.75)	(23, 0.88)	(24, 0.80)	(16, 0.72)	(20, 0.82)
Hr 3	0.02 ± 0.02	0.08 ± 0.03	0.001 ± 0.12	0.11 ± 0.03	n.d.	n.d.	0.16 ± 0.06
/d	(27, 0.13)	(11, 0.42)	(5, 0.00)	(19, 0.42)			(13, 0.39)
range	**0.06-0.09**	**0.08-0.24**	**0.08-0.16**	**0.08-0.16**	**0.18**		**0.10-0.16**

3.3.2.4. Standard emission rates of VOCs

The standard emission rates, E_{St}, were calculated for a temperature of 30°C from the same fits used to derive β-coefficients. Tables 3.11-3.13 summarize E_{St} for the grass measurements in both seasons. Also included in the tables are the CO_2 assimilation values at 30°C, derived from the linear correlation of CO_2 versus temperature. The mature *Trachypogon* tussock Tp2 was not included in Table 3.11 because, for unknown reasons, all emitted VOCs, except methanol, exhibited a negative correlation with temperature. Tp 2/d was also omitted, because methanol, the only emission detected from this specimen, was also negatively correlated with temperature.

There was no significant difference between the average standard emission factors of masses 33, 43, 57 and 73 from mature and young *Trachypogon*, whereas E_{St} from masses 45, 59 and 69 were higher from mature grasses (Table 3.11). Compared to the dry *Trachypogon* grasses, the emission rates from green (young and mature) grass tussocks were higher by at least a factor of 3. The plant-to-plant variability of the emission rates was rather large. Especially for m57 (butene + butanol) the E_{St} from young grasses varied by almost an order of magnitude from 11 to 87 ngC/g/h. For all other compounds, emission rates among the *Trachypogon* specimens measured during a given season, varied generally between a factor of 2-4.

The average E_{St} from mature *Axonopus* (Table 3.12) were higher than E_{St} of the respective dry grasses by more than a factor of 2 (range 2.5-8.3). The plant-to-plant variability was particularly high between the two *Axonopus* measured in the wet season. The plant-to-plant variability for the dry *Axonopus* was lower (between a factor of 1.4-3.3).

The emissions from mature *Hyparrhenia* grasses were 2-19 times higher than those of dry grasses (Table 3.13). The plant-to-plant variations for mature grasses were lower than a factor of 3, and between 2-4 for dry grasses.

The E_{St} of acetic acid (m61, included in Table 3.15) was similar for all dry grass species, namely 5.8 ± 3.2 ngC/g/h for dry *Trachypogon,* 4.4 ± 1.5 ngC/g/h for dry *Axonopus*, and 9.6 ± 2.6 ngC/g/h for dry *Hyparrhenia* grasses. Nevertheless, due to the measurement problems of this acid (Chapter 2), these values may have high uncertainty.

Table 3.11. Standard emission rates in [ngC/g/h] for *Trachypogon plumosus*. Errors are SD from fits to the data.

	CO_2[a]	**m33**	**m43**	**m45**	**m57**	**m59**	**m69**	**m73**
Wet Season / *Trachypogon plumosus* (mature green grass)								
Tp 1	78	81.5 ± 2.8	6.5 ± 21.5	19.2 ± 5.9	44.8 ± 3.6	110.9 ± 2.2	21.3 ± 7.3	27.2 ± 5.0
Tp 3	72	87.7 ± 3.9	3.6 ± 3.0	16.0 ± 5.7	28.7 ± 2.6	31.8 ± 2.4	8.9 ± 4.0	11.0 ± 2.9
Tp 4	37	72.5 ± 2.6	13.7 ± 3.0	60.4 ± 2.8	41.6 ± 3.4	44.3 ± 2.3	n.d.	18.5 ± 3.3
Tp 5	-204	63.6 ± 2.9	n.d.	15.8 ± 5.0	23.1 ± 4.7	43.1 ± 1.9	n.d.	neg. corr.
Average Tp(WS)		**76.3 ± 9.1**	**7.9 ± 4.3**	**27.9 ± 18.8**	**34.5 ± 8.9**	**57.5 ± 31.2**	**15.1± 6.2**	**18.9 ± 6.6**
Dry Season / *Trachypogon plumosus* (young grass)								
Tp 1/y	-935	97.3 ± 1.7	15.6 ± 2.6	17.5 ± 3.3	20.6 ± 4.9	20.0 ± 3.2	n.d.	16.2 ± 2.3
Tp 2/y	-728	106.3 ± 1.9	n.d.	15.5 ± 2.7	16.3 ± 2.4	37.4 ± 1.9	n.d.	19.4 ± 1.9
Tp 3/y	-93	73.7 ± 1.4	15.0 ± 2.1	15.6 ± 4.5	10.8 ± 2.9	47.5 ± 3.9	8.0 ± 1.8	7.2 ± 2.1
Tp 4/y	-68	89.4 ± 1.7	16.6 ± 2.7	13.8 ± 3.2	69.2 ± 2.0	50.1 ± 2.0	n.d.	19.8 ± 2.6
Tp 5/y	-350	39.5 ± 2.1	11.3 ± 2.7	8.8 ± 2.1	87.3 ± 1.6	20.0 ± 4.0	6.0 ± 2.2	36.5 ± 1.8
Average Tp/y		**81.2 ± 23.5**	**14.6 ± 2.0**	**14.2 ± 3.0**	**40.8 ± 31.2**	**35.0 ± 13.0**	**7.0 ± 1.0**	**19.8 ± 9.5**
Dry Season / *Trachypogon plumosus* (dry grass)								
Tp 1/d	-4	23.8 ± 1.7	4.7 ± 2.8	2.1 ± 3.3	7.6 ± 2.6	5.2 ± 2.3	n.d.	2.8 ± 2.2

[a] CO_2 assimilation in µgC/g/h, derived from linear correlations of CO_2 exchange vs. temperature.

Table 3.12. Standard emission rates in [ngC/g/h] for *Axonopus canescens*. Errors are SD from fits to the data.

	CO_2[a]	**m33**	**m43**	**m45**	**m57**	**m59**	**m69**	**m73**
Wet Season / *Axonopus canescens* (mature green grass)								
Ac 1	95	37.0 ± 3.7	n.d.	2.36 ± 8.4	40.0 ± 55.7	no corr.	neg. corr	3.77 ± 3.1
Ac 2	84	181 ± 1.34	n.d.	58.0 ± 2.5	64.1 ± 1.7	57.0 ± 3.9	77.4 ± 1.6	46.9 ± 2.4
Average Ac (WS)		**109 ± 72**	**n.d.**	**30.3 ± 27.2**	**52.1 ± 12.1**	**57.0**	**77.4**	**25.3 ± 21.6**
Dry Season / *Axonopus canescens* (dry grass)								
Ac 1/d	23	23.2 ± 2.1	5.3 ± 1.9	3.9 ± 2.2	11.9 ± 2.0	7.0 ± 2.3	n.d.	3.0 ± 2.4
Ac 2/d	-76	27.9 ± 1.8	4.4 ± 19.8	6.6 ± 3.6	n.d.	n.d.	n.d.	n.d.
Ac 3/d	-5	75.7 ± 1.6	11.9 ± 6.1	n.d.	17.3 ± 2.2	n.d.	n.d.	n.d.
Average Ac/d		**42.2 ± 23.2**	**7.2 ± 3.3**	**5.3 ± 1.3**	**14.6 ± 2.7**	**7.0**	**n.d.**	**3.0**

[a] CO_2 assimilation in µgC/g/h, derived from linear correlations of CO_2 exchange vs. temperature.

Table 3.13. Standard emission rates in [ngC/g/h] for *Hyparrhenia rufa*. Errors are SD from fits to the data.

	CO$_2$[a]	**m33**	**m43**	**m45**	**m57**	**m59**	**m69**	**m73**
Wet Season / *Hyparrhenia rufa* (mature green grass)								
Hr 1	-122	81.6 ± 4.0	n.d.	53.3 ± 2.5	92.2 ± 2.0	129.3 ± 2.4	n.d.	90.7 ± 19.5
Hr 2	-160	107.3 ± 5.7	n.d.	134.2 ± 5.5	neg. corr.	77.4 ± 85.0	68.6 ± 9.7	neg. corr.
Hr 3	-2400	98.2 ± 1.8	n.d.	neg. corr.	97.1 ± 1.5	neg. corr.	neg. corr.	86.48 ± 2.1
Average Hr (WS)		**95.7 ± 10.7**	**n.d.**	**93.8 ± 40.4**	**94.7 ± 2.5**	**103.4 ± 26.0**	**68.6**	**88.6 ± 2.1**
Dry Season / *Hyparrhenia rufa* (dry grass)								
Hr 1/d	-14	31.0 ± 1.5	5.3 ± 3.8	2.6 ± 14.1	5.7 ± 3.9	n.d.	n.d.	3.3 ± 2.8
Hr 2/d	-90	68.5 ± 1.4	6.0 ± 4.1	8.5 ± 2.8	22.0 ± 1.6	11.6 ± 0.2	6.7 ± 2.3	9.7 ± 2.0
Hr 3/d	-312	32.5 ± 1.9	13.6 ± 2	neg. corr.	11.9 ± 2.2	n.d.	n.d.	3.6 ± 8.4
Average Hr/d		**44.0 ± 17.4**	**8.3 ± 3.8**	**5.6 ± 2.9**	**13.2 ± 6.7**	**11.6**	**6.7**	**5.5 ± 3.0**

[a] CO$_2$ assimilation in µgC/g/h, derived from linear correlations of CO$_2$ exchange vs. temperature.

3.4. Discussion

3.4.1. Plant-to-plant variability of VOC emissions

The *intra*-species variability of the sum of emitted carbon was found to be similar for all grasses, varying within a range of a factor of 1.5-2.6 (Table 3.14).

Table 3.14. Range of total VOC standard emission rates in [ngC/g/h] for savanna grasses

	Mature grass			Young grass	Dry grass		
ΣE_{St}	Tp	Ac	Hr	Tp/y	Tp/d	Ac/d	Hr/d
Range	145-311	209-484	282-447	177-258	46	39-105	48-126
Average	224	347	372	206		66	79

The standard emission rates of individual VOCs varied between a factor of 2-4 within the same species (section 3.3.2.4). The highest variability was observed in the E_{St} of acetaldehyde (m45), butene+butanol (m57) and acetone (m59) especially from green grasses (Tables 3.11-3.13). Stress is a possible explanation for different rates of increases in emissions. Leaf wounding leads to the release of several C_6-compounds, such as (Z)-3-hexenal (detected at mass 81), (Z)-3-hexenol (m83) and hexanal (m101) (Kirstine *et al.*, 1998; de Gouw *et al.*, 1999; Karl *et al.*, 2001a) –which are responsible for the odor of freshly mown grass (Hatanaka, 1993)– and the C_5 compounds 1-penten-3-ol and methylbutanals (Fall *et al.*, 2001), both detected at mass 69. Wounding also has been reported to enhance the emissions of methanol, acetaldehyde, acetone and MEK (de Gouw *et al.*, 1999; Karl *et al.*, 2001b; Warneke *et al.*, 2002). Temporary enhancement of emission rates of these compounds were also measured in a cutting experiment of *Trachypogon* grass performed in this study (data not shown). It is generally estimated that rates of herbivory in savannas and also forests are substantial (e.g. in savannas, about 10% of the vegetation with a nitrogen content less than 1%, and 80% on fertile soils is typically consumed) (Scholes and Walker, 1993). It is likely that this much herbivory, and other kinds of physical damage to vegetation, will release considerable amounts of these VOCs into the atmosphere throughout the growing season.

High acetaldehyde and ethanol emissions have been identified as response to other stress situations like hypoxia (as produced by flooding), water deficit, high atmospheric ozone concentrations or freezing (Kimmerer and Kozlowski, 1982; Fukui and Doskey, 1998; Kreuzwieser *et al.*, 2000). Also physical stress, like rough handling of the vegetation spontaneously induce large emissions of monoterpenes, (Z)-3-hexenol, and C_6-C_{10} aldehydes (Fukui and Doskey, 1998). Prior to the measurements, the grass tussocks could have suffered from physical stress when they were placed into the chamber, which always implies handling. Leaf wounding could have been caused naturally by herbivore attack, also during the measurements. In general, no significant emissions of C_6-compounds (see above) were detected, with the exception of Tp3 (wet season), which showed daytime emissions of m81 and m83 of 1.8 and 1.3 nmol/g/h respectively, and Ac1 and Ac2 (wet season), both with emissions lower than 3.5 and 1.8 nmol/g/h of m81 and m83 respectively. Mass 69, on which isoprene and the C_5 wounding compounds mentioned above are detected, only correlated with masses 81 and 83 for Ac2. Therefore, it is probable that the emission detected on m69 for Ac2 (77.4 ngC/g/h, Table 3.12) is mainly due to a wounding/stress compound and not isoprene, perhaps the emissions of other compounds (e.g. methanol, acetaldehyde) were also enhanced due to some kind of stress factor.

Differences in metabolic or enzymatic activity may also have caused the variability observed in VOCs emissions. But nothing can be speculated since no additional information could be derived from the present data or the literature.

As expected, due to the variation on the emission rates discussed, a plant-to-plant variation in the composition of VOC emissions was also observed. The proportional contribution of the individual compounds to the total sum of VOCs emission of all measured grasses is shown in Figure 3.10.

Methanol (m33) was the main contributor to the total emissions of most *Trachypogon* grasses, accounting for 18-54% of the total VOCs emission. Exceptions were Tp1 (wet season), for which acetone (m59) was the highest emission (36%), and Tp5/y (dry season), whose emission of m57 represented 40% of the total (and methanol only 18%). Acetone was another major constituent of the emission of most individuals, ranging from 17-36% in mature, 10-26% in young grasses. Butene+butanol (m57) constituted ~15% of the emissions from mature grasses, whereas for young grasses the range was between 8-41%. The contribution of all other masses was generally below 10%.

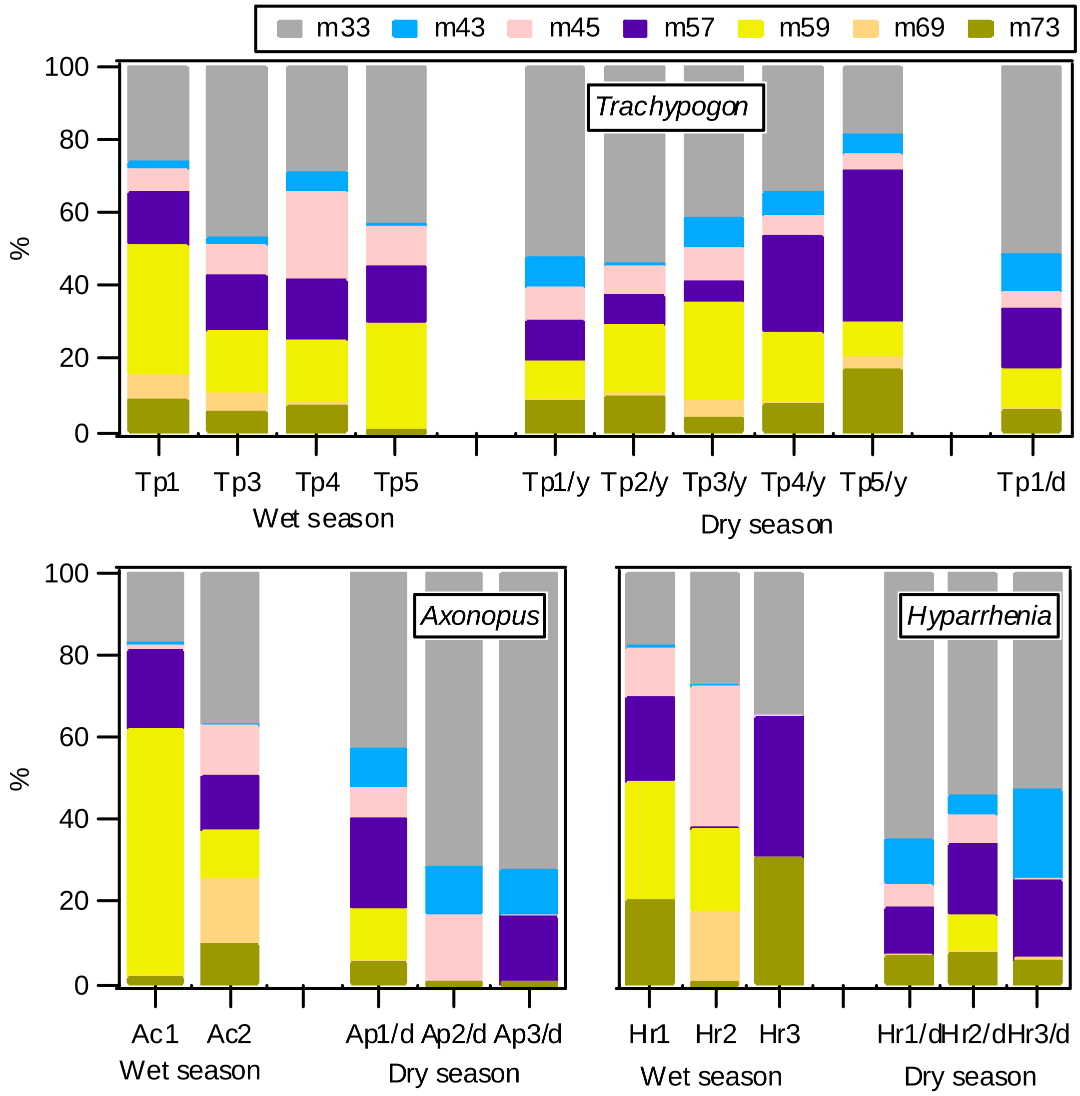

Figure 3.10. Percentage contribution of the detected VOCs to the sum of total VOCs emission from savanna grasses.

The *Axonopus* measured in the wet season exhibited a very different emission pattern. For the first specimen, Ac1, acetone was the major emission (60%), and methanol the second (18%), whereas for Ac2, methanol accounted for almost 40% and acetone 12% of the total emission. Methanol contributed between 42-72% of the emission from dry *Axonopus* grasses. This high variability is mainly because not all measured specimens emitted all compounds.

Very unequal patterns of emission were observed for mature *Hyparrhenia* grasses. For Hr1 acetone was the most important emission (29%), for Hr2, it was acetaldehyde (m45) with 35%, and for Hr3 the share of both methanol and m57 was ~35%. The contribution of methanol to the emissions from dry grasses was between 53-65%, and the share of m57 was between 12-19%. For Hr3/d, propene (m43) emission was relatively high, and represented 22% of the total VOCs emitted by this individual.

In summary, the plant-to-plant variability in the total amount of emitted VOCs was found to range within a factor of 2 and 3, whereas the emission of individual compounds may vary by up to a factor of 4. A variability in the composition of VOC emissions was also observed. For most of the mature grasses, methanol was the major emission accounting for 20-54% of the total emitted carbon; but for some individuals other compounds like acetone, acetaldehyde and butene+butanol were the predominant emissions. Less variability was observed in the emissions from dry grasses: methanol was the major emission and contributed to 40-75% of the total. Physical stress due to handling when the grass tussocks were placed in the chamber, and also leaf wounding by insects, as well as differences in metabolic or enzymatic activity may be possible explanations for the intraspecific differences in emission rates and composition.

3.4.2. Interspecies variability of emissions

The average and range of the standard emission rates determined for mature and dry grasses is presented in Table 3.15.

Mature grasses: the interspecific variability of total VOC emission was relatively small. *Hyparrhenia* showed the highest total emission (372 ngC/g/h), which was similar to the emission from *Axonopus* (347 ngC/g/h) and only a factor of 1.6 higher than those of *Trachypogon* (224 ngC/g/h). The variability of the individual VOCs was higher. The ratios between standard emission rates from *Hyparrhenia* and *Trachypogon* emissions were in a range of 1.3-4.7. The lowest difference was found for methanol and the largest for the MEK emissions. The ratios between *Hyparrhenia* and *Axonopus* emissions were between 0.9-3.5. The methanol emissions from *Axonopus* were the highest measured, but an enhanced emission due to stress during the measurements of the second specimen (Ac2) cannot be ruled out (see previous section).

Table 3.15. Average standard VOC emission rates in [ng C/g/h] from tropical grasses

	Trachypogon plumosus	*Axonopus canescens*	*Hyparrhenia rufa*
m33 / methanol			
mature (green) grasses/wet season	76.3 (63/88)	109 (37/181)	95.7 (82/107)
dry grasses/dry season	23.8 ± 1.7	42.2 (23/76)	44.0 (31/69)
m43 / propene + others			
mature (green) grasses/wet season	7.9 (n.d./14)	Dep.	n.d.
dry grasses/dry season	4.7 ± 2.8	7.2 (4/12)	8.3 (5/14)
m45 / acetaldehyde			
mature (green) grasses/wet season	27.9 (16/60)	30.3 (2/58)	93.8 (53/134)
dry grasses/dry season	2.1 ± 3.3	5.3 (n.d./7)	5.6 (3/9)
m57 / butene + others			
mature (green) grasses/wet season	34.5 (23/45)	52.1 (40/64)	94.7 (92/97)
dry grasses/dry season	7.6 ±2.6	14.6 (n.d./17)	13.2 (6/22)
m59 / acetone			
mature (green) grasses/wet season	57.5 (32/111)	57.0	103.4 (77/129)
dry grasses/dry season	5.2 ± 2.3	7.0 ± 2.3	11.6 (n.d./12)
m61 / acetic acid			
mature (green) grasses/wet season	Dep.	n.d.	n.d.
dry grasses/dry season	5.8 ± 3.2	4.4 (3/5)	9.6 (7/11)
m69 / isoprene / C_5-alcohols			
mature (green) grasses/wet season	15.1 (n.d./21)	77.4	68.6 (n.d./69)
dry grasses/dry season	n.d.	n.d.	6.7 (n.d./7)
m73 / MEK			
mature (green) grasses/wet season	18.9 (11/27)	25.3 (4/47)	88.6 (86/90)
dry grasses/dry season	2.8 ± 1.8	3.0 (n.d./3)	5.5 (3/10)
Total VOC emission			
mature (green) grasses/wet season	224 (145/311)	347 (209/484)	372 (281/447)
dry grasses/dry season	46	66 (39/105)	79 (48/126)

Note: given are averages, emission range in parentheses (or ± SD when only data for one specimen exist). n.d. is not detected; n.m. not measured; Dep, means only deposition was observed.

Dry grasses: the highest emissions from dry grasses were also from *Hyparrhenia*. The differences of the total VOC emission were similar to those of mature grasses, i.e. the highest difference –of a factor of 1.6– was between *Hyparrhenia* and *Trachypogon* (79 and 46 ngC/g/h, respectively, Table 3.15).

The average proportional contribution of the measured compounds to the total VOC emission of mature, young and dry grasses is shown in Figure 3.11.

Mature grasses: the emission distribution was similar for *Trachypogon* and *Axonopus*: together methanol and acetone accounted for more than half of the total VOCs emission (methanol was the major emission representing 27-32%, and acetone the second with 24%). The other VOCs contributed in comparable amounts to the total emission, with the exception of m69, which corresponds to 20% of the *Axonopus* emission, and m43, which was not emitted by this grass species. For *Hyparrhenia* the emitted compounds were almost equally distributed, each accounting for 13-19%. The major differences between this grass species and the other two were the contribution of methanol, which was only 18%, and MEK (m73), which accounted for 16%. Like *Axonopus*, mature *Hyparrhenia* grasses did not emit propene (m43).

Dry grasses: there was no significant difference in the emission distribution of dry grasses. Methanol represented about half of the VOCs emissions, the share of butene+butanol (m57) was ~17% and acetone represented between 9-13%. The contribution of masses 43, 45 and 73 were all <10%.

In summary, the interspecific variability of total VOCs emission of both mature and dry grasses was relatively low, with the largest difference (a factor of 1.6) observed between the emissions of *Hyparrhenia* and *Trachypogon*. The average proportional contribution of the individual compounds to the total emission was very similar between *Trachypogon* and *Axonopus*, for which methanol and acetone made up ~50% of the emissions, whereas for *Hyparrhenia* the emitted compounds were almost equally distributed, each accounting for 13-19%. No significant difference was observed in the emission pattern of dry grasses. For all species, methanol represented about half of the total VOC emission.

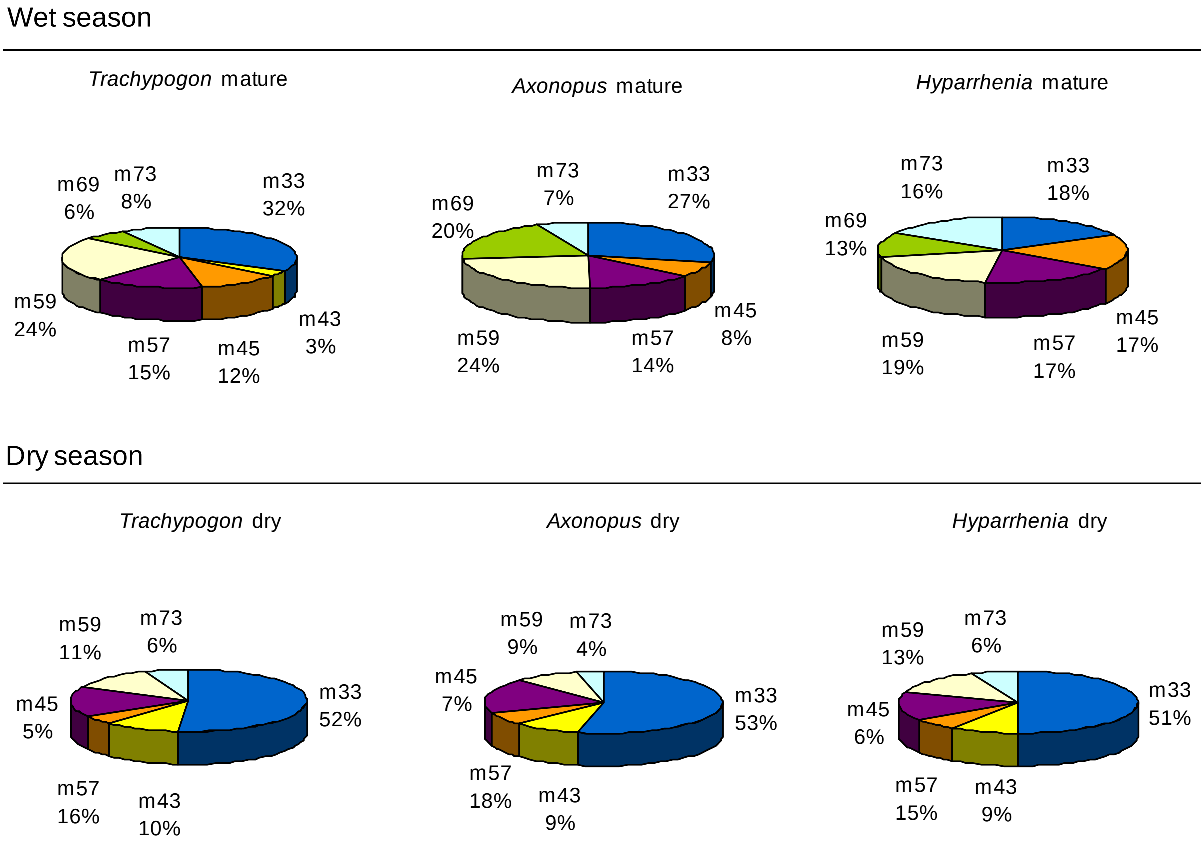

Figure 3.11. Average proportional contribution of individual VOCs to the sum of carbon emission from grasses in the wet and dry season.

3.4.3. Developmental stage and VOC emissions

The discussion about the influence of development state on emissions will be based on the results from *Trachypogon* grasses only. An estimation of the seasonal variation of the emission of VOCs, calculated taking into account the developmental differences and temperature dependence of the emissions, as well as the net primary productivity (NPP) of the Calabozo savanna, will be given in section 3.4.5.

In spite of the unfavorable environmental conditions during the dry season, especially the low humidity of the soil, it is surprising that the burned *Trachypogon* regrow almost immediately, without rains, and that the new leaves stay green until the wet season begins. A priori one would expect a very low biological activity of the plants in this season, and consequently, low emissions. Nevertheless, the total VOC emissions of mature *Trachypogon* (wet season) were on average, only a factor of 1.13 higher than the emissions from young grasses in the dry season, but almost a factor of 5 higher than those from dry grasses (Figure 3.12).

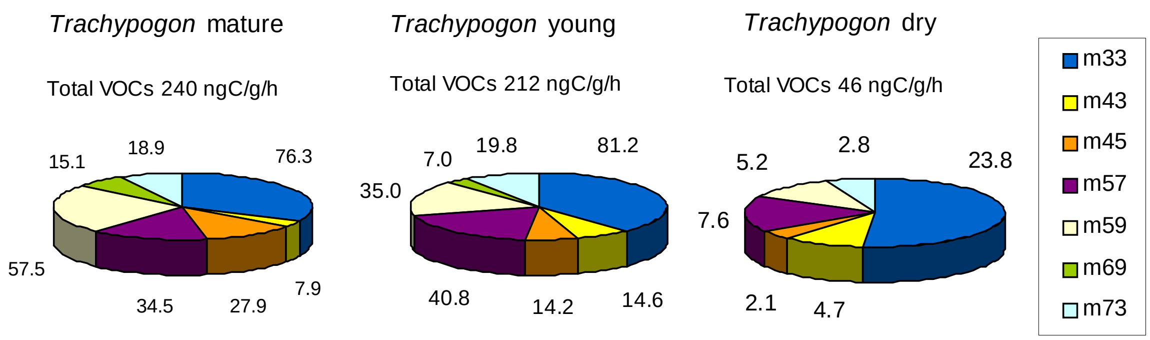

Figure 3.12. Comparison of VOC emissions [ngC/g/h] from mature, young and dry *Trachypogon* grasses.

However, some compounds, namely methanol, propene and butene+butanol, were emitted in higher rates from young grasses:

Methanol (m33), which is produced in significant amounts during cell wall maturation as a product of pectin demethylation (Nemecek- Marshall *et al.*, 1995), was expected to be emitted in much higher rates by young leaves, but the E_{St} from young grasses was only 1.06 times higher than the emission from mature grasses (Table 3.15). Previous studies, which investigated the effect of leaf development on methanol emission (Macdonald and Fall, 1993b; Nemecek-Marshall *et al.*, 1995), have found that the emissions were higher when the leaves are young and expanding than when they reach maturity. However, it is important to note that in those studies *mature* leaves are the first fully expanded leaves, and *young* leaves are unfolding leaves. In our work, it was impossible to assess the age of the young grass, because no information about the date when the savanna was burned is available. The burned *Trachypogon* individuals start to regrow few days after the fire producing a tuft of green leaves that remain alive until the beginning of the rains when they grow as fast as the unburned plants and reach a similar biomass by August-October (Baruch and Bilbao, 1999). Therefore, most likely a large fraction of the grass blades were already fully expanded, or they were not actually growing anymore due to the dry conditions. On the other hand, as the intense growing stage begins with the rainy season, and the grasses keep continuously growing for 4-6 months, methanol emissions might therefore be rather constantly high during most of the wet season.

Methanol was also the highest emission from dry grasses, but the emission rate was a factor of ~3.4 lower than those from green grasses. Pectin demethylation occurs not only during growth and development, but also during aging and senescence of plant tissues. (Nemecek-Marshall *et al.*, 1995; Galbally and Kirstine, 2002, and references therein). Additionally it is known that oxygenated VOCs (including methanol and acetone) are produced within the leaves by nonenzymatic thermochemical reactions, so called Maillard reactions (Warneke *et al.*, 1999). Actually, Warneke *et al.* (1999) found that emission of oxygenated VOCs from dead plant material after "roasting" (at 50°C) and subsequent wetting could be a significant atmospheric source of these gases. However, in their experiment dead grass produce much less methanol than beech leaves and oak and spruce needles, and also the release of VOCs became gradually lower after several heating-wetting-drying cycles, a situation that resembles the savanna environment in the wet season. The increasing of the methanol nighttime ambient concentrations after a rain event (occurred between 17:40-20:00) in the dry season up to 23 ppb, which is more than twice the maximum mixing ratio observed on average at night in this season (~10 ppb, Fig. 3.3), suggests that the wetting of dry grass, soil, or both may be an important regional source of methanol which is difficult to account for.

Higher emissions of mass 57 (tentatively identified as 1- and 2-butene, butanol) were also measured from young grasses. Fukui and Doskey (1998) observed highest emissions of 2-methylpropene and 1-butene in early summer (end of June). Butanol was detected at the same grassland site in a subsequent study, but was not quantified (Fukui and Doskey, 2000).

Emission rates of mass 43 (likely propene, cyclopropane, 2- and 1-propanol) and mass 73 (MEK) were the in the same range in young and mature grasses.

Standard emission rates were higher from mature than young grasses for following compounds:

Acetaldehyde (m45) emissions were higher from mature grasses approximately by a factor of 2 (Table 3.15). Several studies have shown that leaves of higher plants emit ethanol and acetaldehyde as a physiological response to flooding (Kreuzwieser *et al.*, 1999a; Holzinger *et al.*, 2000; Rottenberger, 2003). The metabolic source of these emissions is alcoholic fermentation in the roots, which produces acetaldehyde and ethanol from pyruvate in a two-step process (see Scheme 2 in section 3.1.1.2). The mature grass samples have been measured during the wet season at favorable conditions for this sort of acetaldehyde emissions, whereas the young samples have been measured under very dry conditions. A second mechanism, termed the *pyruvate overflow mechanism*, has been recently discovered following the observation of transient release of acetaldehyde from tree leaves during light-dark transitions (Holzinger *et al.*, 2000; Karl *et al.*, 2002a). During such a transition, the levels of cytosolic pyruvic acid rise rapidly, triggering the cytosolic enzyme pyruvate decarboxylase reaction and acetaldehyde is formed from the excess pyruvate (Karl *et al.*, 2002a). Acetaldehyde can either be oxidized to acetate (Scheme 3, section 3.1.1.2) or released to the atmosphere via stomata. Karl *et al.* (2002) proposed that, since such emission bursts were seen after few minutes of darkening, this mechanism may be important in plant canopies, which are subjected to sunflecks (i.e. variations in the PAR) throughout the day. It is possible that rapid changes in PAR could trigger small but frequent releases of acetaldehyde. Again, fast changes between full sunlight and overcast conditions are in favor of acetaldehyde emissions during the wet season, therefore the difference between young and mature Trachypogon rather reflects meteorological conditions than the developmental stage of this species.

The average acetone (m59) standard emission rate of the mature *Trachypogon* grasses was a factor of 1.7 higher than from young grasses. Acetone can be produced by numerous mechanisms in biological systems (Fall, 2003), known pathways in plants are decarboxylation of acetoacetate (Scheme 3) and cyanogenesis (Scheme 4). Among the thousands of plant species that have been reported to be cyanogenic, some belong to the family of grasses (e.g. sorghum, crabgrass, Bermuda grass) (Aikman *et al.*, 1996; Vetter, 2000), but no specific information about *Trachypogon* or the other studied grass species could be found. Since acetone is one of the main emissions from grasses, more work to investigate which is the production mechanism of acetone is needed. It would be interesting to test if this species emit also HCN, since simultaneous emissions of acetone and HCN were observed from cyanogenic plants (several clover species and cassava) after wounding (Custer *et al.*, 2003).

The standard emission of m69 from mature *Trachypogon* ranged from not detected up to 21 ngC/g/h, the emission from young grasses was a factor of 2 lower. Studies on the influence of leaf development on isoprene emissions have shown that the highest isoprene emission potential occurs when leaves are fully expanded, at the same time when isoprene synthase is at its maximum (Fall, 1999).

In general, measurements of young grasses under wet soil conditions (early wet season) are needed. The emission rates and pattern of emitted VOCs may be significantly different to those of mature grasses.

3.4.4. Comparison with other studies

The standard emission rates (normalized to 30°C) of total VOCs from all mature grasses in this study were found to range between 0.24 and 0.37 μgC/g(dw)/h (Table 3.15). Kirstine *et al.* (1998) found typical total VOCs emission rates (normalized to a leaf canopy temperature of 30°C and a PAR equal to 1000 $\mu E/m^2/s$) from grass pasture in South-eastern Australia of about 0.41 μgC/g(dw)/h, and 1.9 μgC/g(dw)/h from clover. Fukui and Doskey (1998) reported total VOC emissions of 5.5 ± 0.9 μgC/g/h around noontime on sunny days from a grassland site in the Midwestern United States.

In Table 3.16, the standard emission rates of the VOCs from mature (wet season) and dry grasses (dry season) obtained in this study are compared with the reported emissions from herbaceous vegetation for other sites of the world. Strictly speaking, of course, these measurements cannot be compared directly, since the environmental conditions, plant species, measurement techniques and normalization methods (if applied) are different; but they give an overview of the, up to now, little information about VOCs emission from grassy vegetation.

Table 3.16. Observed emission rates of VOCs from herbaceous vegetation

	Plant Species	Emission rate ng C/g (dw)/h	Observations	Reference
Methanol / m33				
Venezuelan savana	3 grasses			This work
	Wet season	76-109	normalized to 30°C	
	Dry season	24-44		
Victoria, Australia	Grass	45-61	normalized to PAR 1000 $\mu E/m^2/s$ and 30°C	1
	Clover	285-627		
Argonne, Illinois	Mixture of herbaceous	412/632	1992 and 1993; noon, sunny days 15-34°C	2
Innsbruck, Austria	Meadow grass	150	14:00 LT, sunny, 19°C	3

Table 3.16 continued

Acetaldehyde / m45				
Venezuelan savanna	3 grasses			This work
	Wet season	29-94	normalized to 30°C	
	Dry season	2-6		
Victoria, Australia	Grass	53-66	normalized PAR 1000 µE/m^2/s and 30°C	1
	Clover	<10		
Argonne, Illinois	Mixture of herbaceous	54/106	1992 and 1993; noon, sunny days 15-34°C	2
Butene + others / m57				
Venezuelan savanna	3 grasses			This work
	Wet season	35-95	normalized to 30°C	
	Dry season	8-15		
Argonne, Illinois	Mixture of herbaceous	3.1/5.4	2-methylpropene and 1-butene. 1992 and 1993; noon, sunny days 15-34°C	2
Straßhof, Austria	Grassland	1-5.4	1-butanol	
Acetone / m59				
Venezuelan savanna	3 grasses			This work
	Wet season	57-103	normalized to 30°C	
	Dry season	5-12		
Victoria, Australia	Grass	45-66	normalized to PAR 1000 µE/m^2/s and 30°C	1
	Clover	247-437		
Argonne, Illinois	Mixture of herbaceous	149/127	1992 and 1993; noon, sunny days 15-34°C	2
Isoprene / m69				
Venezuelan savanna	3 grasses			This work
	Wet season	15-69	normalized to 30°C	
	Dry season	<7		
Argonne, Illinois	Mixture of herbaceous	7.8/6.9	1992 and 1993; noon, sunny days 15-34°C	2
Straßhof, Austria	Grassland	0.2-1.5	sunny, 25°C	5
China	Different Grasses	<100	Portable PID, leaf cuvette	6
MEK / m73				
Venezuelan savanna	3 grasses			This work
	Wet season	19-89	normalized to 30°C	
	Dry season	3-6		
Victoria, Australia	Grass	1.6-8.6	normalized to PAR 1000 µE/m^2/s and 30°C	1
	Clover	855-950		
Straßhof, Austria	Grassland	2.8	sunny, 25°C	5

1. Kirstine et al (1998); 2. Fukui and Doskey (1998); 3. Warneke et al, (1999); 4. MacDonald and Fall (1993b) ; 5. König et al., (1995); 6. Klinger et al (2002)

Methanol emissions from green Venezuelan savanna grasses are well within the range observed from grasses in Australia and Austria (Kirstine *et al.*, 1998; Warneke *et al.*, 1999), at least a factor of 2.5 lower than clover emissions (Kirstine *et al.*, 1998) and a factor of 3.5 lower than the emissions from a grassland in Illinois (Fukui and Doskey, 1998). The emission rates from the dry grasses were close to the lower end of the emissions from Australian grasses.

The mean standard emission rate of the compounds detected at mass 43 (e.g. propene, cyclopropane, 2- and 1-propanol) was 7.9 ngC/g/h for mature *Trachypogon* grass. Kirstine *et al.* (1998) determined a mean propanol emission rate of 2 and 8 ngC/g/h from clover and grass, respectively.

Acetaldehyde (m45) emissions from mature grasses were within the range of emissions measured previously from other grasslands.

Emission of mass 57 was considerably higher than the emissions of 2-methylpropene and 1-butene from a US site (Fukui and Doskey, 1998), and 1-butanol from grassland in Austria (König *et al.*, 1995). This suggests that the emission of mass 57 from savanna grasses is due to more compounds than butenes and butanol.

Acetone (m59) emissions were comparable to the observed from grasses by Kirstine *et al.* (1998), and lower by more than a factor of 2.3 than clover emissions The emissions observed by Fukui and Doskey (1998) were higher than the emission from Venezuelan grasses by a factor of at least 1.2.

Mass 69 (isoprene, 2-methyl-3-buten-2-ol (MBO) and other C_5-alcohols). C_5-alcohols were detected from rye and rape, but not from grasses (König *et al.*, 1995). Mass 69 emissions from mature savanna grasses were higher than isoprene emissions from grasses measured in the US and Austria (König *et al.*, 1995; Fukui and Doskey, 1998), and comparable to the emission of different grass species measured in China (Klinger *et al.*, 2002). In that study, 386 plant species, many of them graminoids, were screened for isoprene and monoterpene emissions with a portable photoionization detector (PID) and a leaf chamber (~20 cm^2 of leaf surface). In a previous study, (Klinger *et al.*, 1998), the same technique was applied within the framework of the Experiment for the Regional Sources and

Sinks of Oxidants (EXPRESSO) in a 800-km transect from grassland to primary rainforest in central Africa. No isoprene emission from African grasses was found.

Butanone (MEK) emission from mature savanna grasses was higher than from those from other grassland sites but lower by at least an order of magnitude than the emission from clover, for which it was the most important emission, accounting for 45-50% of the total VOC emissions (Kirstine *et al.*, 1998), whereas it accounted for less than 2% of the grass emissions.

For all studied grasses, the oxygenated compounds accounted for 66-76% of the total emissions. Kirstine *et al.* (1998) found that the emissions from an Australian grassland were principally light oxygenates including methanol (13%), ethanol (19%), acetaldehyde (15%), and acetone (14%). Together, these four compounds accounted for 59-68% of the sum of carbon emissions from grass pasture. For the grassland site in Illinois, Fukui and Doskey (1998) reported that the identified hydrocarbons represented between 18-30%, and the oxygenated VOCs 80-70% of the total carbon emissions in 1992 and 1993, respectively. Methanol was the major VOC emitted at that site, accounted for 50% and more of the total emissions.

3.4.5. Extrapolation of VOC emissions

Based on the results for *Trachypogon* grasses, the dominant species of the herbaceous plants in Venezuelan savannas, methanol, acetaldehyde, acetone and MEK fluxes were calculated for the Venezuelan and tropical savanna grasses. An estimated seasonal variation of the emissions for the Calabozo savanna is also presented. This upscaling to a landscape flux considered the standard emission rates, the temperature dependence and the aboveground biomass density.

3.4.5.1. VOCs source strength of tropical grasslands

Monthly data on aboveground live biomass and total dead matter for burned and unburned plots are available for 10 months during 1969 for the savanna at the Estación Biológica de Los Llanos in Calabozo (San José and Montes, 1998, http://www.daac.ornl.gov/NPP/site_des/clb_des.html.). Total Net Primary Productivity (NPP, above and below ground) was estimated at 682 g/m^2/yr for unburned and 755 g/m^2 for burned plots, although later estimates range from 365 to 968 g/m^2/yr (40-50% of production below ground). The other input parameters were the average standard emission factors, E_{St} (Table 3.11), and the temperature dependence, β (Table 3.8), for each compound obtained from the *Trachypogon* measurements in the wet and dry seasons. Mean diurnal emission courses for mature, young and dry *Trachypogon* were calculated by adjusting the daily course of temperature observed during the wet and dry season to the mean monthly maximum and minimum temperatures measured in Calabozo (16 years average between 1968-1984) (San José and Montes, 1998).

Further it was assumed that that 50% of the savanna is burned annually (Scholes and Walker, 1993), and for estimating the VOCs source of tropical savanna grasses, the aboveground biomass data from the Calabozo area was used, which may be rather low for some areas. A recent review by House and Hall (2001), reports a range of aboveground NPP for tropical savannas and grasslands between 140-2500 g(dry matter)/m^2, with an average of 837 g(dm)/m^2, and the average of the Calabozo savanna is 478 g(dm)/m^2 (Appendix 8.4, Table 8.2). On the other hand, the extent of savannas is also uncertain due to the variation in classification of this biome and the sparsity of data from these areas. The estimates range from 15-33 $\times 10^6$ km^2 (Whittaker and Likens, 1975; Atjay *et al.*, 1979; Olson *et al.*, 1983). For the extrapolations we used the estimate for tropical savannas by Scholes and Hall (1996) of 16.1 $\times 10^6$ km^2 (~11% of the global land surface) as lower limit, and House and Hall's (2001) estimate of 27.6 $\times 10^6$ km^2 (~20% of the land surface, also including "warm or hot shrub and grasslands in the tropics") as upper limit. As an example, the estimation for methanol is shown in Table 3.17, and the results for the estimated VOC source strength of the Venezuelan and all tropical savannas are shown in Table 3.18.

Table 3.17. Estimated flux of methanol for Venezuelan and tropical savannas

	Aboveground biomass[a] (g dry matter/m^2)				Monthly methanol Flux[d] ($mgC/m^2/mth$)	
	not burned		burned		not burned	burned
Month	live	dead	live	dead	live+dead	
1	100	1025	0	0	22	0
2	50	1175	27	0	23	2
3	12	815	33	0	15	2
4	27	1000	26	95	18	3
5	110	1025	40	190	20	5
6	150	720	150	260	14	10
7	290	337	310	380	13	14
8	325	630	315	411	18	15
9	320	840	360	360	23	18
10	250	910	310	400	23	18
11	200	936	267	456	21	18
12	150	990	230	520	19	17
					229	120
Annual emission[b] ($mgC/m^2/yr$)					175	
Venezuelan Savanna[a] (~$3x10^5$ km^2) (GgC/yr)					52	
Tropical Savannas[c] ($17\text{-}27x10^6$ km^2) (TgC/yr)					2.8-4.4	

[a] NPP data of the Calabozo savanna and Venezuelan savanna area from San José and Montes (1998). NPP for November and December was interpolated. The savanna was burned in January.

[b] Assuming 50% of the savanna area is burned annually.

[c] Tropical savanna area from House and Hall (2001) and references therein.

[d] Monthly emission calculation based on monthly mean max. and min. temperature in Calabozo (San José and Montes, 1998)

Table 3.18. Estimated sources of VOCs from tropical savanna grasses

	Annual flux[a] ($mgC/m^2/yr$)	Venezuelan Savanna (GgC/yr)	Tropical Savanna (TgC/yr)
		0.3×10^6 km^2	$16 – 27 \times 10^6$ km^2
Methanol	175	52	2.8 – 4.4
Acetaldehyde	37	11	0.6 – 0.9
Acetone	84	25	1.4 – 2.1
MEK	46	14	0.7 – 1.2

[a] Assuming half of the savanna area is burned every year

The global budget of methanol is very uncertain, and the biogenic share is even less constrained. Galbally and Kirstine (2002) estimated an average global methanol source of 55 TgC/yr (included sources are: higher plants, biomass burning, atmospheric production, anthropogenic, decay of dead plant material and ocean sources). Based on global NPP estimates which indicate that 62.4% of the NPP is in the Northern Hemisphere, 37.6% in the Southern Hemisphere (Cao and Woodward, 1998), and that the fraction of NPP that comes from grasses is 34% (Field *et al.*, 1998), they predict a total global emission of methanol from flowering plants of ~38 TgC/y, from which 3.8 TgC/y are predicted for grasslands and 33.8 TgC/y for other terrestrial plant biomes (Galbally and Kirstine, 2002). The annual emission of methanol estimated here for tropical savanna grasses (2.8-4-4 TgC/y) agrees very well with the grassland source estimated by Galbally and Kirstine (2002), and also with a previous estimate of Kirstine *et al.* (1998) of 5 TgC/y (they made a global extrapolation of methanol, acetaldehyde and acetone emissions for grasslands, based on their speciation studies –which showed that each of these compounds made up ~15% of the total emission from grasses– and on the NPP global inventory by Guenther *et al.*, 1995). Other estimates for vegetation methanol sources, namely >100 TgC/yr (Guenther *et al.*, 1995), 19-47 TgC/yr (Singh *et al.*, 2000), and 105 TgC/y (Heikes *et al.*, 2002, based on Guenther *et al.,* 1995, and Singh *et al.*, 2000), are much higher than our estimated savanna grasses source, but these estimates refer to global vegetation and not only to grasses. If 38-105 TgC/y is taken as the range of global methanol source from vegetation, the estimated emission for tropical savannas calculated here may represent about 3-12% of this source.

The sources of acetone are also not well known. Global sources of 35 TgC/yr (Singh *et al.*, 2000) and 59 TgC/yr (Jacob *et al.*, 2002) have been estimated. Jacob *et al.* (2002) recommend a primary biogenic source of 20 TgC/yr, nearly twice as large as that of Singh *et al.* (2000). Recent plant emission and flux date suggest even larger vegetation emissions (Schade and Goldstein, 2001; Karl *et al.*, 2002b; Villanueva-Fierro *et al.*, 2004), and model results based on foliar emission and satellite derived leaf area index obtained a global biogenic acetone source of 30-105 TgC/yr (Potter *et al.*, 2003). Potter´s predicted acetone emissions from wooded grassland and savanna is 8-25 TgC/yr (land area 22×10^{6} km^2). The terrestrial vegetation source from Jacob *et al.*, (2002) resolves a contribution from grasslands to the global budget of 7 TgC/yr (based on Kirstine´s 1998 estimates), and from other vegetation of 11 TgC/yr. Both estimates for grasslands and savannas are considerably higher than the estimated here for tropical savanna grasses (1.4-2.1 TgC/yr).

Acetaldehyde is produced in the oxidation of a variety of hydrocarbons, and is also emitted directly from anthropogenic activities and biogenic processes. But, on a global scale, very little is known about the magnitude of acetaldehyde sources and no global inventory is presently available (Singh *et al.*, 2004). Biogenic emission of acetaldehyde has been reported for several tree species as well as grass under various physiological conditions (e.g. normal photosynthesis, root flooding, light-dark transitions, wounding) (de Gouw *et al.*, 1999; Holzinger *et al.*, 1999; Kreuzwieser *et al.*, 2000; Kesselmeier, 2001; Villanueva-Fierro *et al.*, 2004). Also, measurements made on a canopy-scale are limited (Schade and Goldstein, 2001; Karl *et al.*, 2002b; Karl *et al.*, 2003a). However, Singh *et al.* (2004) estimated a biogenic source of 25 (7-42) TgC/yr, assuming –based on the available emission studies– a median emission value of 381 ngC/g/h at 30°C, and using a recent version of the Guenther *et al.* (1995) model. The estimated contribution of savanna grasses (~1 TgC/yr) to the global biogenic source calculated by Singh *et al.* (2004) is of only 4%.

Little is known about the sources of methyl ethyl ketone (MEK) and no global estimates exist (Singh *et al.*, 2004). The available data presently do not allow a quantitative estimation of MEK biogenic sources, however a first tentative estimate of 4 TgC/yr is given by Singh *et al.* (2004). On the basis of this value, the contribution of savanna grasses to the global biogenic MEK emissions estimated here would be important (representing ~30%, Table 3.18). Nevertheless, these numbers should be considered with care, since both are very rough estimates.

Because of the complexity of sources and lack of measurement data, the estimations of global sources of oxygenated VOCs are very uncertain, and especially biogenic emissions are poorly quantified. There is a need for more measurements of oxygenated VOCs in several ecosystems, especially tropical savannas and forests. Research should be focused on long-term measurements of both, ambient mixing ratios and biogenic emissions, in order to account for variations in VOC fluxes due to temperature, light and plant developmental stage. An estimate of the annual variation of the emission of some VOCs from the savanna grass in Venezuela is presented below.

3.4.5.2. Seasonal variation of VOCs emission from the Venezuelan savanna grasses

Figure 3.13 shows the calculated annual cycle of emission fluxes for several VOCs. It was assumed that half of the savanna area was burned in January. The highest emission fluxes were calculated for the wet season (May-November), especially between September and October when also the *live* aboveground biomass reached its maximum (Table 3.17). The average emission of acetaldehyde, acetone and MEK in the wet season was a factor of ~2 higher than the fluxes in the dry season. The methanol flux was only a factor of 1.4 higher in the wet season, which shows the influence not only of the young grasses, but also the dry grasses in the methanol fluxes during the dry season.

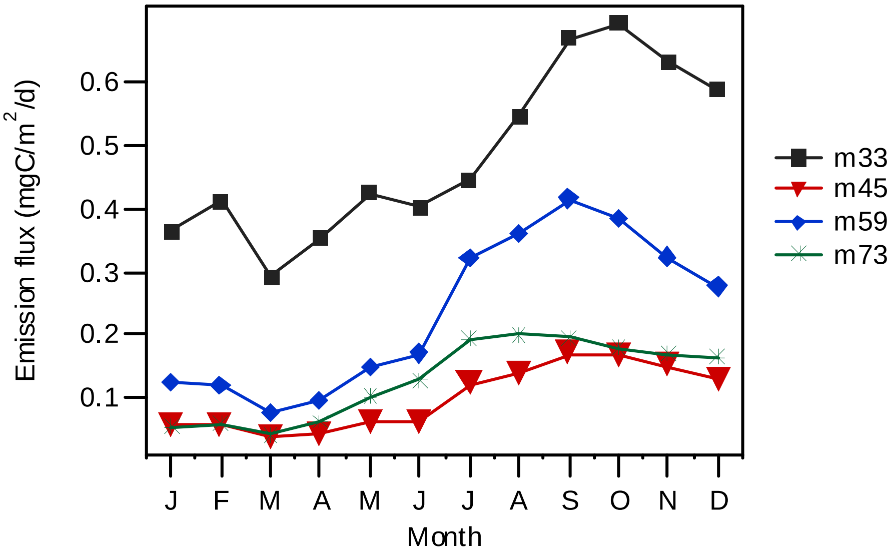

Figure 3.13. Calculated flux of selected VOCs for the Venezuelan Savanna

Fukui and Doskey (1998) recorded the highest emissions of methanol, acetaldehyde and acetone in summer. Methanol emissions increased in the Illinois grassland site gradually during spring and early summer to a peak in midsummer, and declined again in fall to levels similar to those observed in spring. The peak methanol emission rate they measured was a factor of 2-3 higher than during spring or fall.

3.5. Summary and conclusions

The VOC emissions of three savanna grass species (*Trachypogon plumosus, Axonopus canescens* and *Hyparrhenia rufa*) were investigated at Calabozo, in the central savanna area of Venezuela. The measurements were made in the wet season during September/October 1999, and in the dry season during March/April 2000.

The VOC emissions showed a diurnal variation that followed closely the diurnal cycle of temperature and radiation. For this reason, a high variability in emission ratios was found due to the natural fluctuations of the environmental conditions at the measurement site. In general, the emissions correlated best with temperature, and therefore a normalization of the VOC emission rates to a standard temperature (30°C) allowed for interspecies and seasonal comparisons.

The temperature dependence was modeled by means of the emission algorithm typically used to simulate monoterpenes emission (Guenther *et al.*, 1993). The parameter describing the temperature dependence of individual VOC emissions β, ranged between 0.08-0.23 K^{-1} for all species. The variations of β were random without a noticeable interspecific or seasonal trend.

Methanol (m33) was the primary emission of all grass species. With a standard emission range of 79-109 ngC/g/h for green (young and mature) grasses, and 24-44 ngC/g/h for dry grasses, methanol accounted for about 30% and 50% of the total VOCs emission of green and dry grasses, respectively. Acetone (m59) was the second most abundant emission. Its emission range from green grasses (35-103 ngC/g/h) is comparable to those of methanol, but the emission from dry grasses was considerably lower (5-12 ngC/g/h). Acetaldehyde (m45) and butene+butanol (m57) were emitted from green grasses in a range between 14-95 ngC/g/h.

The sum of VOCs emission rate for all green grasses was 200-400 ngC/g/h. The oxygenated species (methanol, acetaldehyde, acetone and MEK) represented 70-75% of the total carbon emitted, and the remaining 30% was olefins and other not identified species. On average, less than 0.1% of the carbon assimilated by photosynthesis during daytime is reemitted as VOCs.

The total sum of emitted VOCs was found to vary between a factor of 2-3 within plants of the same species, and by a factor of 1.6 among the different grass species. The intra- and interspecific variability in emission rates of the individual compounds were larger, and could vary by almost a factor of 5 for some compounds (Table 3.15). Physical stress due to handling when the grass tussocks were placed in the chamber, and also leaf wounding by insects, as well as differences in metabolic or enzymatic activity may be possible explanations for the observed differences.

An estimation of the VOCs source strength of grasses in tropical savanna areas was made using the VOCs temperature dependence and aboveground NPP data from the Calabozo site. The calculated annual source of methanol for savanna grasses (3-4.4 TgC, Table 3.18) may represent up to 12% of the current estimated emission from vegetation. The estimated contribution of acetone and acetaldehyde from savannas is of minor importance for the global biogenic sources of these compounds. The contribution of savanna grasses to the biogenic source of MEK might be as high as 30%, but the estimated global source is poorly quantified.

To our knowledge, these are the first determinations of VOC emissions –other than isoprenoids– from grasses in a tropical savanna ecosystem. We corroborated the findings of previous studies made in temperate grasslands, which reported that grasses are not a major source of isoprene and monoterpenes, but they could contribute significantly to fluxes of oxygenated compounds, some of which play important roles in atmospheric chemistry. Methanol, for instance, can have a significant impact on the oxidizing capacity of the atmosphere, since its oxidation leads to the formation of formaldehyde, whose photolysis and oxidation by OH produces HO_2 radicals, which chiefly react with NO to produce NO_2, the precursor of ozone.

Due to the vast area that savannas cover globally, the emissions from this biome are important to the global budget of methanol and maybe also for other oxygenated compounds, for which information about sources and sinks are very scarce.

4. Fluxes of VOCs from tropical savanna trees

4.1. Introduction

Savannas form a continuum between tropical forests and grasslands. The relative abundance of woody and herbaceous species is dependent on environmental conditions and seasonal and interannual variations (House and Hall, 2001). The plant available moisture and nutrients, which are a function of soil properties, topography and hydrology, seem to be the major determinants of the tree-grass balance (House and Hall, 2001; Hoffmann *et al.*, 2004). The physiognomy of the Calabozo study area and its surroundings varies between *savanna grasslands* and *savanna woodland* with a tree cover ranging approximately from 2-15% (Sarmiento and Monasterio, 1971). Groups of trees, usually called “matas”, are also common, with sizes that vary between less than 12 m in diameter to one hectare or more. They are considered remnants of the deciduous dry forest that covered much larger areas some years ago (San José and Montes, 1989).

This study reports on the exchange of VOCs between three different tropical tree species and the atmosphere. The results will be analyzed in a similar way as in the previous chapter of savanna grasses.

4.2. Method

4.2.1. Tree enclosures and measured species

Three of the most common trees species of the Venezuelan savanna were chosen for the measurements: *Byrsonima crassifolia* (Malpighiaceae, common name nance, in Spanish Manteco) is a small evergreen tree, 4 to 10 m in height, with a crown reaching close to the ground. Leaves are opposite, tightly clustered at the end of branches, dark, shiny green on the top, densely pubescent on the underside, *Cochlospermum vitifolium* (Cochlospermaceae, common name in Spanish Carnavalito), a small tree, in general no more than 7 meters tall, usually with a leaning trunk and irregular branching. The leaves are star-shaped, with pointed lobes, and *Curatella americana* (Dilleniaceae, is known as sandpaper tree, and in Spanish as chaparro), which is a twisted, thick-barked shrub/tree with pubescent branches when young.

The dynamic plant enclosure system and measurement method were the same as for the grasses, and was described in chapter 3 (sections 3.2.2 - 3.2.4). The studied trees were all tree saplings, since they had to be small in order to fit into the chamber (which could enclose a plant of max. 1 m in height and 30 cm in diameter), but it was not possible to estimate their exact age. The date of the measurements, dry weights and leaf area of the studied trees are given in Table 4.1. The measurements in the dry season (2000) were not conducted on the same individuals measured previously in the wet season in 1999, since the study area was burned in the intervening period.

No data for *C. americana* is presented for the wet season, although two trees of this species were in fact investigated during that campaign, but the first specimen was measured during a “static chamber” experiment, and the second was used for a leaf damage experiment. The static chamber was simulated by turning off the pump, and thus interrupting the airflow through the chamber. The purpose of this experiment was to compare the results of both the dynamic and the static enclosure techniques. The static chamber, turned out to be unsuitable for trace gas exchange measurements with plants. Three major problems were encountered: first of all, after closing the chamber the temperature inside the chamber steadily increased between 1-2 °C every minute, whereas the CO_2 concentration declined very rapidly. These effects most likely stressed the enclosed plant and may have perturbed its normal biological function (e.g. photosynthetic activity and stomatal behavior) and hence altered its VOCs emission rate and/or composition. Additionally, the condensation misted over the inner walls of the chamber in just 2-3 minutes, which changed the incoming solar radiation intensity. On the other hand, the condensation on the Teflon foil represents also a source of error by the loss of water-soluble compounds onto the chamber walls. These problems may be overcome in part by using larger chambers (the volume of the chamber at the time of this experiment was ~60 L). In previous studies, static chambers have been used to measure emission from grasslands (Fukui and Doskey, 1998; Kirstine *et al.*, 1998). The volume of the chamber used by Kirstine was 275 L, and they report only occasional water condensation on the chamber walls. Fukui and Doskey´s chamber had a volume of 90 L, and they also report water condensation as well as occasional nonlinear changes of VOCs concentration in the chamber with the time length it remains closed (Fukui and Doskey, 1996). Due to these disadvantages, all the results presented here were obtained using the dynamic chamber.

Table 4.1. Dry weight and leaf area of trees investigated during the wet season (September-October 1999) and dry season (March-April 2000)

species	date of measurement	dry weight (g)	leaf area (m^2)
Wet season			
Byrsonima crassifolia			
Bc 1/ws	11-12 Oct	20.0	0.11
Bc 2/ws	12 Oct	74.1	0.43
Cochlospermum vitifolium			
Cv 1/ws	10 Oct	11.7	0.16
Cv 2/ws	11 Oct	25.1	0.33
Dry season			
Byrsonima crassifolia			
Bc 1/ds	31 Mar-01 Apr	17.4	0.12
Bc 2/ds	31 Mar-01 Apr	47.3	0.34
Bc 3/ds	01-02 Apr	8.9	0.05
Bc 4/ds	03-05 Apr	18.13	0.11
Bc 5/ds	03-05 Apr	24.64	0.19
Curatella americana			
Ca 1/ds	31 Mar-01 Apr	24.9	0.17
Ca 2/ds	05-06 Apr	11.9	0.10
Cochlospermum vitifolium			
Cv 1/ds	05-06 Apr	3.3	0.03
Cv 2/ds	05-06 Apr	1.9	0.04

4.3. Results

4.3.1. Meteorological conditions

Average radiation, ambient temperature, relative humidity and temperature inside the sample chamber during daytime measurements are given in Table 4.2. More details can be found in Chapter 3, section 3.3.1.

Table 4.2. Meteorological conditions and temperature inside the chamber during the tree measurements. Data are daytime means (10:00-16:00 LT); SD in parentheses.

	Solar Radiation ($W\ m^{-2}$)	Ambient Temperature (°C)	Chamber Temperature (°C)	Rel. Humidity (ambient) (%)
Rainy season				
Byrsonima crassifolia				
Bc 1/ws	700.6 (514.1)	31.6 (4.4)	37.9 (7.4)	72.1 (10.8)
Bc 2/ws	414.9 (292.6)	29.3 (3.1)	34.0 (4.9)	78.7 (7.1)
Cochlospermum vitifolium				
Cv 1/ws	781.3 (302.3)	32.5 (1.4)	37.4 (2.3)	65.8 (5.5)
Cv 2/ws	850.4 (400.9)	34.6 (1.7)	39.9 (3.2)	52.9 (4.4)
Dry season				
Byrsonima crassifolia				
Bc 1/ds	872.3 (235.7)	35.7 (1.4)	42.0 (3.4)	32.6 (4.6)
Bc 2/ds	756.5 (343.5)	35.8 (1.2)	42.4 (3.0)	32.4 (4.5)
Bc 3/ds	766.8 (202.1)	36.7 (2.5)	43.2 (4.3)	38.5 (7.9)
Bc 4/ds	668.4 (305.6)	35.3 (1.7)	42.1 (3.7)	40.2 (4.6)
Bc 5/ds	704.9 (300.2)	34.9 (1.5)	41.7 (2.7)	41.0 (4.6)
Curatella americana				
Ca 1/ds	872.5 (249.6)	35.8 (1.4)	42.4 (3.2)	32.2 (5.0)
Ca 2/ds	739.9 (325.7)	35.5 (1.7)	41.2 (3.4)	41.3 (5.3)
Cochlospermum vitifolium				
Cv 1/ds	570.1 (443.4)	35.1 (1.4)	39.1 (5.4)	42.4 (4.0)
Cv 2/ds	553.7 (379.7)	35.1 (0.6)	38.7 (4.3)	41.8 (2.1)

4.3.2. Exchange of VOCs

The daytime (10:00-16:00 LT) average exchange rates for the measured tree species are presented in Table 4.3. The nighttime emission rates are included in appendix 8.5, Table 8.3.

The CO_2 assimilation measurements during the study of Bc1/ws and Bc2/ws, and the *Cochlospermum* specimens in the dry season, were not possible due to technical problems of the instrument. The CO_2 assimilation of the studied saplings ranged on average between 60-90 µmol/g/h during high solar radiation conditions (750-800 W/m^2) in both seasons. A significantly lower CO_2 uptake was observed for Bc3/ws, which was measured under lower radiation levels.

The main emission of *Byrsonima* was m69, which was emitted at similar rates in both wet and dry season (on average 400-460 nmol/g/h). Mass 69 is attributed to isoprene since an emission of 2-methyl-3-buten-2-ol (MBO) is very unlikely in that it has been detected only from pine trees (Guenther *et al.*, 1996b; Harley *et al.*, 1998), and pentenols (which are released after leaf wounding), if emitted, are expected to be of minor importance, compared to isoprene. Methanol (m33) and butene+butanol (m57) were also important emissions with average emission rates of ~10 nmol/g/h in the wet season, and 42 and 4 nmol/g/h respectively, in the dry season. The emission rates of all other detected compounds were below 5 nmol/g/h, and acetic acid (m61) was mostly deposited.

Isoprene, with an emission rate of ~2000 nmol/g/h, was also the highest emission from *Cochlospermum* saplings in the wet season, but in the dry season, methanol was the most prominent emission (about a factor of 1.7 higher than isoprene emission). The average methanol emission rate was almost a factor of 10 higher in the dry season (1272 nmol/g/h) than in the wet season (132 nmol/g/h). Other important emissions were m57, m43 (mostly propene), and methacrolein (MACR) and methyl vinyl ketone (MVK) (both detected at mass 71). MACR and MVK are usually reported as products of the oxidation of isoprene with OH radicals (Carter and Atkinson, 1996), but these compounds were also found to be directly emitted by holm oak (Holzinger *et al.*, 2000) and birch (Koppmann, 2003). The highest monoterpene emissions (m81+m137) were recorded from *Cochlospermum* saplings in the dry season. Both, emission as well as deposition of acetic acid (m61) and acetaldehyde (m45) was measured in both seasons.

Table 4.3. VOC exchange rates [nmol/g/h] and CO_2 assimilation from tropical savanna trees in the wet and dry season. Data are 10-min averages of daytime (10:00-16:00 LT) measurements. n.d. means not detected; n.m. not measured. Radiation (Rad) and temperature inside the chamber (T) are also shown.

	Rad	**T**	**CO2**	**m33**	**m43**	**m45**	**m57**	**m59**	**m61**	**m69**	**m71**	**m73**	**m81+m137**
	($W m^{-2}$)	**(°C)**	**($\mu mol\ g^{-1} h^{-1}$)**					**($nmol\ g^{-1} h^{-1}$)**					
						Wet season / ***Byrsonima crassifolia***							
Bc 1/ws	701	38	n.m.	8.52	n.d.	0.86	12.54	3.00	-21.31	447.60	4.59	0.97	1.81
Bc 2/ws	415	34	-19.79	9.44	4.03	1.54	7.82	2.35	n.d.	355.11	3.92	0.88	2.87
Average Bc/ws			**-19.79**	**8.98**	**4.03**	**1.20**	**10.18**	**2.67**	**-21.31**	**401.35**	**4.26**	**0.93**	**2.34**
						Wet season / ***Cochlospermum vitifolium***							
Cv 1/ws	781	37	-116.48	96.36	20.89	n.d.	41.82	n.d.	-36.88	2140.23	23.60	2.21	11.00
Cv 2/ws	850	40	-68.75	166.90	n.d.	n.d.	37.46	11.21	n.d.	1951.16	23.73	n.d.	35.33
Average Cv/ws			**-92.62**	**131.63**	**20.89**	**n.d.**	**39.64**	**11.21**	**-36.88**	**2045.70**	**23.67**	**2.21**	**23.17**
						Dry season / ***Byrsonima crassifolia***							
Bc 1/ds	872	42	-62.51	65.48	7.60	1.66	6.01	6.78	1.87	672.73	2.15	2.61	0.18
Bc 2/ds	757	42	-40.04	49.54	2.66	0.48	3.02	3.50	n.d.	338.40	0.93	1.29	0.58
Bc 3/ds	767	43	-33.04	7.20	1.26	n.d.	n.d.	n.d.	n.d.	139.59	0.99	n.d.	n.d.
Bc 4/ds	668	42	-81.12	36.07	4.06	-2.10	2.15	1.18	-1.37	498.64	0.94	n.d.	0.34
Bc 5/ds	705	42	-86.47	49.36	2.73	-3.50	3.12	0.23	-6.40	668.08	0.92	1.36	0.17
Average Bc/ds			**-60.64**	**41.53**	**3.66**	**-0.87**	**3.58**	**2.92**	**-1.97**	**463.49**	**1.19**	**1.75**	**0.32**
						Dry season / ***Curatella americana***							
Ca 1/ds	873	42	-71.58	50.83	3.25	n.d.	4.65	6.76	n.d.	n.d.	n.d.	2.48	0.92
Ca 2/ds	740	41	-50.00	34.97	3.91	n.d.	5.99	2.35	4.84	5.79	1.54	2.40	13.24
Average Ca/ds			**-60.79**	**42.90**	**3.58**	**n.d.**	**5.32**	**4.56**	**4.84**	**5.79**	**1.54**	**2.44**	**7.08**
						Dry season / ***Cochlospermum vitifolium***							
Cv 1/ds	570	39	n.m.	1584.94	36.41	27.62	28.77	25.54	40.08	990.40	11.01	11.05	4.12
Cv 2/ds	554	39	n.m.	959.01	24.35	n.d.	15.82	12.68	21.18	460.20	4.06	6.15	4.83
Average Cv/ds				**1271.98**	**30.38**	**27.62**	**22.30**	**19.11**	**30.63**	**725.30**	**7.54**	**8.60**	**4.48**

Methanol was the most important emission from *Curatella* in the dry season. Its emission range (50-70 nmol/g/h) was comparable to the observed for *Byrsonima.* All other emissions were below 10 nmol/g/h. The total sum of VOCs emission of this species was about a factor of 10 and 28 lower than the total emission from *Byrsonima* and *Cochlospermum,* respectively, in the dry season.

The ratio of carbon released as VOCs to the carbon assimilated by photosynthesis during daytime is shown in Table 4.4. Between 2-9% of the CO_2 gained by *Byrsonima* was emitted as VOCs, from which more than 95% was isoprene. For *Cochlospermum* the range observed in the dry season was higher (9-15%), but also isoprene accounts for ~95% of all emitted carbon. The percentage of assimilated carbon emitted from *Curatella* was only between 0.2-0.3%. Isoprene was detected in only one of the two individuals measured (Ca2/ds), with very low emission rates (Table 4.3). For this specimen, the highest loss of carbon was due to emission of monoterpenes and methanol.

Table 4.4. Carbon gained by daytime (10:00-16:00) CO_2 assimilation and percentage emitted as VOCs by tropical savanna trees.

	Carbon gain by photosynthesis (μgC g^{-1} h^{-1})	Total VOC-C emitted (μgC g^{-1} h^{-1})	Percentage of C emitted as VOCs
Wet season			
Byrsonima crassifolia			
Bc 1/ws	n.m.	28.18	n.m.
Bc 2/ws	-237.4	23.64	9.53
Cochlospermum vitifolium			
Cv 1/ws	-1397.7	134.89	9.65
Cv 2/ws	-825.0	126.83	15.37
Dry season			
Byrsonima crassifolia			
Bc 1/ds	-750.1	42.29	5.64
Bc 2/ds	-480.5	21.45	4.47
Bc 3/ds	-396.4	8.55	2.16
Bc 4/ds	-973.5	30.76	3.16
Bc 5/ds	-1037.6	41.06	2.69
Curatella americana			
Ca 1/ds	-858.9	1.42	0.17
Ca 2/ds	-600.0	3.17	0.53
Cochlospermum vitifolium			
Cv 1/ds	n.m.	85.23	n.m.
Cv 2/ds	n.m.	42.79	n.m.

4.3.3. Diurnal cycle

Figures 4.1 to 4.3 show the diurnal cycles of the emission rates of several VOCs, along with meteorological (radiation and chamber temperature) and plant physiological (CO_2 assimilation) data for one specimen of each species measured in the dry season. The data are hourly means ± SD of 2-days measurements.

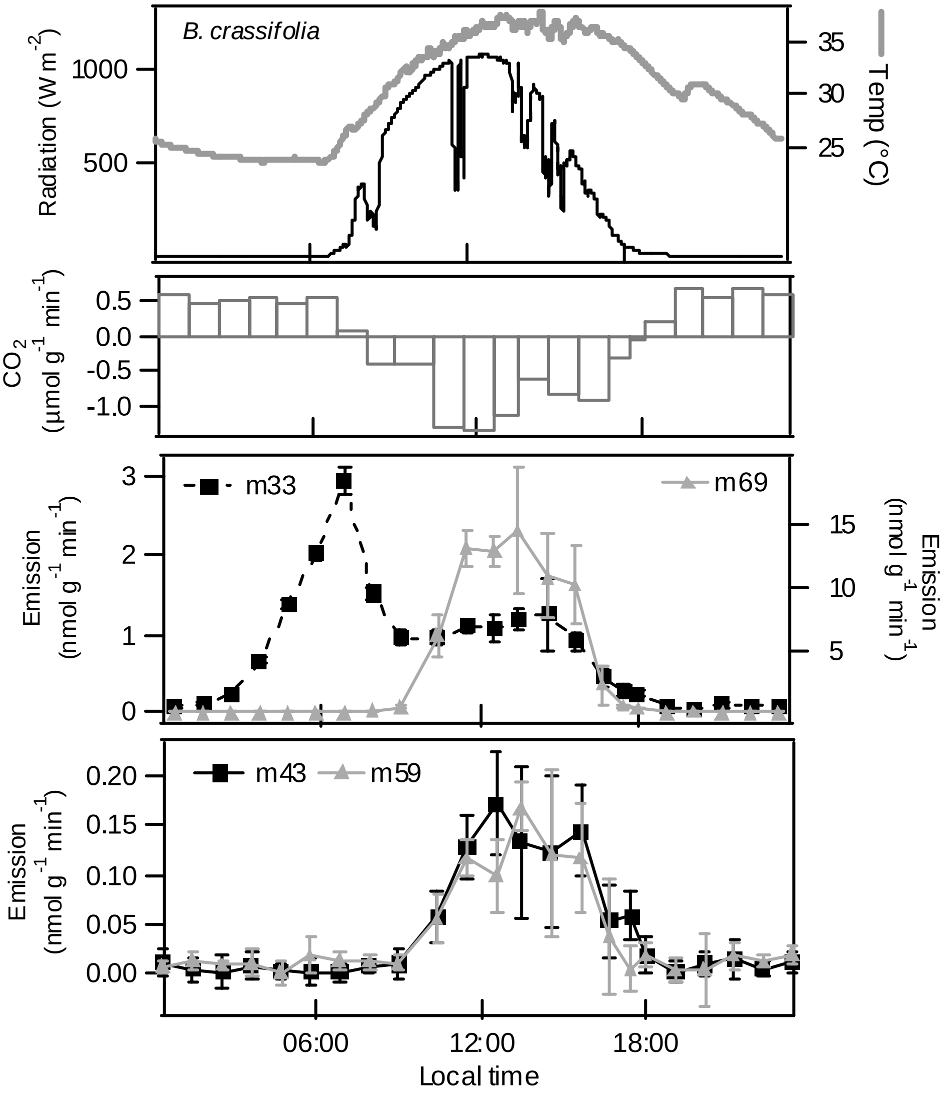

Figure 4.1. Mean diurnal cycle of selected VOC emission rates for *Byrsonima crassifolia* in the dry season, together with meteorological data and CO_2 assimilation. Shown here Bc1/ds, investigated on 31 March-1 April, 2000.

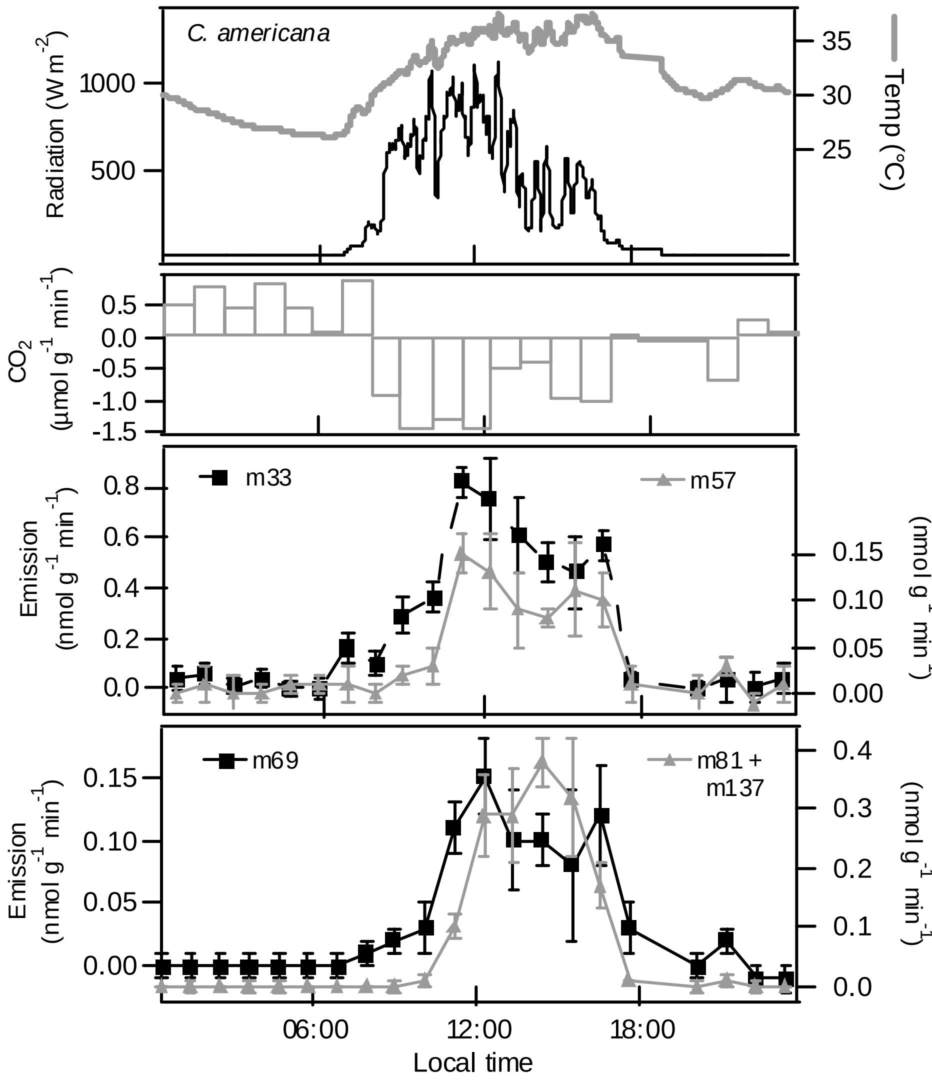

Figure 4.2. Mean diurnal cycle of selected VOC emission rates for *Curatella americana* in the dry season, together with meteorological data and CO_2 assimilation. Shown here Ca2/ds, investigated on 5-6 April, 2000.

The diurnal cycle of methanol (m33) emission of *Byrsonima* (Fig. 4.1) exhibited a completely different shape than those of *Curatella* (Fig 4.2) and *Cochlospermum* (Fig 4.3). In all 5 *Byrsonima* specimens studied, the same diurnal course was observed. A release of methanol was detected from around 03:00 LT onwards. Emission rates increased steadily and reached a maximum after sunrise, between 06:00 and 07:30. The emission declined in the following two hours, stabilized between 9:00 and 15:00 and continued to decline afterwards until very low levels were measured in the night. The maximum emissions during this *morning burst* were between 3-5 nmol/g/min, which is more than 4 times the average daytime emission of this species (42 nmol/g/h, Table 4.3). For *Curatella* instead, only a small burst around 07:00 was observed, which was ~4 times lower than the maximum emission of this species at noon (Fig. 4.2).

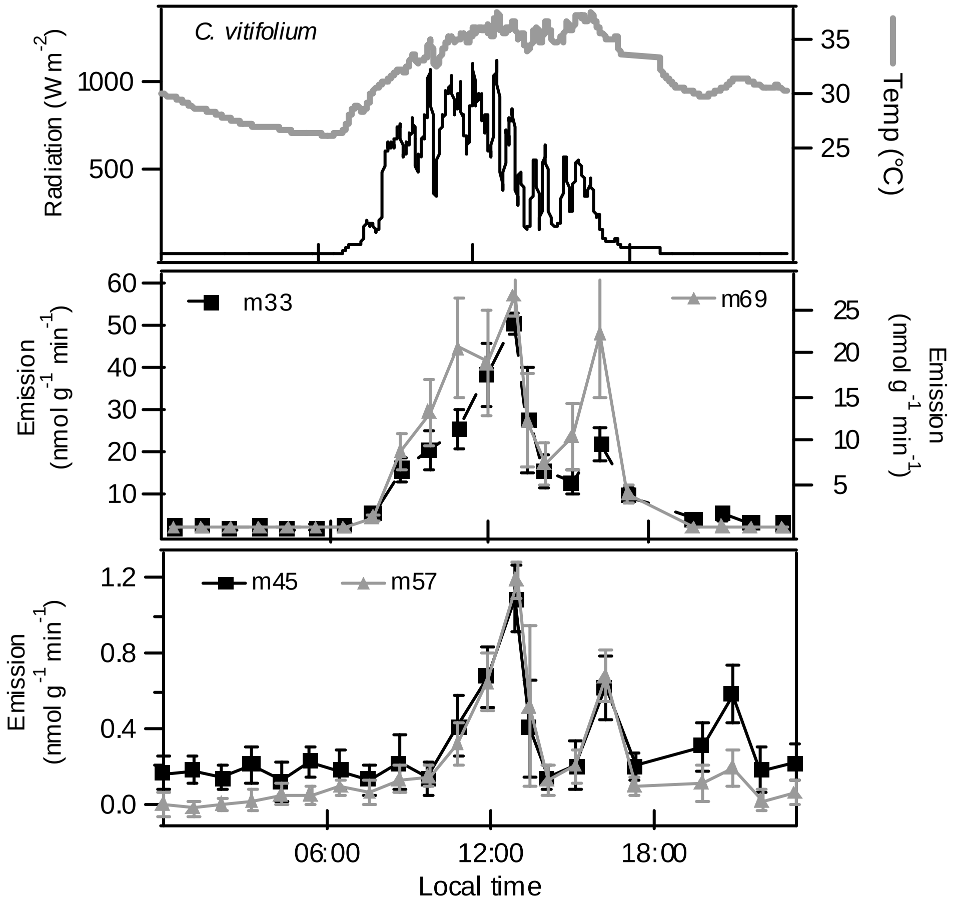

Figure 4.3. Mean diurnal cycle of selected VOC emission rates for *Cochlospermum vitifolium* in the dry season, together with meteorological data. No CO_2 assimilation measurements could be made. Shown here Cv1/ds, investigated on 5-6 April, 2000.

Predawn methanol emissions and morning emission bursts have been experimentally observed before (Macdonald and Fall, 1993b; Nemecek-Marshall *et al.*, 1995), and also that the emissions followed changes in stomatal conductance, i.e. stomatal opening to a certain degree was also occurring during the night. These phenomena are consistent with the build up of methanol in the leaves during periods of stomatal closure, and release after the gas-phase conductance starts to rise (Niinemets and Reichstein, 2003a). The amount of methanol emitted during the morning burst is proportional to the amount accumulated during the night. Additionally, as soon as there is an increase in the partial pressure between the leaf intercellular air space and the atmosphere, any increase in stomatal conductance will lead to a certain burst of emission, which could explain the emissions before sunrise. Unfortunately, the stomatal conductance could not be determined in this work, due to interferences probably from the soil water evaporation (Chapter 3, section 3.3.2.1).

The methanol diurnal profile of *Cochlospermum* (Fig. 4.3), followed closely the radiation and temperature changes, as was also observed for the grasses (Chapter 3). No morning emission burst was observed. Niinemets and Reichstein (2003b) found that differences in leaf architecture, in particular leaf liquid volume to area ratio, also modified the emission response to changes in stomatal aperture. The leaf structure of both trees, *Cochlospermum* and *Byrsonima* is actually very different when they are mature, and even more different when they are not completely developed. The leaves of the *Cochlospermum* saplings measured in the dry season were in a very early development stage, the *Byrsonima* leaves were also young, but probably already fully developed, as the leaf area range, which is similar in both seasons, suggests (Table 4.1, see also section 4.4.3). Whereas the area of *Chlospermum* leaves were at least a factor of 5 larger in the wet than in the dry season (WS 0.16-0.34 m^2; DS 0.03-0.04 m^2).

Other compounds shown in the previous figures, like isoprene (m69), propene and other $C_3H_7^+$ fragments (m43), butene+butanol (m57) and acetone (m59) exhibited similar diurnal cycles, with highest emissions at highest radiation and temperature levels, with the difference that the increase of isoprene emissions in the morning is time-shifted to about one hour later. The fast response of the emissions to changes in radiation, and subsequently, temperature, can be observed for *Curatella* and *Cochlospermum* (Figs. 4.2 and 4.3), which were both investigated in the same period. The monoterpenes (m81+m137) were the only compounds that did not reflect a change in the emission rate during the time when radiation was low (Fig. 4.2). Usually there is not an instantaneous light influence on terpene emissions in the case of monoterpene-storing plant species (e.g. Lerdau *et al.*, 1997; Llusià and Peñuelas, 2000). Thus, if the emitted monoterpenes were derived from storage pools (e.g. glandular trichomes, resin ducts), short-term alterations in synthesis would not be immediately reflected in the emission rates (Monson *et al.*, 1995).

4.3.4. Temperature and light dependence of VOCs emissions

The temperature and radiation dependencies of VOC emission rates were analyzed proceeding as described in Chapter 3, section 3.3.2.2. The results were similar to those found for grasses, i.e. mainly exponential correlations of VOC emissions with temperature, and in general better correlations with temperature than radiation. As was also found for VOC emissions from grasses, the emission algorithm for monoterpenes (Guenther *et al.*, 1993), which only depends on temperature, described the emissions better than the isoprene algorithm which includes the light (PAR) dependency. Accordingly, the emission data were normalized to a standard temperature of 30°C, in order to evaluate seasonal, intra- and interspecific emission variability. The standard temperature of 30°C is rather in the lower end of the observed daytime temperatures in the savanna (see Table 3.3, page 45), but it is the most commonly used in the literature for emission-normalization purposes, and it therefore allows for comparison with previous studies.

The values for the temperature dependence of emissions (β-factors) from the studied trees are presented in Tables 4.5 and 4.6. Acetic acid (m61) was not included in the tables, since the only important emission was measured from *Cochlospermum* in the dry season. On average, β-coefficients varied by a factor of 1.7 between 0.13 and 0.22 K^{-1} (with a minimum of 0.05 and a maximum of 0.7 K^{-1}). No seasonal trend was observed in the values. In general, the β-factors for *Byrsonima* were higher for the saplings measured in the wet season (Table 4.5), while those for *Cochlospermum* were generally higher in the dry season (Table 4.6).

4.3.5. Standard emission rates of VOCs

The standard emission rates (E_{St}) calculated from the temperature correlation equations for a temperature of 30°C, are summarized in Tables 4.7 and 4.8. Also included in the tables is the CO_2 assimilation at 30°C, derived from the linear correlation of CO_2 versus temperature.

The plant-to-plant variability of the emissions ranged mainly between factors of 1.3-3 for all tree species. Exceptions were the monoterpene (m81+137) emissions of *Byrsonima* and *Curatella* in the dry season, and isoprene of *Byrsonima* in the dry season, whose intraspecies E_{St} varied by factors of 8, 6 and 5, respectively.

Table 4.5. Values for the temperature dependence, β [K^{-1}], of VOCs emissions from *Byrsonima crassifolia*. Errors are SD from fits to the data. Numbers in parentheses give *n*, number of measurements, and the correlations coefficients (R^2) for fits of *lnE* versus (T-T_{ref}).

	m33[a]	**m43**	**m45**	**m57**	**m59**	**m69**	**m71**	**m73**	**m81+m137**
				Wet Season / *Byrsonima crassifolia*					
Bc 1/ws	0.22 ± 0.10 (5, 0.71)	n.d.	0.12 ± 0.10 (3, 0.56)	0.16 ± 0.03 (5, 0.89)	0.10 ± 0.07 (3, 0.71)	0.49 ± 0.13 (5, 0.83)	0.30 ± 0.13 (5, 0.65)	0.05 ± 0.04 (5, 0.32)	-0.02 ± 0.05 (6, 0.04)
Bc 2/ws	0.15 ± 0.03 (10, 0.77)	0.23 ± 0.04 (10, 0.82)	0.14 ± 0.06 (7, 0.55)	0.38 ± 0.05 (15, 0.81)	0.17 ± 0.03 (18, 0.70)	0.70 ± 0.08 (14, 0.87)	0.42 ± 0.11 (9, 0.67)	0.26 ± 0.07 (14, 0.51)	0.34 ± 0.09 (12, 0.57)
range	**0.15-0.22**	**0.23**	**0.12-0.14**	**0.16-0.38**	**0.10-0.17**	**0.49-0.70**	**0.30-0.42**	**0.05-0.26**	**0.34**
				Dry Season / *Byrsonima crassifolia*[b]					
Bc 1/ds	0.13 ± 0.02 (21, 0.76)	0.18 ± 0.02 (27, 0.76)	0.10 ± 0.02 (24, 0.49)	0.13 ± 0.02 (29, 0.71)	0.14 ± 0.02 (28, 0.73)	0.25 ± 0.04 (17, 0.76)	0.16 ± 0.02 (19, 0.75)	0.11 ± 0.02 (28, 0.52)	0.18 ± 0.02 (18, 0.77)
Bc 2/ds	0.12 ± 0.01 (24, 0.82)	0.16 ± 0.02 (24, 0.71)	0.11 ± 0.03 (19, 0.39)	0.13 ± 0.02 (28, 0.65)	0.16 ± 0.02 (23, 0.84)	0.21 ± 0.07 (18, 0.37)	0.09 ± 0.02 (18, 0.49)	0.14 ± 0.02 (29, 0.55)	0.12 ± 0.04 (18, 0.32)
Bc 4/ds	0.09 ± 0.02 (21, 0.50)	0.21 ± 0.03 (15, 0.76)	n.d.	0.09 ± 0.02 (25, 0.48)	0.06 ± 0.03 (18, 0.28)	0.17 ± 0.02 (12, 0.84)	0.17 ± 0.04 (13, 0.65)	0.09 ± 0.03 (22, 0.24)	0.07 ± 0.03 (19, 0.21)
Bc 5/ds	0.08 ± 0.02 (21, 0.48)	0.17 ± 0.04 (18, 0.52)	n.d.	0.13 ± 0.02 (29, 0.56)	0.12 ± 0.02 (14, 0.66)	0.26 ± 0.03 (13, 0.84)	0.19 ± 0.02 (12, 0.90)	0.14 ± 0.02 (28, 0.64)	0.09 ± 0.02 (16, 0.50)
range	**0.08-0.13**	**0.16-0.21**	**0.10-0.11**	**0.09-0.13**	**0.06-0.16**	**0.17-0.26**	**0.09-0.19**	**0.09-0.14**	**0.07-0.18**

[a] The data of methanol early morning emission peak were not included in the correlation.

[b] Bc3/ds was not included since its emissions were significantly lower and the correlation worse than those from the other individuals measured.

Table 4.6. Values for the temperature dependence, β [K^{-1}], of VOCs emissions from *Curatella americana* and *Cochlospermum vitifolium*. Errors are SD from fits to the data. Numbers in parentheses give *n*, number of measurements, and the correlations coefficients (R^2) for fits of *lnE* versus *(T-T$_{ref}$)*.

	m33	**m43**	**m45**	**m57**	**m59**	**m69**	**m71**	**m73**	**m81+m137**
				Dry Season / *Curatella americana*					
Ca 1/ds	0.15 ± 0.01 (29, 0.80)	0.13 ± 0.03 (24, 0.42)	n.d.	0.07 ± 0.02 (30, 0.21)	0.17 ± 0.02 (28, 0.70)	n.d.	n.d.	0.13 ± 0.02 (28, 0.55)	0.27 ± 0.05 (19, 0.68)
Ca 2/ds	0.13 ± 0.03 (17, 0.51)	0.12 ± 0.04 (14, 0.47)	n.d.	0.18 ± 0.04 (17, 0.60)	0.22 ± 0.05 (7, 0.83)	0.19 ± 0.02 (14, 0.92)	0.09 ± 0.03 (13, 0.46)	0.13 ± 0.02 (18, 0.68)	0.36 ± 0.06 (12, 0.76)
range	**0.13-0.15**	**0.12-0.13**	**n.d.**	**0.07-0.18**	**0.17-0.22**	**0.19**	**0.09**	**0.13**	**0.27-0.36**
				Wet Season / *Cochlospermum vitifolium*					
Cv 1/ws	0.08 ± 0.03 (9, 0.52)	0.01 ± 0.09 (8, 0.00)	n.d.	0.04 ± 0.07 (8, 0.04)	n.d	0.24 ± 0.07 (9, 0.64)	0.07 ± 0.09 (8, 0.09)	-0.13 ± 0.17 (7, 0.11)	0.00 ± 0.08 (9, 0.00)
Cv 2/ws	0.07 ± 0.02 (5, 0.83)	n.d.	n.d.	0.11 ± 0.02 (5, 0.91)	0.12 ± 0.05 (5, 0.70)	0.16 ± 0.03 (5, 0.90)	0.15 ± 0.01 (5, 0.99)	n.d.	0.19 ± 0.02 (5, 0.95)
range	**0.07-0.08**	**no corr.**	**n.d.**	**0.04-0.11**	**0.12**	**0.16-0.24**	**0.15**	**Neg.**	**0.19**
				Dry Season / *Cochlospermum vitifolium*					
Cv 1/ds	0.15 ± 0.02 (21, 0.83)	0.08 ± 0.01 (21, 0.63)	0.06 ± 0.01 (21, 0.46)	0.13 ± 0.02 (18, 0.76)	0.08 ± 0.02 (21, 0.47)	0.38 ± 0.05 (21, 0.73)	0.10 ± 0.03 (19, 0.45)	0.12 ± 0.02 (21, 0.71)	0.10 ± 0.02 (20, 0.51)
Cv 2/ds	0.21 ± 0.02 (19, 0.84)	0.13 ± 0.03 (15, 0.52)	n.d.	0.22 ± 0.05 (12, 0.64)	0.07 ± 0.05 (10, 0.22)	0.37 ± 0.06 (15, 0.78)	0.07 ± 0.03 (16, 0.22)	0.10 ± 0.04 (16, 0.36)	0.06 ± 0.03 (14, 0.25)
range	**0.15-0.21**	**0.08-0.13**	**0.06**	**0.13-0.22**	**0.07-0.08**	**0.37-0.38**	**0.07-0.10**	**0.10-0.12**	**0.06-0.10**

Table 4.7. Standard emission rates in [ngC/g/h] for *Byrsonima crassifolia*. Errors are SD from fits to the data.

	CO_2[a]	**m33**	**m43**	**m45**	**m57**	**m59**	**m69**	**m71**	**m73**	**m81+m137**
				Wet Season / *Byrsonima crassifolia*						
Bc 1/ws	n.m.	14.9 ± 4.4	n.d.	66.2 ± 4.2	111 ± 1.8	68.7 ± 2.5	115 ± 9.5	8.5 ± 10.1	22.8 ± 2.2	No corr.
Bc2/ws	38.4	54.7 ± 1.5	28.3 ± 1.8	22.5 ± 2.1	54.6 ± 2.6	37.2 ± 1.8	597 ± 4.4	20.0 ± 5.0	9.0 ± 3.9	50.4 ± 4.7
Average	**38.4**	**35 ± 28**	**28.3**	**44 ± 31**	**83 ± 40**	**53 ± 22**	**356 ± 341**	**14 ± 8**	**16 ± 10**	**50**
				Dry Season / *Byrsonima crassifolia*						
Bc 1/ds	24.9	149 ± 2.1	26.8 ± 2.5	9.8 ± 2.7	54.7 ± 2.1	26.9 ± 2.1	1592 ± 4.9	12.3 ± 2.7	21.3 ± 2.7	2.3 ± 3.0
Bc 2/ds	-115.2	113 ± 1.8	13.5 ± 2.9	2.0 ± 4.4	28.2 ± 2.5	11.6 ± 2.1	1130 ± 23.2	11.9 ± 2.9	8.7 ± 3.4	5.8 ± 7.1
Bc 4/ds	-153.6	152 ± 2.2	9.8 ± 3.5	n.d.	56.7 ± 2.1	31.0 ± 2.4	3413 ± 2.5	4.4 ± 4.2	17.0 ± 3.2	18.6 ± 3.2
Bc 5/ds	-277.2	231 ± 2.1	11.0 ± 4.2	n.d.	39.2 ± 2.3	10.0 ± 1.9	1900 ± 3.2	4.2 ± 2.0	15.4 ± 2.2	6.3 ± 2.4
Average	**-129 ± 120**	**161 ± 50**	**15 ± 8**	**5.9 ± 5.5**	**45 ± 14**	**20 ± 11**	**2008 ± 998**	**8.4 ± 4.5**	**16 ± 5**	**8.2 ± 7.1**

[a] CO_2 assimilation in µgC/g/h, derived from linear correlations of CO_2 exchange vs. temperature.

Table 4.8. Standard emission rates in [ngC/g/h] for *Curatella americana* and *Cochlospermum vitifolium*. Errors are SD from fits to the data.

	CO_2[a]	m33	m43	m45	m57	m59	m69	m71	m73	m81+m137
					Dry Season / *Curatella Americana*					
Ca 1/ds	-52.8	85.9 ± 2.0	19.0 ± 4.5	n.d.	61.9 ± 3.2	16.4 ± 2.9	n.d.	n.d.	19.9 ± 2.8	2.0 ± 7.9
Ca 2/ds	-9.6	66.4 ± 3.1	28.1 ± 3.5	n.d.	26.7 ± 3.7	6.4 ± 4.4	32.5 ± 1.7	22.7 ± 2.6	19.6 ± 2.2	11.8 ± 8.7
Average	**-31 ± 31**	**76 ± 14**	**24 ± 6**	**n.d.**	**44 ± 25**	**11 ± 7**	**33**	**23**	**20 ± 0.3**	**6.9 ± 7.0**
					Wet Season / *Cochlospermum vitifolium*					
Cv 1/ws	-271.2	681.0 ± 1.8	485.8 ± 6.5	n.d.	1685.8 ± 4.2	n.d.	24169.2 ± 4.1	No corr.	388.9 ± 27.8	1478.6 ± 5.2
Cv 2/ws	-424.8	970.8 ± 1.5	n.d.	n.d.	577.3 ± 1.6	110.7 ± 2.8	22291.5 ± 2.0	240.2 ± 1.2	n.d.	556.2 ± 1.8
Average	**-349 ± 108**	**826 ± 205**	**486**	**n.d.**	**1131 ± 783**	**111**	**23230 ± 1327**	**240**	**389**	**1017 ± 652**
					Dry Season / *Cochlospermum vitifolium*					
Cv 1/ds	n.m.	3190.4 ± 1.7	470.6 ± 1.6	307.7 ± 1.6	247.4 ± 1.8	330.7 ± 1.8	826.2 ± 5.4	157.8 ± 2.4	117.2 ± 1.7	140.3 ± 2.1
Cv 2/ds	n.m.	1630.1 ± 1.8	267.3 ± 2.4	n.d.	108.4 ± 3.7	278.8 ± 3.3	1002.9 ± 4.3	132.1 ± 2.3	89.4 ± 2.6	275.2 ± 2.2
Average		**2410 ± 1103**	**369 ± 144**	**308**	**178 ± 98**	**305 ± 37**	**915 ± 125**	**145 ± 18**	**103 ± 19**	**208 ± 95**

[a] CO_2 assimilation in μgC/g/h, derived from linear correlations of CO_2 exchange vs. temperature.

Some plants did not emit acetaldehyde (m45) at all, and the emission of most individuals was below 70 ngC/g/h, only one *Cochlospermum* specimen in the dry season showed an emission close to 300 ngC/g/h.

High interspecies variability was also observed. The standard emissions of *Curatella* were in general lower than the E_{St} of the other two species. Its methanol emission, for instance, was a factor of 2 lower than the emission from *Byrsonima*, and a factor of 30 lower than those of *Cochlospermum* (in the dry season). *Curatella* is also a very low isoprene and monoterpene emitter.

The standard emission rates of *Cochlospermum* were significantly higher than those of *Byrsonima*. *Cochlospermum*'s methanol (m33), propene (m43), methacrolein and methyl vinyl ketone (MACR+MVK, m71)[4], methyl ethyl ketone (MEK, m73) and monoterpenes (m81+m137) average emission rates were up to ~20 times higher than those of *Byrsonima*. Acetone (m59) and butene+butanol (m57) were found to be between a factor of 2-15 higher.

A seasonal difference in standard emission rates was observed for nearly all emissions from *Byrsonima* and *Cochlospermum*, but the seasonal trend was not the same for all compounds. The highest methanol standard emission rates, for both tree species, were found in the dry season, whereas butene+butanol, MACR+MVK, and monoterpene emission rates were higher in the wet season. Interestingly, the isoprene emission from *Byrsonima* was higher in the dry season by about a factor of 6, whereas for *Cochlospermum* the emission rate was 25 times higher in the wet season. No seasonal variability was observed for propene standard emissions, which were within one standard deviation in both seasons for both tree species.

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[4] MACR and MVK are produced by the oxidation of isoprene, thus, production inside the chamber cannot be excluded. Nevertheless, direct emission has been also observed in laboratory measurements (Holzinger *et al.*, 2000).

4.4. Discussion

4.4.1. Plant-to-plant variability of VOC emissions

The amount of emitted VOCs (sum of VOCs) during a given season varied among plants of the same species between a factor of 1.1 and 2.8 (see next section, Table 4.9). A similar range of intraspecies variability (1.5-2.6) was observed for savanna grasses (Chapter 3, Table 3.14). The highest variability was observed among the *Byrsonima* individuals in the dry season, whose total emissions ranged from 1.3-3.7 µgC/g/h. Interestingly, only little variation in the percentage composition of the different VOCs emitted by these specimens in this season was found: isoprene accounted for more than 80%, and methanol for 4-10% of the emissions (Figure 4.4).

On the other hand, a rather large variability in the emission patterns of the *Byrsonima* saplings in the wet season was observed (Fig. 4.4). While for Bc1/ws isoprene and butene+butanol contributed each to ~28% of the total emission, for Bc2/ws isoprene represented ~70% of all carbon emitted.

For the *Cochlospermum* saplings measured in the wet season both the amount of emitted VOCs as well as its emission pattern were very uniform. The mean total emission was 27 µgC/g/h, from which isoprene represented 83 and 90% for Cv1/ws and Cv2/ws, respectively. For the two saplings measured in the dry season, the distribution was different; the share of isoprene was only 14 and 27%, and methanol, which accounted for ~50% of the total, was the most important emission.

For the first *Curatella* specimen measured (Ca1/ds), methanol and butene+butanol were the prominent compounds (42 and 30% respectively), followed by minor fractions (~9%) of propene, acetone and MEK. For Ca2/ds methanol accounted for 30%, and all other emissions, except for acetone, contributed similarly with 9-15% to the total emissions.

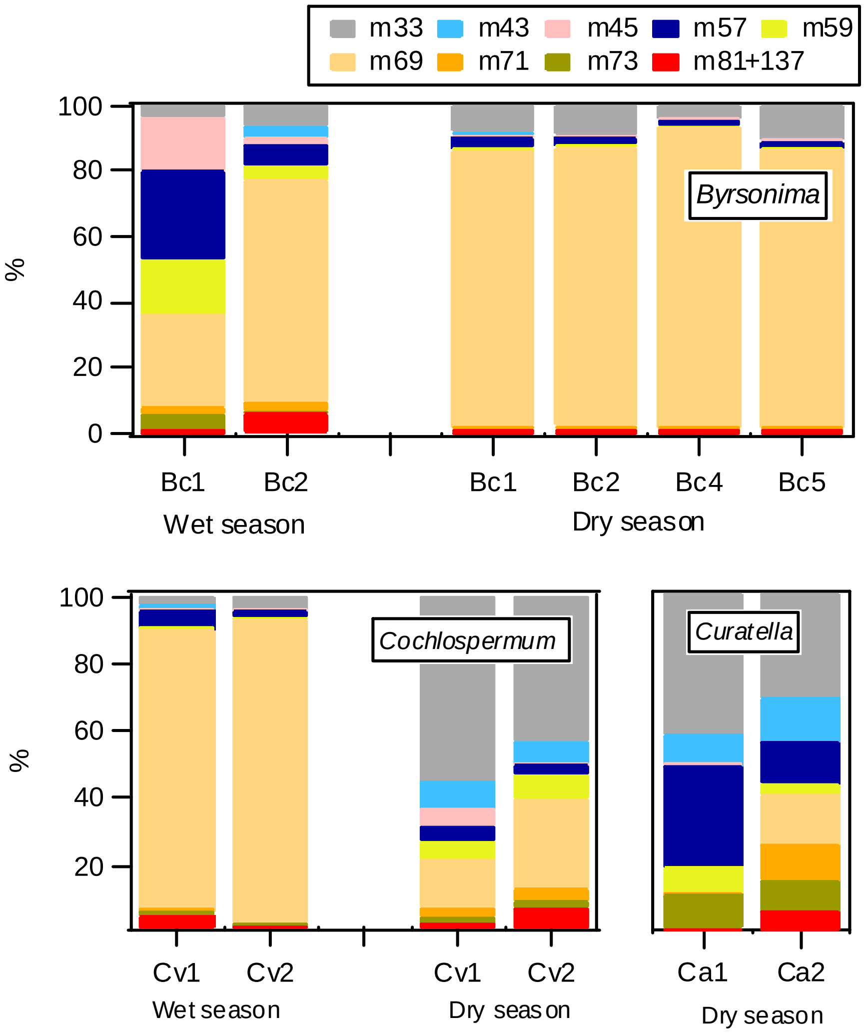


Figure 4.4. Intraspecific variability of the percentage contribution of the detected VOCs to the total emission from savanna trees

Little is known about the environmental and physiological controls on biogenic VOC emissions other than isoprene and monoterpenes. It is a fact that emission rates of all plant-emitted VOCs depend on temperature, and many compounds depend also on light (Guenther *et al.*, 2000). The empirical algorithms currently used to predict plant emissions are based on these environmental variables (e.g. Guenther *et al.*, 1993; Guenther *et al.*, 1995), however a series of physiological and physicochemical factors (e.g. elevated CO_2, leaf nitrogen concentration, heat stress, mechanical damage, stomatal closure due to water or salinity stress, and characteristics of the compound such as its solubility, volatility and diffusivity) (Lerdau and Gray, 2003; Niinemets *et al.*, 2004, and references therein), which determine the rate of compound synthesis and control its emission, are not included (Niinemets *et al.*, 2004). The intraspecific variation in the composition of VOC emissions has been even much less investigated. Only a handful of studies investigated the differences in the emission composition of monoterpene emissions from oak trees (*Quercus ilex*) (Peñuelas and Llusià, 1999; Staudt *et al.*, 2001) and Scots pine (Komenda and Koppmann, 2002; Komenda *et al.*, 2003), and they ascribe the high variability in the spectrum of monoterpenes emitted to genotypic differences and not environmental influences. Thus, even when we eliminated the effect of temperature by normalizing the emission rates of savanna trees to a standard temperature of 30°C, there are many other factors that cause variability of VOCs production and emission, which are difficult to identify and, especially in field measurements, impossible to control.

4.4.2. Interspecies variability of emissions

Large differences in emission rates were observed also among the different tree species. Table 4.9 summarizes the average standard emission rates determined for the investigated species in both seasons. The highest emissions were measured from *Cochlospermum*. The VOCs total sum of this species in the wet season was 42 times higher than the emission from *Byrsonima*. This enormous difference was principally due to the high isoprene emission of *Cochlospermum* (23 μgC/g/h), which was higher than those of *Byrsonima* by a factor of 65 (0.35 μgC/g/h). Isoprene accounted for 44% of the total emission of *Byrsonima,* while for *Cochlospermum* it represented as much as 85% (Fig. 4.5). In the dry season, the total emission from *Cochlospermum* was only two times higher than those of *Byrsonima*. Nevertheless, the differences of the individual compounds were generally much higher (ranging between a factor of 6-51), with isoprene as the only exception (i.e. the isoprene emission of *Cochlospermum* was about half of the emission of *Byrsonima).* In the dry season, isoprene was the main emission of *Byrsonima*, accounting for 88% and methanol only for 7% of all the emitted carbon. Methanol was the main emission of *Cochlospermum* (49%), followed by isoprene whose share was only 19%.

Curatella was in general a very low-emitting tree species. Its sum of emission was 10 and 20 times lower than the total emission of *Byrsonima* and *Cochlospermum,* respectively (Table 4.9). About one third of the emitted carbon was coming from methanol (Fig. 4.5), 19% from butene+butanol and 10% from propene. Isoprene was only detected in one of the two measured individuals (Table 4.8), and its standard emission rate was very low (33 ngC/g/h), which means that the mean isoprene emission from *Cochlospermum* is higher by a factor of 27, and that of *Byrsonima* by a factor of 60.

Table 4.9. Average VOCs standard emission rates from tropical trees[a]

	Byrsonima crassifolia	*Curatella americana*	*Cochlospermum vitifolium*
m33 / methanol			
Wet season	35 (15/55)	n.m.	826 (681/971)
Dry season	161 (113/231)	76 (66/86)	2410 (1630/3190)
m43 / propene + others			
Wet season	28 (n.d./28.3)	n.m.	486 (n.d./486)
Dry season	15 (10/27)	24 (19/28)	369 (267/470)
m45 / acetaldehyde			
Wet season	44 (22/66)	n.m.	n.d.
Dry season	6 (n.d./10)	n.d.	308 (n.d./308)
m57 / butene + others			
Wet season	83 (55/111)	n.m.	1131 (577/1685)
Dry season	45 (28/55)	44 (27/62)	178 (108/247)
m59 /acetone			
Wet season	53 (37/69)	n.m.	111 (n.d./110)
Dry season	20 (10/31)	11 (6/16)	305 (279/330)
m69 /isoprene			
Wet season	356 (115/597)	n.m.	23230 (22292/24169)
Dry season	2008 (1130/3413)	33 ± 2	915 (826/1003)
M71 /MACR+MVK			
Wet season	14 (9/20)	n.m.	240 ± 1.2
Dry season	8 (4/12)	23 ± 3	145 (132/158)
m73 / MEK			
Wet season	16 (9/23)	n.m.	389 (n.d./389)
Dry season	16 (9/21)	20 ± 0.3	103 (89/117)
M81+ m137/monoterpenes			
Wet season	50 ± 5	n.m.	1017 (556/1479)
Dry season	8 (2/19)	7 (2/12)	208 (140/275)
Sum of VOCs emission [μgC/g/h]			
Wet season	0.64 (0.4/0.9)	n.m.	27.0 (24.7/28.9)
Dry season	2.3 (1.3/3.7)	0.22 (0.21/0.24)	4.8 (3.8/5.8)

[a] Units are [ngC/g/h], except total VOCs emission in [μgC/g/h]
Given are averages, emission range in parentheses (or ± SD when data for only one plant exist). n.d. not detected, n.m. not measured.

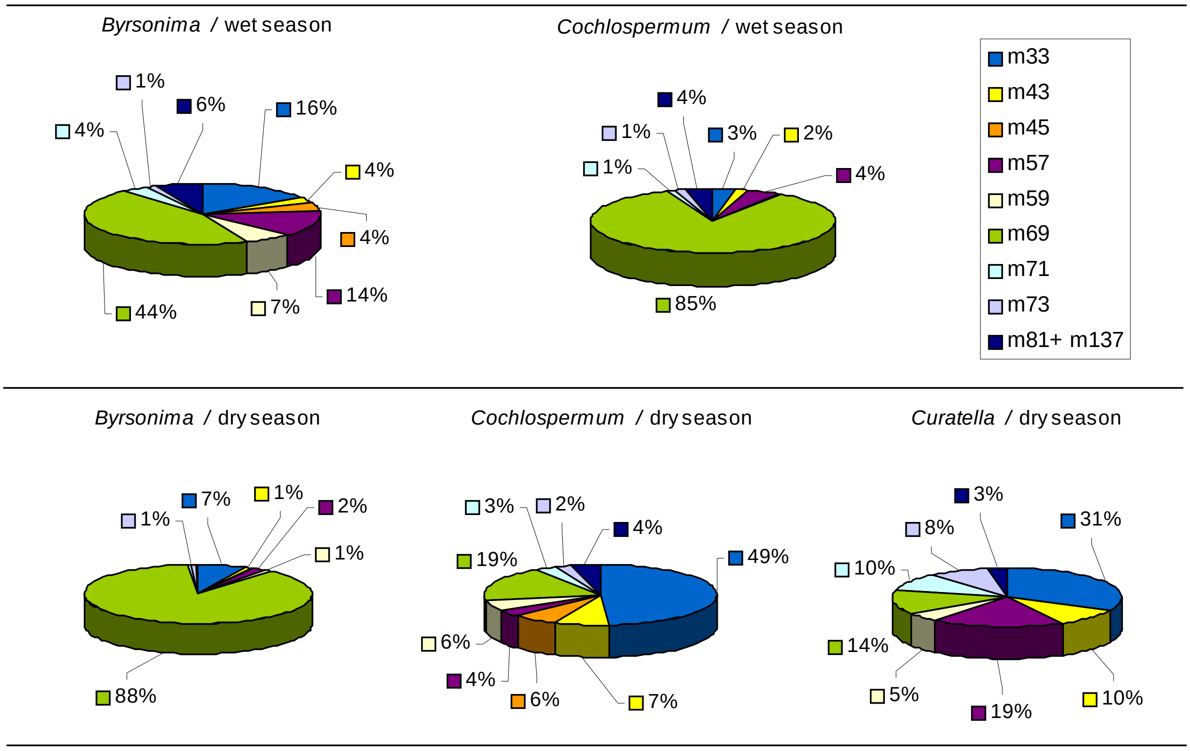


Fig 4.5. Average proportional distribution of individual VOCs to the sum of carbon emission from savanna trees.

4.4.3. Seasonal/developmental variations in VOC emissions

Byrsonima and *Cochlospermum* tree saplings were measured during one wet and one dry season, and the measurements could, unfortunately, not be made on the same individuals, since the wet season campaign was first (September-October 1999), and the measurement site was burned in the following dry season, prior to the dry season field campaign (March-April 2000). Therefore, all saplings studied in the dry season had new leaves, many of which were still expanding. Therefore, the seasonal variability of emission rates of is also a study of their developmental variability, and it is difficult to asses which factor exerts a greater influence on VOC emissions.

The standard emission rates of methanol from both species were higher in the dry than in the wet season: the emissions from *Byrsonima* by a factor of 4.6 and from *Cochlospermum* by a factor of ~3 (Table 4.9). This is in accordance with the fact that methanol is produced in greater amounts during cell wall expansion, for which *Cochlospermum* is a very good example. The tree saplings of this species measured in the wet season were ca. 80 cm high and the majority of leaves was fully developed. On the contrary, the saplings studied in the dry season were less than 40 cm high, and had tiny and delicate leaves. All four measured specimens (wet and dry season) had a similar number of leaves (between 40-60), but the difference in leaf size and leaf dry weight was astonishing: the saplings in the wet season had a leaf area and a dry weight of up to one order of magnitude higher than those in the dry season (Table 4.1). Accordingly, the high emission rates of the young leaves in the dry season are impressive.

A marked seasonal difference in isoprene standard emission rates was also observed. The isoprene emissions from the mature leaves of *Cochlospermum* in the wet season (23 µgC/g/h) were 25 times higher than those from the young and growing leaves in the dry season (~1 µgC/g/h; Table 4.9). This is consistent with previous studies which have shown that the developmental stage of the leaf plays a key role in determining isoprene emission capacity, with leaves of temperate and tropical broadleaf plants not producing isoprene until they were fully expanded (Grinspoon *et al.*, 1991; Kuzma and Fall, 1993). This pattern has been linked to the starting of activity of the enzyme isoprene synthase. Contrarily to *Cochlospermum*, for *Byrsonima* much higher isoprene emissions were measured in the dry than in the wet season. This difference might be attributed to differences in enzyme activity, due to genetic varieties, or as a result of unequal developmental stadiums of the leaves of both species in the dry season. It was not possible to find out if the leaves of the *Byrsonima* individuals were older than those of *Cochlospermum*; but from the size of the individual leaves (which could be verified from the photocopies of the leaves which were made for calculating the leaf area), and from the total leaf area range (Table 4.1) can be said that there was no evident difference in leaf size of the *Byrsonima* specimens measured in both seasons. This suggests that the leaves of the saplings in the dry season were already fully or almost fully developed, which was not the case of the *Cochlospermum* leaves.

Several other environmental factors such as the past temperature conditions (Monson *et al.*, 1992) and nitrogen supply also affect isoprene emission, but these factors are not expected to vary much for the studied specimens, since they were all growing close to each other. On the other hand, water stress, even when photosynthesis fell to zero, was found to have little effect on isoprene emission, however, after rewatering, the emission increased several fold above the pre-stress level, and stayed high for several weeks (Sharkey and Yeh, 2001). It can be speculated that the rainfall events at the beginning of the dry season measurements –which probably occurred after weeks of dryness– might have enhanced the emissions of *Byrsonima* leaves. This effect was probably smaller for the much less developed leaves, and therefore with lower isoprene synthase activity, of *Cochlospermum*.

Monoterpene emissions of both tree species were between 5-6 times higher in the wet season than in the dry season. Recent field works clearly showed that the monoterpene standard emission factor of holm oak (*Quercus ilex*) strongly change with leaf development and leaf age, and is related to the activity of monoterpene synthase in the leaves (Fischbach *et al.*, 2002). Enzyme activities were found to increase rapidly in spring after leaf emergence, reaching maximum values in summer, which declined during the following winter period. On the other hand, significant reductions in monoterpenes emissions have been found for holm oak and other Mediterranean trees under very dry conditions during the summer, which seem to be linked to water limitation generating a lack of carbon substrate, stomatal closing and to low relative humidities decreasing the permeability of the cuticle to gas exchange (Bertin and Staudt, 1996; Llusià and Peñuelas, 1998; Llusià and Peñuelas, 1999; Staudt *et al.*, 2002). According to this, the lower emissions of the saplings measured in the dry season may be due to the water stress usually prevailing this part of the year, and –in the case of *Cochlospermum*– to the early development stage of the leaves.

Other emissions like m57 (butene+butanol) and m71 (MACR+MVK) were also higher in the wet season, whereas for masses 43, 45, 59 and 73 the seasonal difference was not alike for both species (Table 4.9). Karl *et al.* (2003) found higher emissions of acetone (m59) and acetaldehyde (m45) above a hardwood forest during fall. They attributed the higher emissions to senescing and decay of biomass. No studies on seasonal or developmental variations of the emissions of the other compounds were found in the literature.

From the results discussed here a seasonal cycle of VOCs emission rates from the analyzed savanna trees cannot be inferred. Significantly different VOCs emission rates from leaves in different developmental stages were indeed observed, but more measurements on the same individuals over longer timer periods are needed to differentiate between variability of emission rates caused merely by the leaf age and a seasonal influence, likely water/nutrient stress and temperature “history”.

4.4.4. Comparison with other studies

Biogenic emission inventories show isoprene and monoterpenes as the most prominent and best-studied compounds. A recent review by Kesselmeier and Staudt (1999) compiles a number of emission factors of these and other VOCs for standard conditions of temperature (30°C) and light (1000 μmol/m^2/s PAR). Emission factors of isoprene were found to range over more than two orders of magnitude from below detection limit to a maximum of 360 μgC/g/h, an exceptionally high value observed for velvet bean, but emission factors are usually <100 μgC/g/h. Monoterpenes emission factors ranged from below detection limit up to 50 μgC/g/h (most emission factors being <10μgC/g/h). The maximum isoprene and monoterpene emission rates measured here (23 μgC/g/h and 1 μgC/g/h respectively, both from *Cochlospermum* in the wet season, Table 4.9) were rather in the lower end of the range found in the literature (Kesselmeier and Staudt, 1999, and references therein).

The emission of other biogenic VOCs has been poorly investigated. The available data for methanol is shown in Table 4.10. The range of standard emission rates observed for the three savanna tree species measured in this study (0.02-3.2 μgC/g/h) were comparable to the emissions from holm oak (Holzinger *et al.*, 2000), and in the lower range of the other reported emission rates (references 1-3 in Table 4.10).

Table 4.10. Overview of methanol emission rates from vegetation.

	details	Emission rate μg C/g (dw)/h	Observations	Reference
Methanol / m33				
B. crassifolia *C. americana* *C. vitifolium*	Wet and dry season	0.02-0.23 0.07-0.09 0.68-3.19	Normalized to 30°C	This work
Diverse species (14, tree species and agricultural crops)	Mature leaves Young leaves	0.5-17 5-23	Charcoal-filtered air passed through the cuvette	1
Bush bean and soybean cottonwood leaves		2-24 0.4-26		2
Aspen leaves	young	28-43		3
Quercus ilex (holm oak)		0.08-1.4	Maximum: root flooded; minimum: young leaves	4

1. MacDonald and Fall (1993); 2. Nemececk-Marshall et al., (1995); 3. Fall, R. (unpublished data, quoted in Heikes et al. 2002); 4. Holzinger et al., (2000).

Based on measurements reported in the literature, Guenther *et al.* (2000) estimated a methanol emission capacity for North American vegetation of 0.23 µgC/g/h. There are also canopy-scale flux measurements of oxygenated VOCs, including methanol, made over a pine plantation (Schade and Goldstein, 2001), a sub alpine coniferous forest (Baker *et al.*, 2001; Karl *et al.*, 2002b), and a mixed hardwood forest (Karl *et al.*, 2003a), but the fluxes were normalized to LAI (Leaf Area Index, defined as the leaf area per unit ground; and expressed in e.g. mg/m^2/h), hence difficult to compare to emission rates normalized to leaf dry weight.

The standard emission rates of mass 43 –attributed mainly to propene– measured in this work ranged between ‘no emission’ to 486 ngC/g/h (Table 4.9). Hakola *et al.* (1998) measured propene emission rates of young trees in Helsinki during the growing season, and found also great variability: tea-leafed willow emitted up to 700 ngC/g/h, whereas aspen and silver birch emitted less than 50 ngC/g/h.

Acetaldehyde emissions also ranged widely from ‘not detected’ to 308 ngC/g/h, and were between the limits reported by others who found emissions up to 820 ngC/g/h from stone pine, 490 ngC/g/h from holm oak (Kesselmeier *et al.*, 1997; Holzinger *et al.*, 2000), 812 ngC/g/h from cottonwood (Villanueva-Fierro *et al.*, 2004), 588 ngC/g/h from Douglas fir and 49 ngC/g/h from pinyon pine (Martin *et al.*, 1999).

Emissions of mass 57 (attributed to mainly butene and butanol) were found to be between 27 and 1685 ngC/g/h. In the abovementioned study in Helsinki (Hakola *et al.*, 1998), the butene emission rates from different trees ranged from 0-1971 ngC/g/h.

Acetone (m59) emissions varied between not detected to a maximum of 330 ngC/g/h (Table 4.9), and lie within the reported emission ranges of the literature: 734-1253 ngC/g/h from holm oak (Holzinger *et al.*, 2000), 14-428 ngC/g/h from pine, cottonwood and fir (Martin *et al.*, 1999; Villanueva-Fierro *et al.*, 2004), 870 ngC/g/h from Scots pine and 265 ngC/g/h from Norway spruce (Janson and de Serves, 2001). The emission factor derived by Guenther *et al.* (2000), 56 ngC/g/h, is in the lower end of the emission range reported to date.

The standard emission rates of MACR+MVK (m71) and MEK (m73) were in a similar range: m71, 4-240 ngC/g/h and m73, n.d.-389 ngC/g/h (Table 4.9). The emissions of m71 were lower than the observed for holm oak (201-806 ngC/g/h) and the emissions of m73 were within the range measured for holm oak (144-374 ngC/g/h) (Holzinger *et al.*, 2000).

4.5. Summary and conclusions

The results of enclosure measurements of the savanna tree species *Byrsonima crassifolia, Cochlospermum vitifolium* and *Curatella Americana* were discussed in this chapter. The studies with the tree saplings were conducted in Calabozo, during two field campaigns, one in the wet season 1999, and the second in the dry season 2000.

Most VOCs emitted from the trees were found to increase exponentially with temperature. The temperature dependence was modeled using the emission algorithm established by Guenther *et al.*, (1993). The estimates of coefficient β, which establishes the temperature dependence of emission rates, varied from 0.13 to 0.22 K^{-1} for all tree species. Variations were random without a clear seasonal trend and without significant differences among plants of the same species.

By means of the mentioned algorithm, the VOC emissions were normalized to a standard temperature of 30°C, in order to make emissions of different species and seasons comparable. The *standard* emission rates thus determined showed high variability. The interspecies and seasonal/developmental variations, which could be of more than an order of magnitude, were much higher than the plant-to-plant variability, which was around a factor of 3.

The sum of VOCs standard emission rates ranged between 0.64 and 27 μgC/g/h in the wet season, and 0.22 and 4.8 μgC/g/h in the dry season, for all measured species. The highest emissions were from *Cochlospermum* in the wet season. The total emission of this species in the wet season was 42 times higher than the emission from *Byrsonima* (principally due to the high isoprene emission of *Cochlospermum)*, whereas in the dry season, the total emission from *Cochlospermum* was only twice as high as those of *Byrsonima*. *Curatella* was a very low-emitting species; the total emission of this species in the dry season was lower than the emission of the other two species by more than an order of magnitude.

Isoprene and methanol were the most important emissions from *Byrsonima* and *Cochlospermum*, but the standard emission rates of these compounds as well as their relative contribution to the total VOCs emitted was very different. *Curatella* was a very low isoprene emitter, and methanol was the main emission of this species. The *Cochlospermum* individuals measured in the wet season, showed the highest isoprene standard emission rate (on average 23 µgC/g/h), which was about a factor of 70 higher than the emission from *Byrsonima*. Isoprene represented almost 50% of all carbon emitted by *Byrsonima*, and as much as 85% of the carbon emitted by *Cochlospermum* in the wet season. The highest methanol emissions (up to 3 µgC/g/h) were measured from *Cochlospermum* tree saplings in the dry season, whose leaves were still developing, and accounted for 50% of the total emitted carbon, while isoprene accounted for only 19%.

For the two isoprene-emitters *Byrsonima* and *Cochlospermum* the ratio of carbon released as VOCs to the carbon assimilated by photosynthesis was rather high, and varied between 2-15%. Isoprene accounted for most of the emitted carbon from these species. On the other hand, the assimilated carbon lost as VOC emissions from *Curatella* was only ~0.3%, and it was mainly due to methanol and monoterpenes emission.

5. Laboratory measurements of biomass-burning emissions

5.1. Introduction

Between February and March 2001, a series of experimental fires was carried out in Fire Sciences laboratory (FSL) of the USDA Forest Service, in Missoula (Montana, USA). The trace gas emissions from 44 fires of different biomass types from Africa, Indonesia and elsewhere were analyzed with PTR-MS and open-path Fourier transform infrared spectroscopy (OP-FTIR). The OP-FTIR was operated by Robert Yokelson and Ted Christian of the Chemistry Department of the University of Montana in Missoula. Each technique has its strengths and limitations: the PTR-MS quantifies many volatile compounds at ppt levels, but the complex mixture of gases produced by biomass burning makes the compound identification challenging. The OP-FTIR is well suited for identification and quantification of a large number of trace gases, but not below ppb levels (Goode *et al.*, 1999). The codeployment and comparison of both methods helped with optimizing the techniques and provided a comprehensive trace gas analysis of biomass fires.

The controlled conditions during the fire experiments in the laboratory, such as the knowledge of the properties of the fuel and the environment, and the high concentration of the chemical species in the smoke, facilitates an accurate determination of the emission factors of the measured compounds. This is an advantage of lab fires compared to fires occurring in natural vegetation, where is difficult to monitor a single fire from the beginning to the end and the fuel composition is not always known. On the other hand, the experimental fires must be carefully set up, since it is difficult to simulate natural fires in the lab. This applies to the chemistry and also the dynamics of the fires (e.g. the meteorological conditions prevailing during the fire affect the movement of the flame front) (Yokelson *et al.*, 1996; Andreae and Merlet, 2001).

5.2. The combustion process: definitions

The combustion of biomass involves several interconnected heterogeneous processes. They have been described extensively in previous works (Lobert and Warnatz, 1993; Yokelson *et al.*, 1996; Yokelson *et al.*, 1997; Bertschi *et al.*, 2003a), and only a short outline is given here. Thermal degradation of biomass begins with the drying/distilling process in which water and volatile contents of the fuel are released. The pyrolytic process starts when thermal cracking of the fuel molecules (basically cellulose, hemicellulose and lignin) occurs, at about 130°C. Above 200°C the high-molecular weight components are decomposed into char (carbon-enriched, solid intermediate), tar (intermediate molecular weight) and volatile organic compounds (flammable white smoke). In the presence of oxygen, the glowing process begins at ~530 °C. The gas products of the fuel bed are diluted with air to a flammable mixture that forms the flame, in which the relatively reduced compounds are oxidized to simple molecules, particularly CO_2, H_2O, NO and SO_2. This combination of processes is commonly known as “flaming combustion”. When these volatile flammable products are consumed, the flame ceases, and partially oxidized products of pyrolysis and glowing are emitted during the “smoldering combustion”. The diversity of substances emitted is much higher during this phase. The amount of substances emitted from a fire and their relative proportions are determined by the chemical composition of the fuel and to a large extent by the ratio of flaming to smoldering combustion (Andreae and Merlet, 2001). The emission ratio of CO to CO_2 ($\Delta CO/\Delta CO_2$; Δ indicates excess mixing ratio, i.e., concentration above ambient levels) the combustion efficiency (CE, fraction of burned carbon completely oxidized to CO_2) and the modified combustion efficiency (MCE), are useful as indices of the relative amount of flaming and smoldering combustion during a fire. CE is defined as the ratio of carbon emitted as CO_2 to the total carbon emitted (Ward and Hardy, 1991):

$$CE = \frac{[C_{CO2}]}{[C_{CO2}]+[C_{CO}]+[C_{CH4}]+[C_{VOCs}]+[C_{particulates}]+\ldots} \tag{5.1}$$

Thus, CE it is higher when the ratio of flaming to smoldering combustion is higher and has a maximum value of unity in the case of complete combustion, where all carbon is released as CO_2.

For practical purposes, the *modified* combustion efficiency (MCE) is often used instead of the combustion efficiency. Here, carbon compounds other than CO_2 and CO are neglected (Ward and Radke, 1993)

$$MCE = \frac{[CO_2]}{[CO_2]+[CO]} \tag{5.2}$$

In this work the MCE was used to define the periods during which flaming or smoldering was the predominant process during the course of a fire. Pure flaming usually has a MCE of 0.97-0.99 and pure smoldering usually has a MCE of 0.75-0.88 (Yokelson *et al.*, 1996). Whenever both phases were well defined during a burning experiment, the emission estimates will be given for both flaming and smoldering.

The concepts of emission ratio (ER) and emission factor (EF) will be used to quantitatively express the emission of trace gases from fires. The emission ratio relates the molar concentration of a particular species of interest to that of a reference species. Emission ratios are obtained by dividing the excess trace gas species concentrations by the excess concentration of a simultaneously measured reference gas. The selection of the reference gas is usually related to the combustion phase during which the compound of interest is mainly emitted. CO is therefore a suitable reference gas for smoldering, and CO_2 for flaming combustion. As an example, the $ER_{X/CO}$ of compound X relative to CO is given as

$$ER_{X/CO} = \frac{\Delta[X]}{\Delta[CO]} = \frac{[X]_{smoke} - [X]_{ambient}}{[CO]_{smoke} - [CO]_{ambient}} \tag{5.3}$$

Emission factors (EF) were calculated using the carbon mass balance method (e.g. Radke *et al.*, 1988) and are defined as the amount of a compound emitted (M_X) per amount of dry matter burned ($M_{biomass}$), expressed in g/kg $_{\text{dry matter}}$:

$$EF_X = \frac{M_X}{M_{biomass}} = \frac{M_X}{M_C}[C]_{biomass} \tag{5.4}$$

where M_C is the mass of carbon in the biomass consumed (it excludes the carbon that remains in the ash and other residuals) and [C] the fuel carbon content; both parameters can be determined for laboratory fires. The total carbon released is estimated by measuring all carbon compounds emitted from the fire, so that equation (5.4) can then be rewritten as

$$EF_X = \frac{[X]}{[C_{CO2}] + [C_{CO}] + [C_{CH4}] + [C_{VOCs}] + [C_{aerosol}] + \ldots}[C]_{biomass} \qquad (5.5)$$

where [X] is the concentration of species X, and $[C_{CO2}]$ etc. are the concentrations of the carbon-containing species in the smoke.

The emission factor of a compound X can be calculated from its emission ratio relative to compound Y, when the emission factor of compound Y is known:

$$EF_X = ER_{(X/Y)}\frac{MW_X}{MW_Y}EF_Y \qquad (5.6)$$

where MW_X and MW_Y are the molecular weights of the species X and the reference species Y, respectively.

5.3. Experimental

5.3.1. The combustion facility

The combustion facility (see also Yokelson *et al.*, 1996) is in a room that measures 12.5 x 12.5 m x 22 m high (Figure 5.1). A 1.6 m diameter, inverted-funnel exhaust stack with a 3.6 m diameter opening extends from ~2 m above the floor to the ceiling (Figure 5.2a). The room is kept at constant pressure with outside air that has been conditioned for temperature and humidity, and which is then vented through the stack, completely entraining the emissions from the fires burning beneath the funnel. A sampling platform surrounds the stack at 17 m elevation, where all the temperature, pressure and trace-gas measurement equipment for this experiment was deployed (Figure 5.2b).

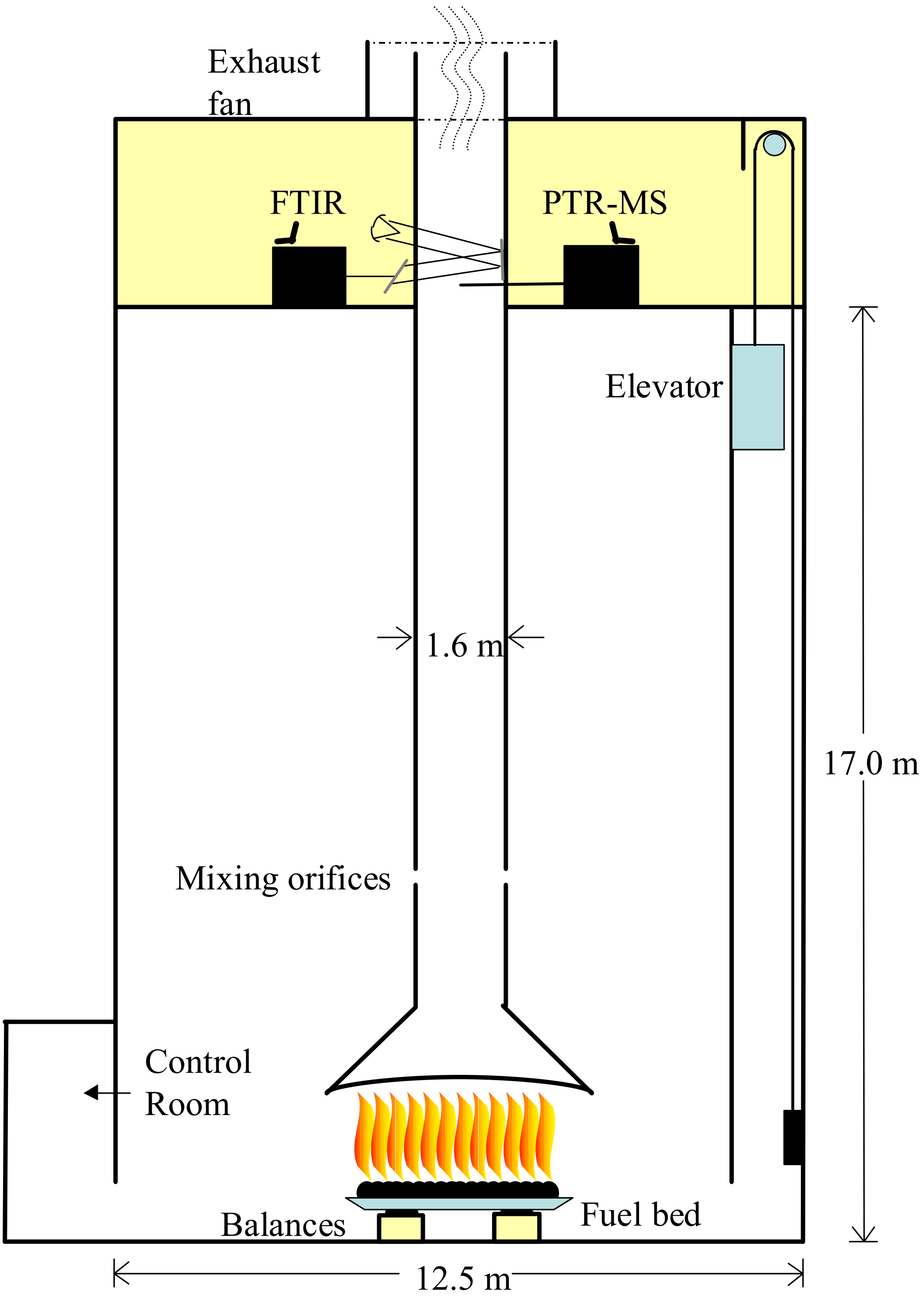


Figure 5.1. Combustion facility at the Fire Sciences laboratory in Missoula

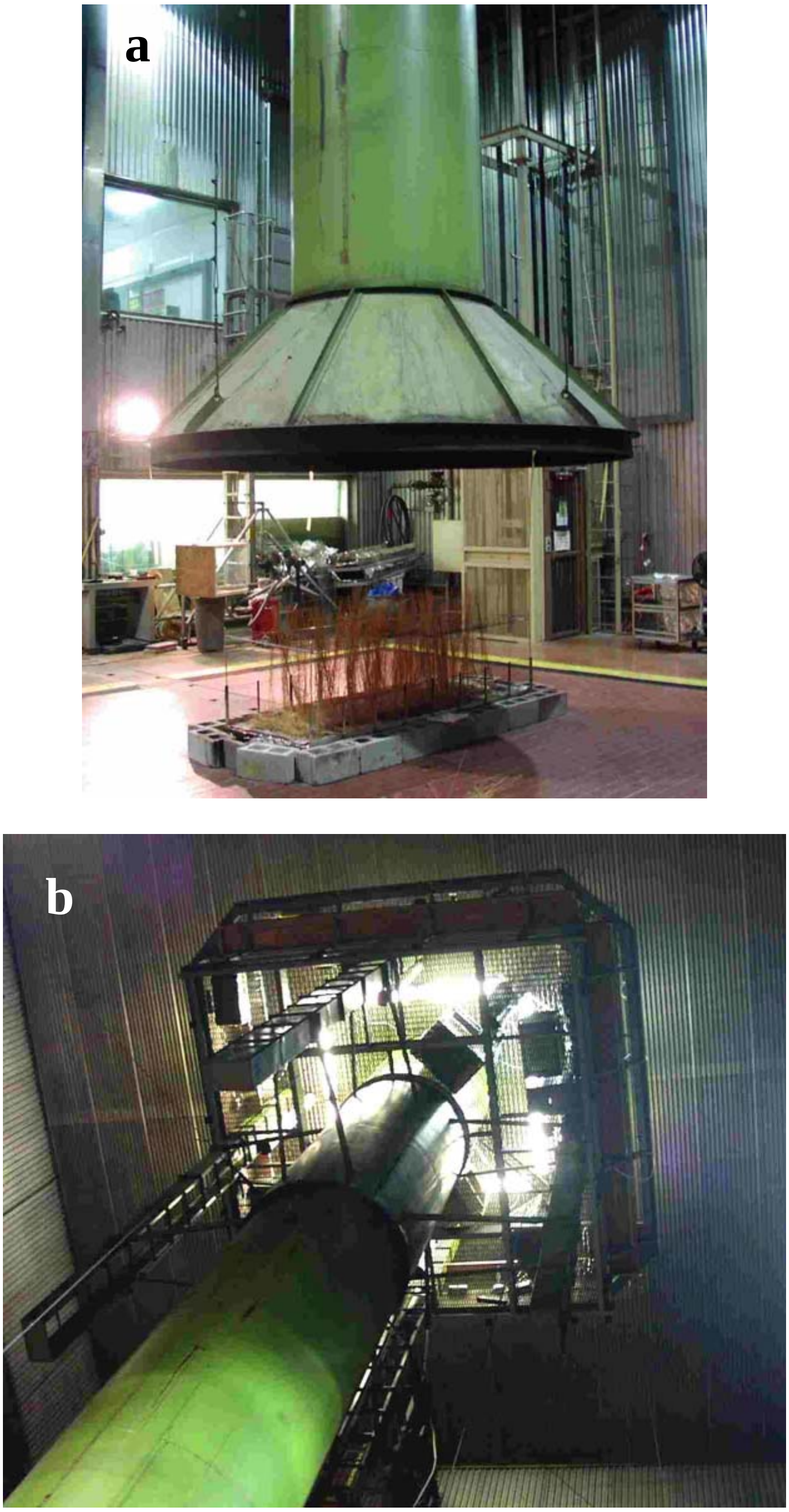


Figure 5.2. Fire Sciences Laboratory (a) fuel bed and inverted-funnel exhaust stack (b) sampling platform (at 17 m height).

Temperature, flow and mixing ratios were constant across the width of the stack at the height of the sampling platform, as determined by moving probes for point measurements to different positions within the stack. The fuel bed was a (80 x 210 cm) tray covered by an inert heat shield, a layer of sand, and is continuous weighed by two electronic balances (Mettler PM34).

5.3.2. Fuel selection and fire simulations

5.3.2.1. African fuels

Descriptions and elemental compositions of all the fuels are presented in Table 5.1. In fourteen of the forty-four experimental fires grass and leaf/twig litter from humid savannas in Zambia (Africa) was burned. There are ~7.7 million km^2 of humid, woodland savannas (also termed tropical dry forests) in the world, of which 5.5 million are in the central African plateau. Half of this area consists of miombo forest (2.8 million km^2) (International Geosphere-Biosphere Program (IGBP), 1997), which constitutes the largest contiguous dry forest/woodland savanna in the world. Miombo tree species are resistant to low/medium intensity fire, so that, underlying grasses and leaf litter are the primary fuels (Shea *et al.*, 1996; Hoffa *et al.*, 1999).

The miombo understory burns about every two years (Shea *et al.*, 1996; International Geosphere-Biosphere Program (IGBP), 1997) and this probably represents more biomass burning than in any other single ecosystem on Earth (International Geosphere-Biosphere Program (IGBP), 1997). Dambos are grassy depressions that occur within the miombo and can occupy up to 40% of the area of the landscape in some areas (International Geosphere-Biosphere Program (IGBP), 1997). Dambos usually burn annually (Hoffa *et al.*, 1999) and this accounts for a large fraction of African fires.

Miombo leaf/twig litter and miombo/dambo grasses were sampled in the western province of Zambia at the end of the dry season, shipped directly to Montana, and stored at low temperature until burning. For these fires, a layer of sand was used to cover the fuel bed, which was design to simulate the sandy miombo soils. For the dambo simulations, the grass was arranged vertically in clumps (held in place with a wire mesh with ~10 x 10 cm grid) in order to achieve as natural an effect as possible. For the miombo simulations, a ~50/50 mixture of grass and leaf/twig litter was used. The litter was dispersed as a layer on the sand.

The fuel loading for grass (dambo) fires was 0.65 ± 0.16 kg/m^2, and the average miombo total fuel loading was 1.0 ± 0.003 kg/m^2. Both are within the range of values measured in central Africa (Shea *et al.*, 1996; Hoffa *et al.*, 1999).

5.3.2.2. Indonesian fuels

Nearly 40% of Indonesian forests have been felled in the last 50 years, and the rate of deforestation is accelerating from 1 million ha/year in the 1980s, to 2 million ha/year after 1996 (Duncan *et al.*, 2003). However, there have been no classical fuel-consumption studies for Indonesian fires, and the relative importance of the fuel types is unknown (Christian *et al.*, 2003). A few studies observed which ecosystems burned in specific provinces of Indonesia during the fires associated with the 1997/8 El Niño haze event over southeast Asia. Peat swamp seems to be the dominant ecosystem that burned in south Kalimantan (Liew *et al.*, 1999), while in east Kalimantan ~75% of the 5.2 million hectares burned was lowland forest (mostly previously logged), secondary forest, plantations and farmland. Of the remaining 25%, 6% was grassland and 6% was peat swamp forest (Siegert *et al.*, 2001). The invasive fire-maintained grass “alang-alang” (*Imperata cylindrica*), appears to account for much of the fuel consumption in Indonesia (Pickford *et al.*, 1992). The burning of rice straw piles, which may smolder for several days, is a common practice in Indonesia and East Asia. The emissions from the following Indonesian fuels were burned: secondary forest floor litter, semak (brush that colonizes clearings), alang-alang, peat, and rice straw. A block of peat of ~25 cm^3 was sampled in south Sumatra, and the other fuels were sampled in Curug village (Bogor District, West Java). The fuel loading for alang-alang in this study (0.62 kg/m^2) was typical for grass loading worldwide, but only ~1/3 the loading of alang-alang measured by Pickford *et al*. (1992) on a single plot in Depok, West Java.

5.3.2.3. Other fuels

Fuels of North American forests (large-diameter hardwood log, shredded hardwood, organic soil, duff and litter) and grass collected near an industrial site in Germany were also burned.

Table 5.1 . Characterization of the fuel types, sorted by country of origin.
Given are averages of two samples of each fuel type. Carbon, hydrogen, nitrogen, and ash content were analyzed by an independent laboratory in the USA on a dry weight basis

Fuel Name	**#fires**	**Fuel Type**	**Origin**	**%H**[a]	**%N**	**%C**	**%ash**	**%C ash free**[a]
Dambo	8	Dry land dambo grass	Zambia	5.90	0.23	46.27	3.35	47.87
Miombo	5	Miombo vegetation type (~50:50 mixture of dambo grass and miombo litter)	Zambia	5.93	0.71	48.91	3.65	50.77
MiomboLitter	1	Miombo litter	Zambia	5.96	1.20	51.56	3.95	53.68
Alang-alang	4	Fire-maintained grass that colonizes after deforestation	Indonesia	5.25	0.78	42.07	10.30	46.89
IndoPeat	1	Peat	Indonesia	4.90	2.12	54.72	6.55	58.56
IndoSFLitter	4	Secondary forest litter	Indonesia	5.50	1.22	47.04	7.15	50.67
Rice straw	3	Rice stalks after grain has been removed	Indonesia	4.73	0.68	35.37	22.25	45.49
Semak	4	Successional shrub/brush after deforestation	Indonesia	5.37	1.33	46.83	6.80	50.24
German grass	3	Grass from heavily industrialized region	Germany	5.73	1.06	45.12	5.40	47.71
NWTDuff	1	Soil, litter, duff - Northwest Territories	Canada	5.09	1.62	56.82	2.80	58.45
Excelsior	2	Quaking Aspen, shredded	USA	5.92	0.06	47.67	0.00	47.67
Cottonwood	1	Hardwood log	USA	5.84	0.04	47.96	1.30	48.59
FirDuff	3	Douglas Fir forest floor duff, soil, litter	USA	4.65	1.06	42.41	20.85	53.58
PPine	3	Ponderosa Pine needles	USA	6.26	0.58	51.40	3.35	53.18
Ppine-FirDuff	1	Ponderosa Pine/Douglas Fir forest floor soil, litter, duff	USA	4.81	0.99	42.99	18.75	52.91

[a] %C ash free is defined as the actual %C that can be volatilized, and is expressed by the following equation: %C ash free = %C/(100 -%ash)x100.

5.3.3. Instrumentation

5.3.3.1. PTR-MS

The PTR-MS was located on the sampling platform and sampled continuously from the emissions stream. The sampling line was a ~2 m, 4 mm inner diameter (i.d.) Teflon tube, whose inlet was placed directly above the center of the OP-FTIR optical path (see description below). The sample line was kept as short as possible in order to minimize wall losses and assure a fast response time, which was around 5 s. A general feature of the PTR-MS technique is that the number of product ions (protonated compounds) must be less than ~5% of the primary ion signal, since too high signals of product ions cause problems of secondary reactions, which could lead to overestimation of substances with high proton affinities. Therefore the maximum mixing ratio of compounds susceptible to proton transfer reaction must be lower than 50 μmol/mol (Holzinger *et al.*, in preparation 2004). The first fuel that was burned (rice straw, which was expected to have very high emissions) met this condition. The next four fires -with different fuels- were also analyzed immediately and it was confirmed that dilution of the smoke was not necessary, since the maximum trace gas mixing ratio of 50 μmol/mol was never reached.

During the experiments, the PTR-MS was operated in one of two modes. In the full mass-scan mode the instrument was configured to scan incrementally from 17 to 142 atomic mass units, with a sample time of 20 ms per mass. In the selected-mass mode the instrument was configured to measure a selection of 30-36 masses, with a sampling time of 0.1 to 0.2 s for each mass. Overall time resolution in both modes was about 4 to 8 s.

Before each fire, the background air was measured for 2-5 min, and the average mixing ratios were subtracted from the fire emissions. The PTR-MS computer was synchronized with the rest of the data acquisition.

5.3.3.2. OP-FTIR

A total of eighteen substances were measured by OP-FTIR, eight of which are important compounds that cannot be measured by PTR-MS because of their low proton affinity (e.g. Methane (CH_4), ethylene (C_2H_4), acetylene (C_2H_2), nitric oxide (NO)), and others, whose quantification is difficult because their proton affinity is close to that of water (e.g. formaldehyde (HCHO), hydrogen cyanide (HCN)), or tend to stick to the surfaces (e.g. formic acid (HCOOH), ammonia (NH_3)).

The OP-FTIR was positioned on the sampling platform so that the open white cell spanned the stack directly in the rising emissions stream for continuous (0.83 s resolution) scanning. The system consists of a MIDAC model 2500 spectrometer, a 1.6 m base-path, open multipass cell, and an MCT (mercury-cadmium-telluride), LN_2-cooled detector. The path length was set to 57.7 m and the spectral resolution was 0.5 cm^{-1}. A detailed description of the system, and the spectral analysis technique employed can be found elsewhere (Yokelson *et al.*, 1997; Yokelson and Bertschi, 2002; Bertschi *et al.*, 2003a).

5.3.3.3. Canister sampling and other instruments

A total of eighteen stainless steel canisters were sampled during different burning phases of selected fires. The evacuated canisters were filled in less than 10 s to ambient pressure *("quick cans")* by means of a "cross" manifold and a 4 mm i.d. stainless steel sampling tube that opened next to the PTR-MS inlet. The sample line pressure was logged on the data system, so that the filling time was precisely known. The canisters were qualitatively analyzed by GC-MS in Mainz by Rolf Hofmann. The analysis was made in scan mode so that library comparisons could be made in order to confirm the presence of the compounds measured by PTR-MS and look for other emitted compounds.

Another set of fifty-eight canisters, forty-eight of which were filled at a linear rate, over a precisely known period, and twenty-eight quick cans, were analyzed by GC-FID for CO_2, CO, and C_1-C_4 hydrocarbons by the USDA Forest Service. In addition, seven quick cans taken during the fires were analyzed at the UC Irvine with GC-FID/GC-MS/GC-ECD. Mixing ratios for seven compounds measured either by FTIR or PTR-MS were obtained (ethylene, acetylene, propylene, isoprene, benzene, toluene, and *p*-xylene).

The sampling line also supplied air for continuous CO_2 (LICOR 6262) and CO (TECO 48C) measurements. The instruments were calibrated daily with NIST traceable standards. The smoke temperature at the platform height (chromel-alumel thermocouple), pressure, stack flow (Kurz mass flow meter model 455) and fuel mass were continuously monitored with 2 s resolution. Background CO_2 (LICOR 6262) was also continuously measured in the room where the combustion facility is located.

5.4. Results and Discussion

5.4.1. Preliminary tests

5.4.1.1. Homogeneity of the smoke

This biomass burning experiment represented also the first intercomparison of PTR-MS and OP-FTIR. The FTIR was deployed with its optical path spanning the smoke column 17 m above the fire (i.e. integrating the whole diameter of the stack), and the PTR-MS sample inlet, was placed in the center of the stack (above the center of the optical path of the OP-FTIR). If the assumption is made that the smoke was well mixed at the height at which both instruments were sampling/measuring, the burning experiments could perfectly well be used for an intercomparison of both techniques. In order to test this, during a long and stable smoldering fire (fir duff 2), the PTR-MS inlet was moved to several different positions within the stack. Figure 5.3 shows in the upper graph (a) that the ratio of PTR-MS methanol (point-source) to OP-FTIR methanol (path integrated) is independent of position, as the PTR-MS inlet is repeatedly moved from the center of the stack (80 cm) to within 4 cm of the stack wall. In (b) can be seen that there is no position dependence for acetic acid, which is a stickier compound. This indicates that the smoke was well mixed at the height of the platform.

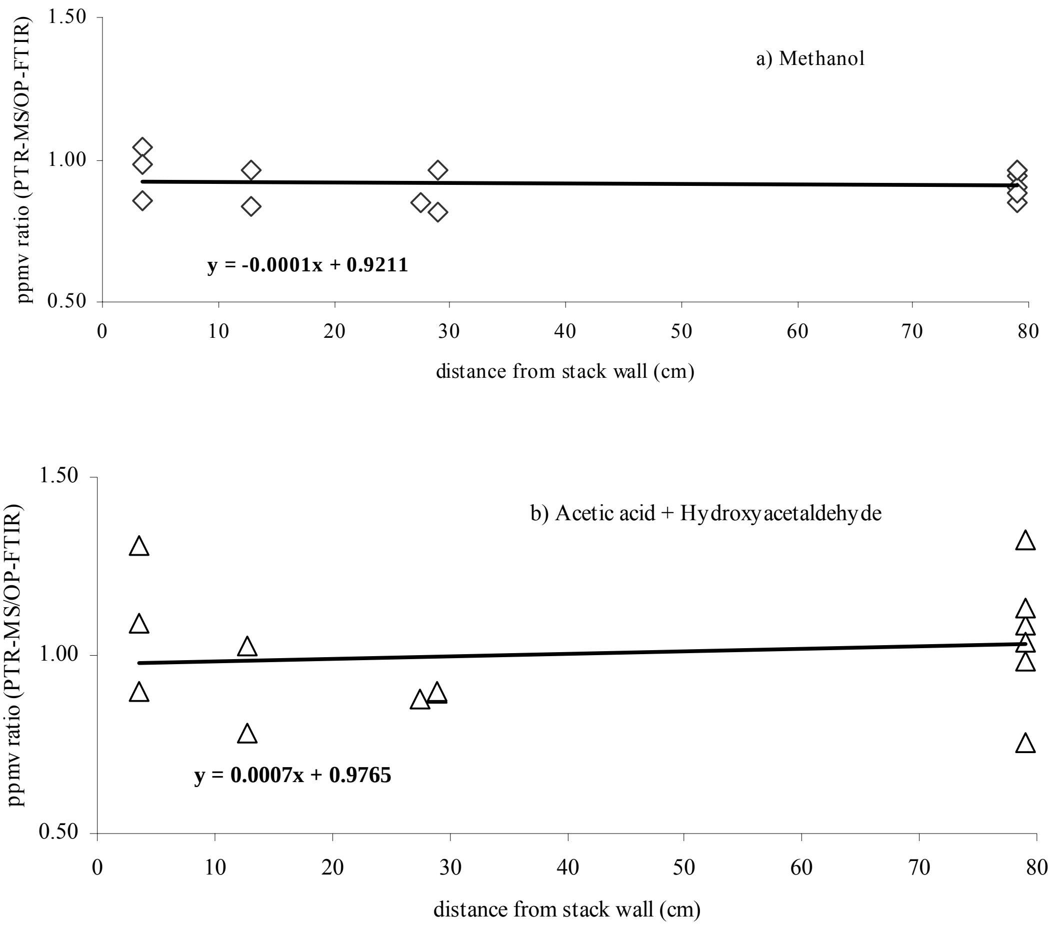


Figure 5.3. Inlet position test to verify the homogeneity of the smoke at the height of the sampling platform. The ratio of PTR-MS to OP-FTIR (a) methanol (mass 33) and (b) acetic acid + hydroxyacetaldehyde (mass 61). Values are 5 min averages.

5.4.1.2. Influence of particles

Another test was performed during the same fire as described in section 5.4.1.1. to evaluate if the presence of particles arising from the fires interfered with the measurements. For this test, a second PTR-MS inlet was placed in the stack, from which the sample was led through a Teflon filter (pore size 0.2 µm); the smoke was alternatively sampled with both inlets. The results shown in Table 5.2 indicate that particles did not interfere with the measurements. Consequently, for subsequent fires the inlet was used without any filter.

Table 5.2. Filtered PTR-MS inlet test. PTR/FTIR ratio switching every 5 min between a *filtered* and an *unfiltered* PTR-MS inlet.

	PTR/FTIR ratio	
	methanol	acetic acid
filter	1.032	1.017
no filter	0.985	1.156
filter	0.987	1.142
no filter	0.968	1.101
filter	0.990	1.242
no filter	1.041	1.251
filter	0.997	1.139
avg with filter	1.001	1.135
avg w/o filter	0.998	1.169

5.4.2. Compound identification

The identification and quantification of VOCs with the PTR-MS becomes more difficult as the complexity of the sample increases (i.e. unknown mixtures of compounds). With the combination of instruments deployed in this experiment, it was possible to obtain reliable mass peak identification for many mass signals.

The OP-FTIR measured ten gases which have a proton affinity higher than that of water; for these compounds it was therefore possible to obtain not only qualitative support for the PTR-MS mass peak identifications, but also a quantitative comparison. A quantitative comparison with the UCI canisters and a qualitative comparison with the Mainz canisters was also possible.

To quantify the comparison between the PTR-MS and OP-FTIR instruments, the excess mixing ratio of a specific mass measured by PTR-MS was integrated over the whole fire, and divided by the integrated excess mixing ratio of the compound measured by FTIR. The average ratio is hereafter abbreviated PT/FT. For calculation of the averages and standard deviations, the highest and lowest ratio for each compound were discarded, in each case n indicates the number of fires used for the calculation (n varies because the fires with a very low signal-to-noise ratio for a specific compound were excluded). This method was preferred over a linear correlation, because it is not affected by instrumental noise and imperfect synchronization (Christian *et al.*, 2004).

Mass 18 — Ammonia (NH_3) is detected on mass 18. This species has a high proton affinity but readily sticks to certain surfaces, including Teflon. This effect makes quantification of ammonia mixing ratios by PTR-MS very difficult. The OP-FTIR suffers from no such sampling artifacts, and the signal-to-noise ratio (S/N ratio) was high for all fires. Therefore, the results obtained by FTIR are preferred, and no quantitative comparison between the two measurement techniques is pursued for this species.

Mass 28 — hydrogen cyanide (HCN), mass 31 — formaldehyde (HCHO). The FTIR measurement of these gases are more reliable than the PTR-MS measurements, since HCN and HCHO have a proton affinity close to that of water (170.4 kcal/mol), so that the back reaction (deprotonation) is important in the PTR-MS drift tube and their observed concentrations are highly dependent on humidity. Hansel *et al.* (1997) described an approximate method to correct HCHO mixing ratios without calibration, which presumably can be also applied to correct HCN mixing ratios. For the present experiments the correction consists in multiplying the HCN mixing ratios by 4 and the HCHO mixing ratios by 8. As a result the PT/FT ratios of HCN and HCHO are 0.34 and 1.33 respectively.

Mass 33 — methanol (CH_3OH). Excelent agreement was obtained for methanol (PT/FT = 1.04 ± 0.118, n = 38). The methanol IR spectrum (and also that of ammonia) was remeasured in the fire lab in order to verify the calibration, and was found to be accurate to within a few percent (Yokelson *et al.*, 2003b).

Mass 43 — There are several compounds that may contribute to mass 43: propene (C_3H_6) , cyclopropane, 2- and 1-propanol (C_3H_6OH), which have a protonated mass of 61, but lose a water molecule after protonation, producing the $C_3H_7^+$ fragment, which is detected almost 100% at this mass, as well as ~30% of acetic acid (mass 61) that also fragments to mass 43 under normal measurement conditions. To account for the fragmentation of mass 61 (which was primarily acetic acid, together with smaller amounts of hydroxyacetaldehyde), the mixing ratio of mass 43 was decreased by 30% of the adjusted mass 61. The mixing ratios measured at mass 43 were normally higher than the propene mixing ratios measured by OP-FTIR (PT/FT = 2.33 ± 0.89, n = 19), but besides propene, no other compounds with protonated mass 43 were detected by OP-FTIR. Therefore it seems likely that other, as yet unidentified, species contributed to this mass via fragmentation processes.

Mass 47 — The majority of the signal at this mass is postulated to be formic acid (HCOOH), but the PTR-MS accounted for only about half the formic acid measured by the FTIR (PT/FT = 0.417 ± 0.168, n = 38). Losses in the inlet or on metal surfaces of the PTR-MS probably account for this difference, as formic acid readily adsorbs onto many surfaces. Nevertheless, no time delay in the response of the signal at this mass was observed, thus it is possible that the signal came from ethanol (C_2H_5OH), which fragments upon protonation to yield ~10% mass 47 (Williams *et al.*, 2001) or dimethylether (C_2H_6O), but neither of these species was detected by FTIR.

Mass 59 — The FTIR can measure several mass 59 candidates: acetone (C_3H_6O) was not always measurable by the FTIR instrument because the most suitable IR peak is fairly broad and overlapped by complex structure due to other compounds in smoke. Methylvinylether (MVE), an acetone isomer, was measured in all fires. Propanal showed a very noisy signal, and was always around the detection limit. Other candidates, like trimethylene oxide and propylene oxide, which have reasonably strong and isolated IR peaks, and glyoxal, which has been identified as a major product of the fast pyrolysis of biomass (Thamburaj, 2000), were not detected. The GC-MS spectrum shows two close peaks, acetone and propanal, and some smaller peaks at higher retention times, but since propanal was below the detection limit of the FTIR, it can be concluded that the signal at mass 59 is mostly acetone and MVE. These two compounds are combined in the FTIR fraction of the PT/FT ratio, which was 1.29 ± 0.81 (n = 29). The average PT/FT varied with the fuel type: for both the miombo and dambo fires the ratio was <0.7, but for all other fuels the average PT/FT was >1.0. When the relative contribution of acetone and MVE to the total mass 59 signal is calculated for the different fuels, the results show that in the dambo and miombo fires MVE accounts for 70-100% of mass 59, and ~30% (on average) for the other fuel types. Further details of these results will be given in the discussions on African and Indonesian fuels (sections 5.4.5 and 5.4.6, respectively).

Mass 61 — Acetic acid (CH_3COOH) and its isomer hydroxyacetaldehyde (glycolaldehyde) were determined by FTIR and accounted, within experimental uncertainty, for the mass 61 signal (PT/FT = 1.17 ± 0.34, n = 39). As mentioned for mass 43, the mass 61 signal was corrected to account for fragmentation in the drift tube. On average, hydroxyacetaldehyde accounts for 17.8 ± 8.4% of the signal on mass 61 (<10% in mainly smoldering fires like fir duff and indo peat, and >15% in faster burning fires). In the two earlier biomass burning experiments in which smoke was analyzed with PTR-MS (Holzinger *et al.*, 1999, and 2004), appreciable acetic acid was lost in the instrument inlet, but in this experiment the fast response and the good agreement with the FTIR suggest that this problem was overcome by using a shorter inlet. This was possible thanks to the larger combustion facility available in Montana. The wider and longer stack permits more entrainment of air and so no smoke-dilution system (which would make the sampling line significantly longer) was needed.

Mass 69 — Two compounds with protonated mass 69 were detected with FTIR: furan (C_4H_4O) and isoprene (C_5H_8). The FTIR data showed that, in most fires, the PTR-MS signal arose principally from furan and only secondary from isoprene. The PT/FT ratio was 0.783 ± 0.465 (n = 39). The GC-MS spectra of the Mainz canisters also showed a dominant furan peak and some isoprene. The IR spectral analysis for furan is complicated by CO_2 lines at high CO_2, which occurred in almost all grass-type (alang-alang, dambo and miombo) and pine fires. Additionally, for many grass fires the furan S/N ratio was low. To account for this effect, the contribution of furan to the total signal on mass 69 was retrieved from the fires that burned less efficiently (and consequently had good S/N ratio and did not present the interference caused by the high CO_2 levels). On average, the furan/mass69 ratio was 0.59 ± 0.28.

Mass 75 — This mass was attributed to acetol (hydroxyacetone, $C_3H_6O_2$) This compound has not been reported previously in biomass burning emissions, but large emissions were detected by FTIR, especially from the rice straw and other fuels that were consumed primarily by smoldering combustion. Based on these results, the IR cross-section of acetol was measured at five concentrations, and fragmentation and response time tests were performed for the PTR-MS, showing that ~80% is detected at mass 75 and ~20% at mass 57. This fragmentation was accounted for in the PTR-MS results. The average PT/FT ratio was 0.416 ± 0.289 (n = 36), but the FTIR S/N ratio in the majority of fires was very low, and thus the experimental precision was very low. Alternatively, when the fire-integrated PTR-MS mixing ratios were plotted against the FTIR mixing ratios for all fires, the slope (0.81 ± 0.018) of the linear regression gives an estimate on the average ratio that heavily weighs the larger values, which correspond to higher signal to noise. This implies good agreement between FTIR and PTR-MS at high mixing ratios.

Mass 95 — On average, all of the PTR-MS signal on mass 95 could be accounted for by the FTIR phenol (C_6H_6O), but the measurement scatter was very high (PT/FT = 0.843 ± 0.845). The large scatter was mostly due to fires with low S/N ratio, but there was also evidence of contributions of unknown substances to the mass 95 signal at high S/N. Many substances with molecular mass 94 could be potentially detected at this mass, such as other compounds with molecular formula C_6H_6O (e.g. 2-vinyl-furan, Friedli *et al.*, 2002), or C_7H_6, and also nitrogen-containing compounds with formula $C_5H_6N_2$, such as pyridinamine. No other mass 95 candidates were detected by FTIR, however. To investigate the contribution of low S/N ratio to the scatter, a similar plot as for mass 75 was made. The correlation obtained suggests that the agreement was usually excellent at high signal levels, (5 of the 7 fires with highest S/N ratio defined a line with slope 1.02 ± 0.0367) and that other substances may have contributed to mass 95 in the other two fires.

Benzene (C_6H_6), toluene ($C_6H_5CH_3$) and p-xylene, were analyzed in the UCI canisters. Good agreement with the PTR-MS measurements was obtained for benzene (mass 79) and toluene (mass 93), with UCI/PT ratios of 1.2 and 1.3 respectively. The mean UCI/PT ratio for *p*-xylene (mass 107) was ~0.4. This is not very surprising, since other xylenes, as well as ethyl benzene and benzaldehyde are also detected at this mass by PTR-MS and all are emitted in biomass burning (Andreae and Merlet, 2001). Also, small losses of *p*-xylene in the canisters are possible (see Christian *et al.* 2004).

Other important emissions detected in the canisters analyzed in Mainz were:

Mass 42 — This mass was measured with PTR-MS in all fires, and is assigned to acetonitrile (CH_3CN) (Holzinger, 1999). There are no known fragmentation ions at this mass and it is difficult to think of another plausible candidates, especially because compounds detected at an even protonated mass always must contain one odd-valent atom such as nitrogen, which automatically excludes all the molecules containing exclusively carbon, hydrogen and oxygen. A small interference at mass 42 might occur from propyne, propadiene and/or cyclopropene molecules containing one ^{13}C-atom. However the abundance of ^{13}C is only 1.108% of all carbon, and so only ~3% of these compounds contain a ^{13}C-atom. The reaction of O_2^+ with some alkanes or alkenes (Spanel and Smith, 1998) could also cause a signal on mass 42. The O_2^+ ions are an impurity coming from the ion source, but their abundance is usually <2% of the H_3O signal, and therefore the interference should be minor. Acetonitrile was not detected in any FTIR spectra because its IR cross-section is small.

Mass 45 — This mass is postulated to be acetaldehyde (CH_3CHO) (Holzinger *et al.*, 1999). Acetaldehyde was not detected by FTIR, since the only isolated features in the IR spectrum of this compound are too weak, even at the relatively high mixing ratios measured by PTR-MS in the fires, to be readily detectable by FTIR. It was also not possible to attribute any IR absorption lines to other mass 45 candidates such as ethylene oxide. The GC-MS spectrum shows the tailing of the CO_2 peak, a propane peak, acetaldehyde and some small peaks at higher retention times. Since CO_2 and propane are not detected by PTR-MS, and the smaller peaks at longer retention times are probably the result of fragmentation, which does not occur at the lower energies in the PTR-MS, the identification of this mass is supported.

The proposed identities of the 60 significant mass signals that were detected with PTR-MS are presented in Table 5.3. The *proposed ion identity* is based primarily on the results of recent measurements of biomass-burning emissions performed at the Max Planck Institute in Mainz (December 2000-January 2001). Further information of many ion species was obtained by means of analyzing signals at masses m+1 and m+2 (and making use of the known natural isotopic abundances of carbon (^{13}C), oxygen (^{18}O) and nitrogen (^{15}N)) (Holzinger *et al*, in preparation 2004). To maximize precision in this analysis, the isotopic analyses of all fires were combined. Results from single fire measurements were often not precise enough to deduce the number of carbons, thus it cannot be excluded that the identity of a particular mass might be different for individual fires or different fuel types. The assignment of the ionic species to neutral gases was also supported by GC-MS analysis of some canister samples and complemented by previous studies on emissions from biomass burning (Andreae and Merlet, 2001; Friedli *et al.*, 2001) and tobacco smoke (Dalluge *et al.*, 2002). Nevertheless, the identification of some mass signals has to be regarded as uncertain because of the presence of isomers and fragments that can contribute to the signal in many cases. For further evaluations the compounds were classified into 3 sub-groups, namely, partially oxygenated volatile organic compounds (POVOCs), unsaturated + aromatic hydrocarbons, nitrogen-containing compounds (N-compounds, i.e. N-VOCs measured by PTR-MS and HCN + NH_3 measured by FTIR, NO is not included).

Table 5.3. Significant mass signals detected in biomass fires, proposed identification, ion identity and classification by chemical group.

Mass	Possible identification[a]	Proposed ion identity	classification
33	***Methanol***	COH_5^+	POVOC
39	C_3H_3+ fragment	$C_3H_3^+$	Unsat. + Aromatic
41	***1,2-propadiene; 1-propyne; Cyclopropene***	$C_3H_5^+$	Unsat. + Aromatic
42	***Acetonitrile***	$C_2NH_4^+$	N-Compound
43	***Propene, Cyclopropane***; Propanol	$C_3H_7^+$	Unsat. + Aromatic
44	Acetaldimine; Ethenamine; Ethylenimine	$C_2NH_6^+$	N-Compound
45	Acetaldehyde	$C_2OH_5^+$	POVOC
46	NO_2^+ fragment	NO_2^+	N-Compound
49	CH_4S	CSH_5^+; $CO_2H_5^+$	other
53	Butenal	$C_4H_5^+$	POVOC
54	***2-propenenitrile***	$C_3NH_4^+$	N-Compound
55	***1-butyne; 1,2-butadiene; 1,3-butadiene***	$C_4H_7^+$	Unsat. + Aromatic
56	Propanenitrile	$C_3NH_6^+$	N-Compound
57	***1-butene; (Z)-2-butene; 2-Methyl-1-propene;*** Acrolein	$C_4H_9^+$	Unsat. + Aromatic
58	Propenamine; Propanimine	$C_3NH_8^+$	N-Compound
59	***Acetone, Propanal***, Glyoxal, ***Methyl vinyl ether (MVE)***	$C_3OH_7^+$	POVOC
60	Propanamine	$C_3NH_{10}^+$	N-Compound
61	***Acetic acid, Hydroxyacetaldehyde***	$C_2O_2H_5^+$	POVOC
62	Ethylenediamine; 1,1-dimethyl-Hydrazine	$C_2H_7NO^+$	N-Compound
67	***1,3-cyclopentadiene; (E)-3-penten-1-yne; 1-pentene-3-yne***	$C_5H_7^+$	Unsat. + Aromatic
68	***2-Methyl-2-propenenitrile; 2-butenenitrile; 3-butenenitrile;*** Pyrrole	$C_4NH_6^+$	N-Compound
69	***Furan; Isoprene; (E)-1,3-pentadiene; 1,4-pentadiene, Cyclopentene***, Cyclopentanol	$C_5H_9^+$; $C_4OH_5^+$	Unsat. + Aromatic
70	Butanenitrile	$C_4NH_8^+$	N-Compound
71	***cis-(trans)-1,2-dimethyl cyclopropane, Ethyl cyclopropane; 2-methyl-2-butene; 2-methyl-1-butene; 3-methyl-1-butene; 1-pentene; (Z)-2-pentene; 2-methyl-2-propenal; Methyl vinyl ketone (MVK);*** Methacrolein	$C_5H_{11}^+$; $C_4OH_7^+$	Unsat. + Aromatic; POVOC
73	***2-Butanone(methyl ethyl ketone, MEK)***; Butanal	$C_4OH_9^+$	POVOC
75	***Acetol***	$C_3O_2H_7^+$	POVOC

Table 5.3. continued

Mass	Potential identification	Ion identity	classification
79	***Benzene***	$C_6H_7^+$	Unsat. + Aromatic
80	Pyridine	$C_5NH_6^+$	N-Compound
81	$C_4H_4N_2$ (Pyrazine; Diazine; Pyridazine); Cyclohexadiene	$C_4N_2H_5^+$, $C_6H_9^+$	N-Compound; Unsat. + Aromatic
82	Methylpyrrole; C_4H_3NO	$C_5NH_8^+$; $C4NOH_4^+$	N-Compound
83	Methylfuranes	$C_5OH_7^+$	POVOC
84	Pentanenitrile	$C_5NH_{10}^+$	N-Compound
85	1-hexene; C_6-Alkenes	$C_6H_{13}^+$	Unsat. + Aromatic
87	2,3-butanedione; Pentanone	C_5OH_{11}+	POVOC
89	Hydroxybutanone	$C_4O_2H_9^+$	POVOC
91	Butanethiol ($C_4H_{10}S$)	$C_4SH_{11}^+$	other
93	Toluene; 1,3,5-cycloheptatriene	$C_7H_9^+$	Unsat. + Aromatic
94	Methylpyridine	$C_6NH_6^+$	N-Compound
95	***Phenol***; Pyridinamine $C_5H_6N_2$	$C_6OH_7^+$; $C_5N_2H_7^+$	POVOC
96	Pyridineoxide; Dimethylpyrrole	$C_5NOH_6^+$; $C_6NH_{10}^+$	N-Compound
97	Furfural; Dimethylfuran; Ethylfuran	$C_6OH_9^+$	POVOC
99	C_7-Alkenes	$C_7H_{15}^+$	Unsat. + Aromatic
101	Hexanone	$C_6OH_{13}^+$	POVOC
103	Hydroxy-pentanone	$C_5O_2H_{11}^+$	POVOC
104	Benzonitrile	$C_7NH_6^+$	N-Compound
105	Styrene	$C_8H_9^+$	Unsat. + Aromatic
107	***Ethylbenzene; p-xylene; benzaldehyde***	$C_8H_{11}^+$; $C_7OH_7^+$	Unsat. + Aromatic
109	Benzyl alcohol	$C_7OH_9^+$	POVOC
111	Trimethylfuran	$C_7OH_{11}^+$	POVOC
113	C8-Alkenes	$C_8H_{17}^+$	Unsat. + Aromatic
115	$C_5H_{10}N_2O$; $C_6H_{14}N_2$	$C_5N_2OH_{11}^+$; $C_6N_2H_{15}^+$	POVOC
117	Hydroxy-hexanone	$C_5O_2H_{11}^+$	POVOC
118	Benzeneacetonitrile	$C_8NH_8^+$	N-Compound
119	Benzofuran; 3-hydroxyphenylacetylene	$C_8OH_7^+$	POVOC
121	***1-ethyl-2-methyl-benzene; 1-ethyl-3-methyl-benzene***	$C_9H_{11}^+$	Unsat. + Aromatic
123	N,N-Dimethyl-pyridinamines, Niacinamide	$C_7N_2H_{11}^+$; $C_6N_2OH_7^+$	N-Compound
125	$C_7H_{12}N_2$; $C_8H_{12}O$	$C_7N_2H_{13}^+$; $C_8OH_{13}^+$	POVOC; N-Comp
127	C_9-Alkenes	$C_9H_{19}^+$	Unsat. + Aromatic
129	Naphtalene	$C_{10}H_9^+$	Unsat. + Aromatic
135	C_{10}-Benzenes	$C_{10}H_{14}^+$	Unsat. + Aromatic

[a] the compounds in bold italics were either quantitatively (FTIR) or qualitatively (GC-MS) analyzed, or have been reported in the literature as biomass burning emissions (e.g. Andreae and Merlet, 2001; Friedli *et al.*, 2001).

5.4.3. Fire characterization

Table 5.4 summarizes the basic data from forty-four experimental fires of fifteen fuel types. The fire names are listed in alphabetical order. The abbreviated name will be used henceforth to identify individual fires. Fourteen fires were measured in the PTR-MS scan mode and the remaining thirty were measured in the selected masses mode (or multiple-ion detection, mid). The emission factors (EF) were estimated for the entire fire (total, T), and whenever possible, further separated in flaming (F) and smoldering (S) phases. The duration of the fires was very diverse; the grass fires lasted between 3 and 11 min, while duff and peat fires burned for several hours. The combustion factor (CF) is defined as the percentage of the fuel that was consumed. The moisture content was determined by measuring the mass loss after storing an unburned sample at 90°C overnight. Fuel moisture (FM) is expressed as percentage dry weight:

$$FM = \left(\frac{wet - dry}{dry} \right) 100 \tag{5.7}$$

As mentioned in section 5.2, the composition of fire emissions is mainly determined by the chemical content of the biomass (carbon, nitrogen, sulfur, halogens, minerals, etc.), and by the physical and chemical processes which occur during the combustion (the relative contributions of flaming and smoldering combustion). The combustion type predominating in a given fire is influenced by various physical properties of the biomass and the fuel bed, such as the fuel moisture content, density and structure, and the compactness of the fuel bed (i.e. oxygen availability in intense flaming).

Flaming combustion normally dominated in typical grass fires (i.e. alang-alang, dambo, German grass and miombo), characterized by tall, fast moving flames that usually consumed more than 80% of the fuel. If the burning was uniform, as in the case of the miombo fire shown in Fig 5.3, the maxima of the CO_2 and CO peaks were well differentiated, and the transition between flaming and smoldering consumption was clearly distinguishable. During the flaming stage in such a fire the MCE is higher than 0.97. A sharp decrease of the CO_2 emissions occurred when the flames ceased, causing a drop in the MCE. In the transition period of the fire (mixed phase), when spots with small flames were mixed with areas of smoldering combustion, the MCE normally ranged between 0.97 and 0.85.

Table 5.4. Basic information about the individual fires[a]

Fire name	Short name	Meas. mode	EF	Duration (s)	Initial fuel mass (g)	Residue (g)	CF (%)	Fuel Moisture (dry %)
Alang2	al2	mid	F/S/T	260	1158	633	45.3	41.9
Alang3	al3	mid	F/S/T	412	584	148	74.6	10.6
Alang4	al4	mid	F/S/T	240	1153	132	88.6	10.6
Alang5	al5	mid	F/S/T	386	~1119			8.7
Cottonwood1[b]	cw1	scan	T	12571	19930	11320	43.2	14.6
Dambo3	db3	scan	F/S/T	231	734	96	86.9	5.8
Dambo4	db4	scan	F/S/T	283	799	104	87.0	6.6
Dambo7	db7	mid	F/T	219	1308	509	61.1	7.5
Dambo8	db8	mid	F/S/T	237	903	81	91.1	7.5
Dambo9	db9	mid	F/S/T	240	979	34	96.6	7.3
Dambo11	db11	mid	F/S/T	208	1441	55	96.2	10.4
Dambo12	db12	mid	F/T	231	1308	508	61.1	16.4
Dambo13	db13	mid	F/S/T	191	1291	65	94.9	17.3
Excelsior1	ex1	mid	F/S/T	668	709	7	99.0	6.4
Excelsior2	ex2	scan	F/S/T	560	657	1	99.9	6.4
FirDuff2	fd2	mid	T	3856	5023	4159	17.2	14.8
FirDuff3a	fd3a	scan	T	1583	1247	998	20.0	12.3
FirDuff3b	fd3b	scan	T	3622	3028	1732	42.8	12.3
GerGrass1	gg1	mid	F/S/T	519	544	122	77.6	9.2
GerGrass2	gg2	mid	F/S/T	415	479	51	89.3	9.7
GerGrass3	gg3	mid	F/S/T	458	544	101	81.5	21.6
IndoPeat2	ip2	scan	T	8632	2751	2333	15.2	30.5
IndoSFLit1	il1	mid	F/S/T	3127	500	40	92.0	17.1
IndoSFLit2	il2	mid	T	2460	399	54	86.5	17.9
IndoSFLit3	il3	mid	T	1844	411	53	87.0	12.8
IndoSFLit4	il4	scan	F/S/T	1493	510	50	90.2	13.2
MboLit3	ml3	mid	F/S/T	1187	2650	2321	12.4	12.6
Miombo1	mb1	mid	F/S/T	702	1673	438	73.8	8.7
Miombo2	mb2	mid	F/S/T	467	1645	448	72.8	9.5
Miombo3	mb3	mid	F/S/T	698	1659	403	75.7	9.1
Miombo4	mb4	mid	F/S/T	479	1717	540	68.5	10.5
Miombo5	mb5	mid	F/S/T	717	1778	551	69.0	10.4
NWTDuff1	nw1	mid	T	8384	1145	231	79.9	10.7
PPine1	pp1	scan	F/S/T	2501	452	23	94.8	15.9
PPine2	pp2	mid	F/S/T	1975	5020	59	98.8	15.0
PPine3	pp3	scan	F/S/T	2147	5004	224	95.5	15.0
PPineFirDuff1	pf1	scan	T	5398	5342	3114	41.7	15.8
RiceStraw1	rs1	mid	T	2356	656	130	80.2	32.3
RiceStraw2	rs2	mid	T	932	486	157	67.7	20.8
RiceStraw3	rs3	scan	T	1812	684	141	79.3	18.8
Semak1	sk1	scan	T	672	305	39	87.1	26.9
Semak2	sk2	scan	F/S/T	609	176	6	96.4	24.0
Semak3	sk3	mid	F/S/T	2330	455	74	83.8	12.6
Semak4	sk4	scan	F/S/T	1751	415	84	79.8	12.1

[a] The fire names are listed in alphabetical order. Measurement mode (Meas. mode) is either *scan* (from 17 to 142 amu) or *mid* (multiple ion detection). Emission Factors (EF) indicates which emission factors could be estimated F/S, flaming and smoldering; T, total (fire-averaged). Combustion factor (CF) is the percentage of the fuel that was consumed. Moisture content was determined by measuring the mass loss after holding the sample at 90°C overnight.

[b] Cottonwood log, radius=18cm, length=47cm

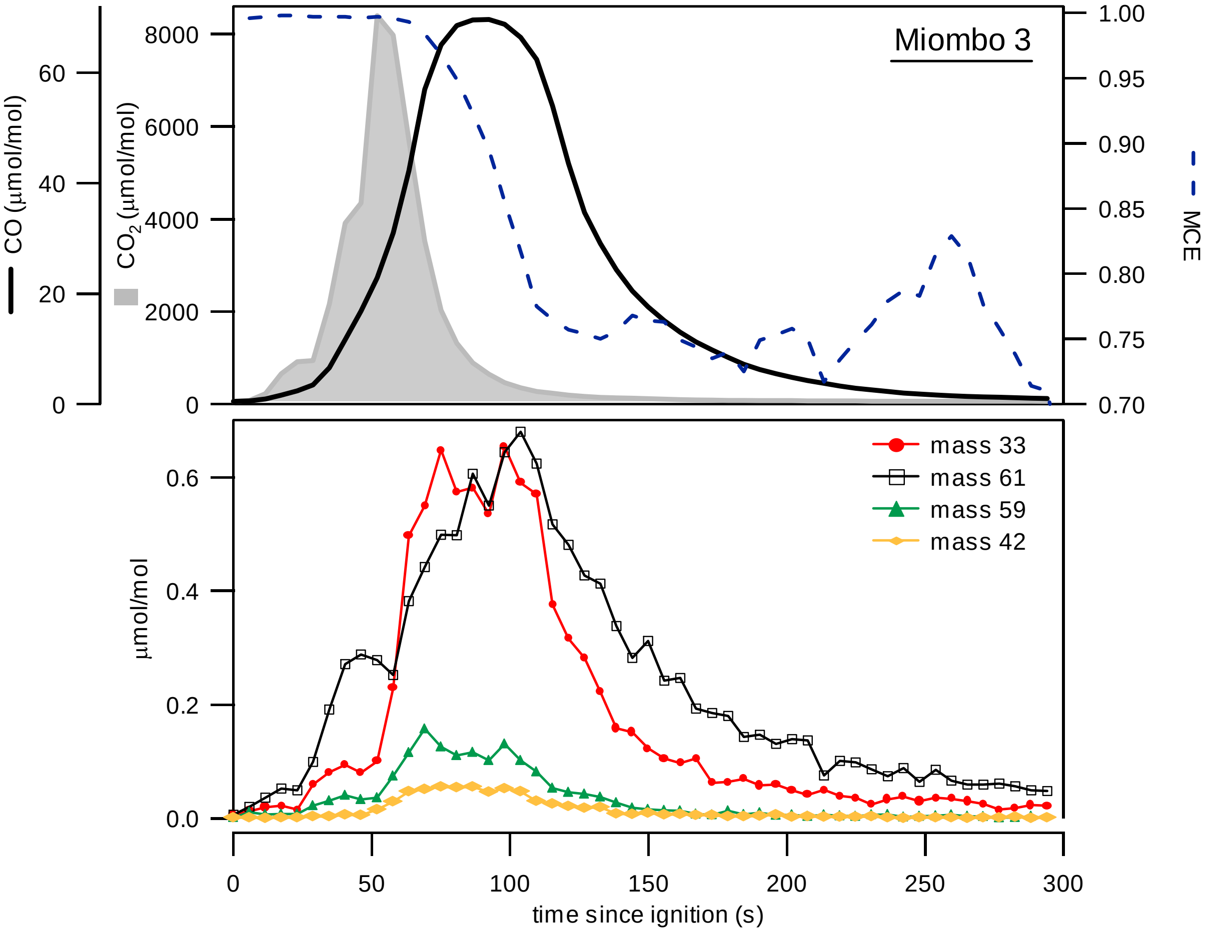


Figure 5.4. Example of the course of a fast and regular fire. The upper panel of the graph shows the mixing ratio (ppm) of CO, CO_2 and the modified combustion efficiency (MCE) during a Miombo fire. MCE values are used to define periods of flaming (MCE > 0.97) and smoldering (MCE 0.85 – 0.75). The lower panel shows mixing ratios of some emitted VOCs measured by PTR-MS: methanol (mass 33), acetic acid and hydroxyacetaldehyde (mass 61), acetone and methyl vinyl ether MVE (mass 59) and acetonitrile (mass 42).

Most measured VOCs were emitted predominantly during the smoldering phase, and therefore correlate better with CO than with CO_2. The maximum emission was usually reached at the beginning of the smoldering phase, when the temperature is still very high, but there are little or no flames. Especially in the case of grass and other fuels that burn very efficiently, the emission then quickly reduces, as also the remaining fuel is burned up. This can be seen in Figure 5.4, where methanol (m33), acetic acid and hydroxyacetaldehyde (m61), acetone and methyl vinyl ether, MVE (m59) and acetonitrile (m42) –species that were emitted from all fires and measured by PTR-MS– are shown.

The fuel moisture affects the course and efficiency of the fire by reducing the flaming (or increasing the smoldering) combustion and thus affecting the emissions. The humidity content of the different fuels can be found in Table 5.4. As an example of the influence of fuel moisture on the fire behavior and the emissions of grass fires, Figure 5.5. shows the amount of fuel burned during the flaming phase versus the fuel moisture content for all of the dambo and miombo fires (upper chart). The moisture content was between ~6 and 17%, and the percentage fuel consumed by flaming ranged between 70 and 100%. The range of the values is high, but nevertheless the trend of less flaming at higher moisture contents is perceptible in Fig. 5.5. When the analogous plot was made using the data from all fuels burned in this study, the correlation became much better ($R^2 = 0.69$); however only dambo and miombo were included in this figure because their burning behavior (and range of emission of trace gases) were similar. The bottom chart of Fig. 5.5 shows that the flaming emission factors of partially oxygenated volatile organic compounds (POVOCs) increased with increasing fuel moisture. Consequently, it can be said that there are two different variables whose effects go in the same direction: the dryer the fuel the more consumption in flaming and the lower are POVOCs emissions.

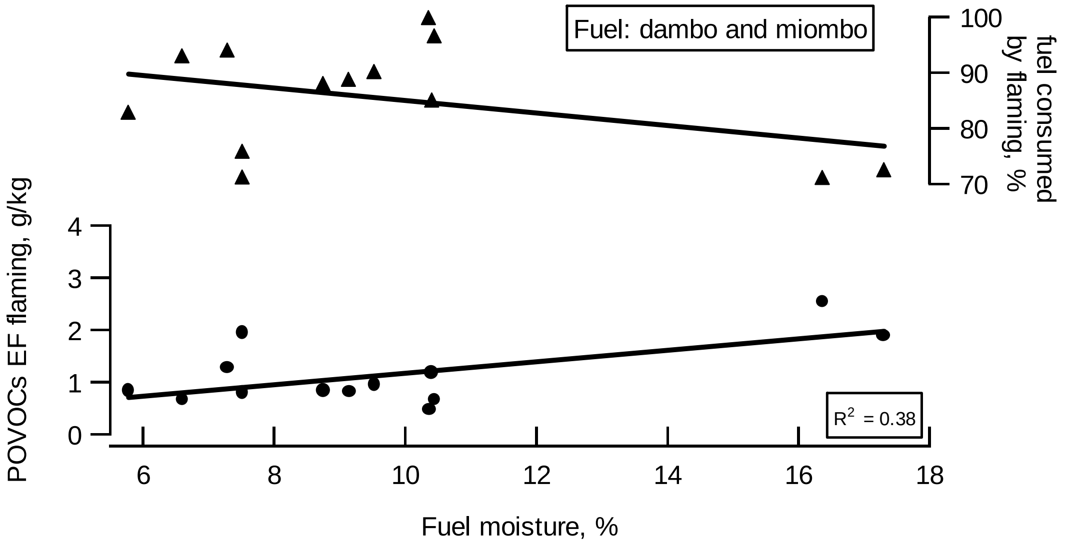


Figure 5.5. Influence of fuel humidity on the amount of fuel burned and POVOCs emissions during the flaming combustion of dambo and miombo fires.

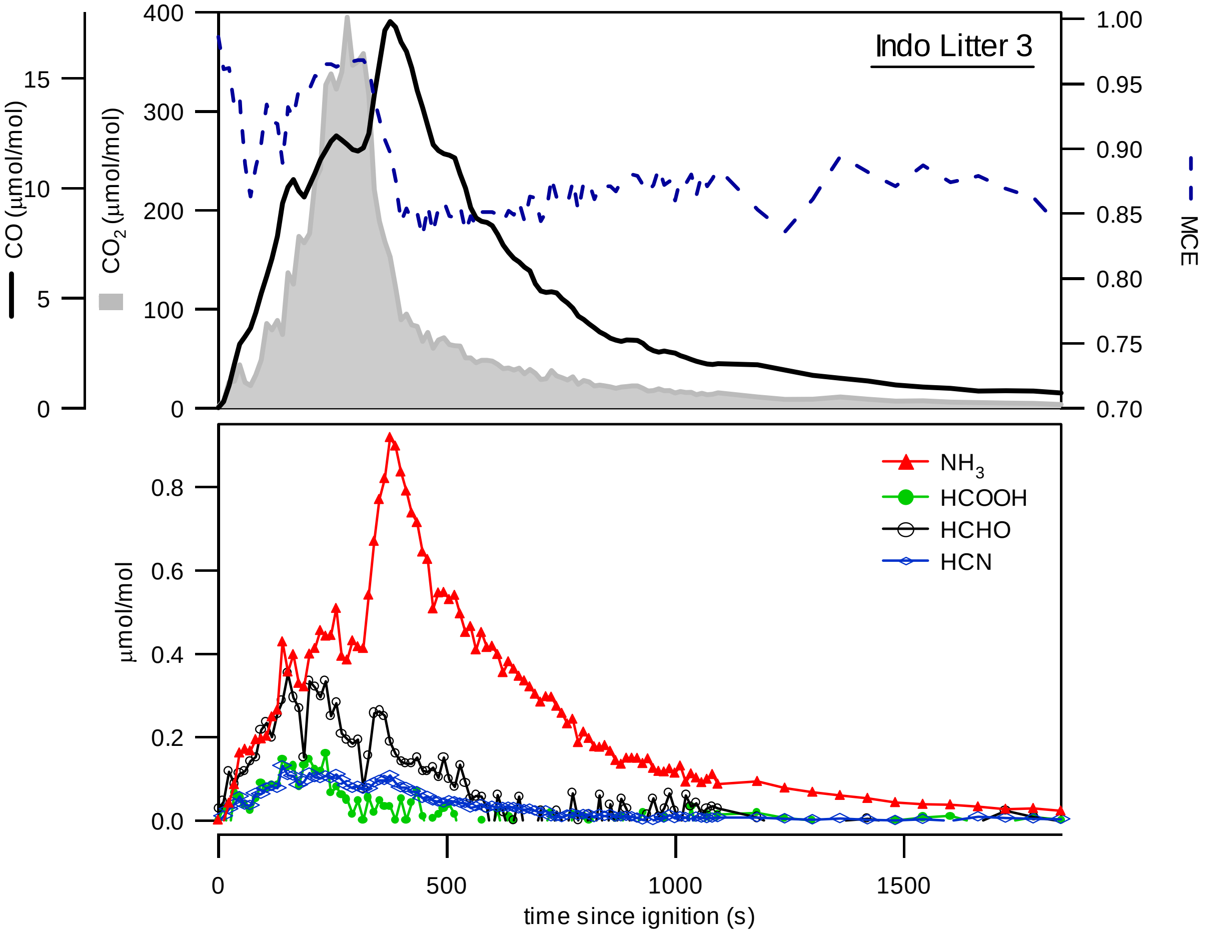


Figure 5.6. Example of the course of a slow and unsteady fire. The upper panel of the graph shows the mixing ratios (ppm) of CO, CO_2 and MCE during a Indo Litter fire. The lower panel shows mixing ratios of some emitted compounds measured by FTIR: ammonia (NH_3), formic acid (HCOOH), formaldehyde (HCHO) and hydrogen cyanide (HCN)

An example of a slow and unsteady fire is shown in Figure 5.6. The Indo litter burned much slower than the grass fires. As the MCE curve shows, there was no clear flaming phase during the first ~200 s, the CO emission rose relatively fast, and the irregular shape of the CO and CO_2 curves indicate that the flames were not increasing as steadily as in the miombo fire (Fig. 5.4). Between 200 and 300 s mainly flaming combustion occurred, but it is interesting to note that the CO_2 peak value was ~20 times lower than that measured in the miombo fire; the CO peak value was 3.5 times lower. Also the emission of trace gases was less uniform, of the four compounds presented here –ammonia (NH_3), formic acid (HCOOH), formaldehyde (HCHO) and hydrogen cyanide (HCN) only NH_3 followed closely the CO curve. The highest emissions of the other compounds occured before the CO peak. Such temporal profiles are caused by the initial heating of the fuel, during which many compounds are released by distillation and pyrolysis. If the flames are not vigorous enough to oxidize the initial products, these may escape unchanged.

5.4.4. Flaming and smoldering emission factors

In most biomass-burning publications, emissions are reported as fire-averaged (or total, EF_{total}), only a few studies in the literature give separate emissions from flaming and smoldering combustion. This deficit is a result of the fact that in field measurements especially, it is difficult to achieve well-separated flaming and smoldering emission measurements, since the area subject to burning is normally large, and there will almost always be overlapping of areas burning with flaming and smoldering combustion. In 75% of the fires in this experiment the flaming and smoldering phases could be analyzed separately. This was done with following goals:

1. Prediction of total emission factors for similar fuel types at different burning efficiencies.
2. Proportion of compound emissions integrated over the flaming and the smoldering phase (i.e. fraction of the total emitted in each burning stage).

Goal two will be discussed in section 5.4.8, and in this section only goal one will be discussed.

Total emission factors (EF_{total}) were *measured* by integrating the emissions over the course of a fire. Separated emission factors for smoldering and flaming combustion (EF_{sm} and EF_{fl}) were obtained by integrating only the periods with flaming or smoldering combustion, respectively. The total emission factors can be calculated from those partial flaming and smoldering emission factors whenever the mass of the fuel consumed, or the MCE for each combustion phase, is known. As mentioned in sections 5.2 and 5.4.3, in this work the criteria to differentiate between flaming and smoldering were the MCE, therefore, the flaming emission factors (EF_{fl}) and smoldering emission factors (EF_{sm}) depend on the threshold values of MCE defining the phases. The validity of the separated EF_{fl} and EF_{sm} can be verified if the agreement between the *calculated* EF_{total} and the actually *measured* EF_{total} for individual fires is good. The EF_{total} can be calculated in two ways based on mass consumption and modified combustion efficiency:

Based on the mass consumption: Ward and Radke (1993) proposed the following equation for estimating EF_{total}:

$$EF_{total} = \frac{(EF_{fl})m_{fl} + (EF_{sm})m_{sm}}{m_{fl} + m_{sm}} \qquad (5.8)$$

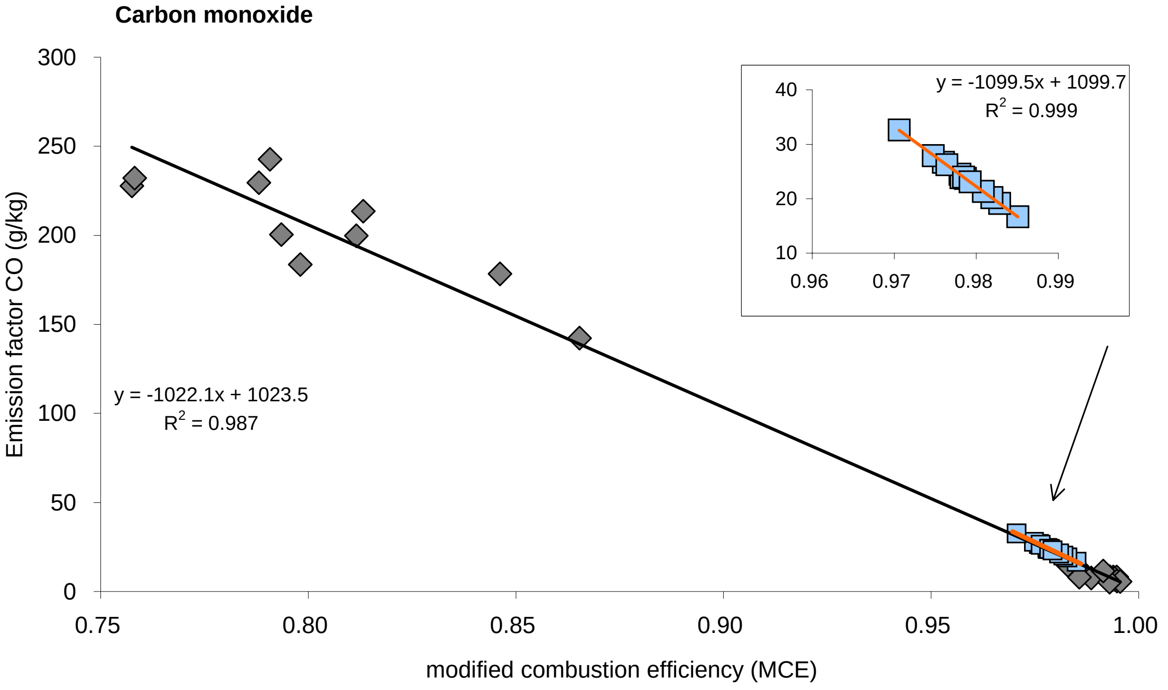
Note that in this equation, it is assumed that all the fuel is consumed during flaming (m_{fl}) or smoldering (m_{sm}); no mixed phase exists. Therefore, to account for all emissions, it was assumed that the mixed phase contributed equally to both combustion phases. In miombo 2 fire, which was burned on March 6th, 2001, the EF_{total}, EF_{fl}, and EF_{sm} of the sum of all VOCs were measured to be 3.03, 1.03 and 22.11 g/kg, respectively. The total fuel mass burned was 1196 gram, 1078 g of which have been burned during flaming and 80 g during smoldering. 38 g have been consumed during the mixed phase. This has been accounted for by increasing the mass of fuel burned during both the flaming and the smoldering phase by 50% of the mass consumed in the mixed phase. According to the relation (5.8) the total VOCs emission factor is calculated to be 2.78 g/kg, which is in very good agreement with the measured value (3.03 g/kg). The approximation is more prone to error where a fire burns with high efficiency, and the *measured* EF_{total} is close to the EF_{fl}. In such cases an incorrect estimation of the fuel burned during smoldering may affect the result considerably, since the smoldering emissions may be higher than the flaming emissions by one order of magnitude or more. The average *measured* EF_{total}/*calculated* EF_{total} ratio for all compounds obtained for this series of experiments was 1.05 ± 0.30.

Based on the relationship of EF with MCE: CO and all the species emitted mainly during smoldering have a negative linear correlation with MCE. Conversely, CO_2 and species emitted in the flaming phase, exhibit a positive correlation with MCE. The EF_{fl} and the EF_{sm} values of each compound measured during an individual fire were plotted against their respective MCE_{fl} and MCE_{sm} values, and regression equations were used to calculate EF_{total} at the MCE_{total} (fire-average MCE). For the miombo2 fire, the same example mentioned above, the correlation of all measured VOCs vs MCE, gave a slope of –88.8 and an intercept value of 89.4. Consequently, at the measured MCE_{total} of this fire (0.976), the calculated EF_{total} was 2.68 g/kg. The average *measured* EF_{total}/*calculated* EF_{total} ratio for all compounds and all fires was found to be 1.06 ± 0.14.

These results show that the *measured* EF_{total} values of individual fires may be calculated using the separated EF_{fl} and EF_{sm} values by both methods. Nevertheless, the MCE-method is more widely applicable, since in natural biomass fires, characterization of the fuel burned is rather difficult, whereas CO and CO_2 are routinely monitored in every field campaign. The emission factors and the extent of correlation between EF and MCE are actually very different for different fuel types. However, if the composition of the biomass burned in a natural fire is similar to the fuels burned in this lab experiment, and the dependence on MCE for some compounds measured both in the lab and in the field is similar, the correlation of EF vs. MCE for a given fuel type may be used as a simple model of emission predictions for compounds that were below their detection limits in the field, or for analogous fires that burned with a different MCE. The correlation of total emission factors and MCE has been successfully used before for this purpose (Hao *et al.*, 1996; Ward *et al.*, 1996; Ferek *et al.*, 1998; Yokelson *et al.*, 1999).

Having confirmed that the EF_{total} of a compound can be calculated from its flaming and smoldering emission factors for an individual fire, we proceed to step two which is to evaluate all fires together that were burned using African Fuels (i.e. dambo and miombo fires). In the same way as it was done for individual fires, the results obtained with the separated emission factors and the total emission factors will be compared. For this analysis the miombo litter fire was omitted, since this fuel is not a complete fuel complex, and also because the calculated MCE_{total} was found to be much lower than the MCE_{total} for other dambo or miombo fires. When computing the regression line, this one point would therefore be given too much weight if included. (Nevertheless, the calculated slopes did not change significantly in most cases after this fire was omitted). Two regression lines were calculated for every compound: one derived from separated emission factors (EF_{fl}, EF_{sm} vs. MCE_{fl}, MCE_{sm}), and the second based on total emission factors (EF_{total} vs. MCE_{total}). Ideally the two regression equations should be identical. By way of an example, the plots derived from the CO and methanol measurements are shown in Figure 5.7.

This figure shows that agreement between the two linear regressions is excellent for CO, but poor for methanol. Similar plots were made for all compounds measured, and the results were satisfactory only for CO and CO_2, whereas for all others, the agreement was poor (similar to that of methanol).



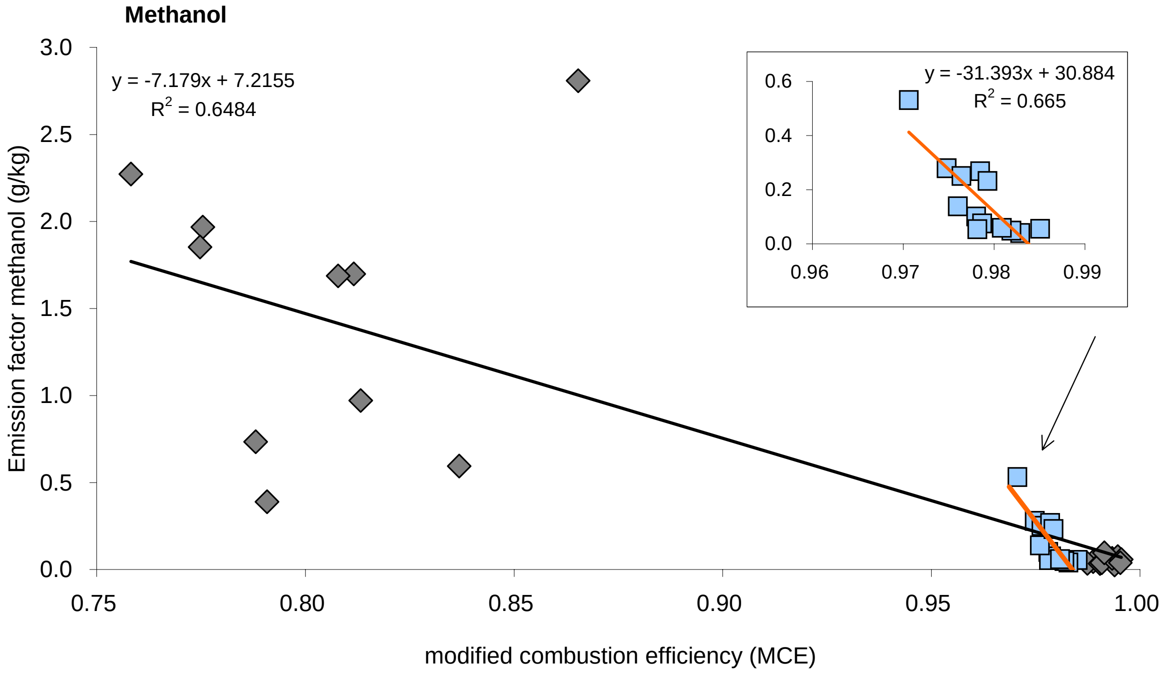


Figure 5.7. Emission Factor (EF) for CO and methanol vs. MCE for African fuels. Two regression lines are shown in each graph: one is calculated from separated EF_{fl} and EF_{sm}, and the other from EF_{total}, which is also shown in detail in the inset.

In other words, if the linear equation obtained with separate EF_{fl} and EF_{sm} is used to calculate –at a specific MCE the emission factor for any compound other than CO and CO_2, the resulting EF will be on average 3 times lower than the obtained by using the regression obtained with the total emission factors and total MCE values. The same analysis was repeated two times for subsets of African fuels, the first done for dambo without miombo and the second for miombo without dambo fires; both producing similar disagreement as the analysis of all African fuels.

The high variability of the EF_{sm} of methanol (Fig. 5.7) suggests that the smoldering emission factors might be underestimated. Similar variabilities were obtained for nearly all other measured trace gases. This hypothesis is supported by the fact that for many compounds the correlations between EF_{total} and high MCE, as obtained in the lab experiments, could be extrapolated to lower MCE values (see African fuels section), thereby reasonably matching EF_{total} and MCE values observed in the field (Christian *et al.*, 2003).

Especially in the grass-type fires, one problem encountered in this experiment was that very little fuel remained after flaming combustion, so that the emissions (measured mixing ratios) were also very low, with a low signal-to-noise ratio. A related problem was a lack of measurement points in the smoldering phase -in most dambo fires the smoldering phase lasted less than one minute. Consequently, the reduced accuracy in these measurements may to a certain extent have caused the scatter in the calculated smoldering emission factors. However, as will be shown below, the large variability cannot be explained by such experimental deficits. In order to check the variability of the emission factors during the course of a fire, "real-time" EF were calculated. In this analysis, the EF for a specific compound was computed for every measurement point, and the same was done for the MCE. The results for a typical grass fire (db13) are shown in Figure 5.8, where the real-time EF of CO, CO_2 and methanol are plotted against MCE. For CO and CO_2, whose signal-to-noise ratio was high for the whole duration of the fire, the real-time EF values correlate very well with MCE, whereas the degree of scatter for methanol is very high during smoldering. The same pattern was observed in all dambo fires and to a lesser degree also in miombo fires. It follows, therefore, that a high degree of variability must be expected in the smoldering emission factors for these fires.

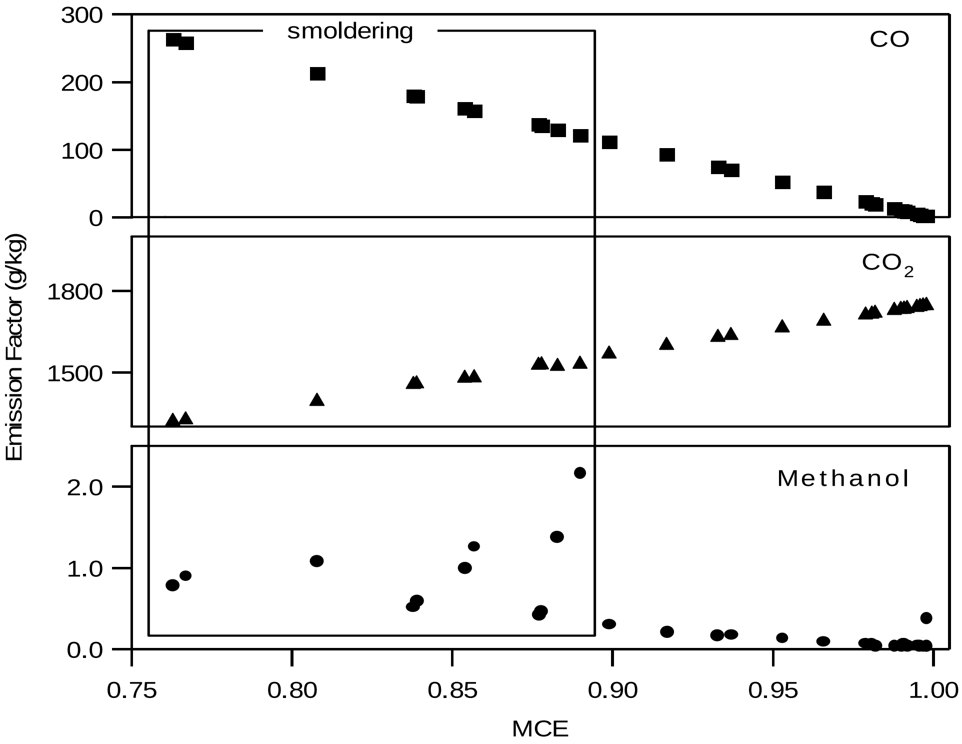


Figure 5.8. Real-time emission factors of CO, CO_2 and methanol vs. MCE for dambo 13. EF and MCE were calculated for every measurement point. The uncertainty in the average methanol EF_{sm} is higher than for CO and CO_2, caused by the high degree of scatter in the individual points.

Real-time EF values were also calculated for the Indonesian fuels, where flaming and smoldering could be separated. If high variability were only a matter of extremely low fuel consumption during smoldering, the correlation of flaming and smoldering EF values and the respective MCE values, should be much better for the Indonesian fuels, where the percentage of fuel consumption by smoldering was found to be as high as 60% in some fires. But the results showed that the tracking of the emission factors of many compounds with MCE was lost towards the end of the fire. Figure 5.8 shows the real-time EF of CO, ammonia and methanol for a semak fire (sk4). The fire burned for 29 minutes in total; the smoldering phase began after ~3 minutes and consumed 55% of the fuel. The data points displayed in blue are the measurements during the last 17 minutes, when approximately 10% of the fuel was left. CO correlates very well with MCE, as did ammonia, which always showed the same temporal profile as CO (Fig. 5.6). From the methanol plot it may be noted that the correlation of EF with MCE at the end of the fire (slope -4.6 g/kg) was very different to that observed during the rest of the smoldering combustion (slope –49 g/kg). Other compounds (not shown in Fig. 5.8) such as acetonitrile, HCN, acetone, and acetic acid, showed the same pattern as methanol, whereas for methane the effect was less pronounced, but with high scattering. The majority of Indonesian fires showed a similar pattern to the one described here, but there were also others in which the EF-MCE correlation was reasonably constant until the end of the fire, but the degree of scatter about the trend line was very high. It follows, therefore, that the estimated smoldering emission factor will have a higher uncertainty when the average is made over few data points –as for the African grass-type fires– or if the scattering of the EF values is very high.

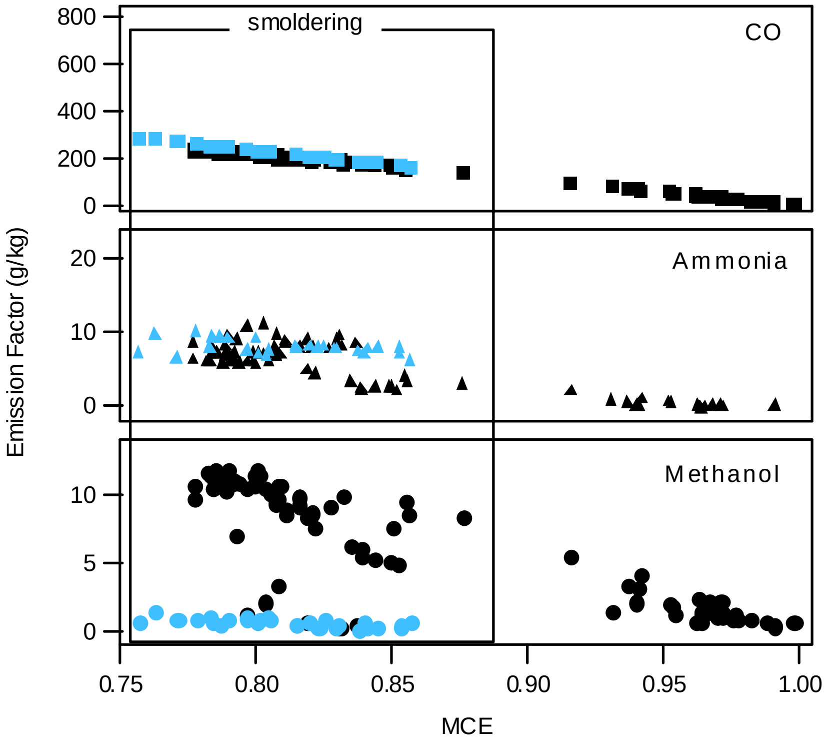


Figure 5.9. Real-time emission factors of CO, ammonia and methanol vs. MCE for sk4.

The results obtained from this study confirm measurements by Yokelson *et al.* (1996) who found that the separation into flaming and smoldering emissions did not work as well for compounds that are also distillation or pyrolysis products of biomass burning (POVOC like methanol, formaldehyde, formic and acetic acid) as it did for primarily flaming or smoldering compounds like CO_2 and CO.

Bertschi *et al.* (2002a) burned duff, logs, and other fuels that can smolder long after flaming, and found that after some hours, the emission of oxygenated compounds from low temperature pyrolysis (e.g. acetic acid, methanol, formaldehyde) were below the detection limit, while other compounds (CO, CO_2, C_1-C_3-alkanes, ethylene, HCN and NH_3) were still being emitted. They proposed that at this point the fresh biomass may be encapsulated by a char layer and also that overlying ash filters the emissions. The same could be true for some Indonesian fuels.

Given the observed difficulties in the calculation of accurate emission factors for flaming and smoldering phases of individual fires, only total-fire results will be used to make any extrapolation from the lab-results. These fires are based on many more data points and are likely to be much more representative than the rather punctual measurements during flaming and smoldering. Nevertheless, the separate emission factors will also be given, in order to show the estimated range of emissions that could be expected from a specific fuel type, and to make estimations of the proportional composition of the emissions.

5.4.5. Emissions from African fuels

Flaming, smoldering and total emission factors and MCE values for the African fuels are presented in Tables 5.5 to 5.7. The emission ratios relative to CO (and CO/CO_2) of African and all other fuels can be found in Appendix 8.6 (Tables 8.4-8.6). The maximum number of fires sampled *(n)* is denoted by the number after the fuel type. The tables show the MCE, CO and CO_2, followed by the compounds measured with FTIR (i.e. nitric oxide, NO; methane, CH_4; ethylene, C_2H_4; acetylene, C_2H_2; ammonia, NH_3, formaldehyde, HCHO; and formic acid, HCOOH), and the protonated masses measured by PTR-MS (among the most important are methanol, m33; acetonitrile, m42; acetaldehyde; butenes, m57; acetone and methyl vinyl ether, m59; acetic acid and hydroxyacetaldehyde, m61; acetol, m75). The emission factors are averages of all fires of the same fuel type, expressed as gram compound emitted per kilogram dry fuel (ash free) burned. The standard deviations (SD) are in parentheses. The absence of SD means that the specific mass was measured in only one fire; or that there was no emission detectable on that mass. The latter was often the case, and therefore the number of detected masses was less in the fires of African fuels compared to the Indonesian fuels (see section 5.4.5.) The sums of emission factors are only for the total emission factors; to sum emission factors for flaming and smoldering emissions would be deceptive, since the two burning phases do not contribute equally to the total emissions of the fire. Note that the *Sum* excludes NO and the major emissions CO_2 and CO. Hereafter, when referring to the total emissions, these compounds will always be excluded, unless explicitly stated.

Table 5.5. Average MCE and emission factors (g compound/kg fuel) for Dambo grass.

	Dambo (n=8)					
	EF Flaming		EF Smoldering		EF Total	
MCE	0.990	(0.003)	0.826	(0.041)	0.981	(0.003)
CO	9.98	(2.349)	197.16	(44.390)	22.00	(3.276)
CO_2	1737.09	(3.576)	1404.32	(80.410)	1717.09	(6.698)
NO	0.690	(0.180)	1.307	(0.327)	0.696	(0.176)
CH_4	0.059	(0.049)	1.142	(1.155)	0.137	(0.091)
C_2H_4	0.122	(0.070)	0.582	(0.444)	0.142	(0.059)
C_2H_2	0.049	(0.020)	0.190	(0.110)	0.058	(0.017)
NH_3	0.008	(0.005)	0.252	(0.176)	0.022	(0.013)
HCN	0.040	(0.005)	0.136	(0.150)	0.044	(0.005)
$HCHO$	0.194	(0.081)	1.965	(1.557)	0.248	(0.106)
$HCOOH$	0.180	(0.048)	1.352	(1.653)	0.200	(0.056)
mass						
33	0.054	(0.033)	0.769	(0.525)	0.072	(0.032)
39	0.004	(0.001)	0.213	(0.185)	0.012	(0.004)
41	0.010	(0.003)	0.168	(0.040)	0.014	(0.002)
42	0.004	(0.003)	0.053	(0.033)	0.007	(0.004)
43	0.057	(0.039)	1.150	(0.983)	0.090	(0.045)
44	0.009	(0.004)	0.091	(0.021)	0.012	(0.000)
45	0.090	(0.059)	0.727	(0.403)	0.102	(0.035)
46	0.008	(0.004)	0.245	(0.223)	0.015	(0.002)
49	0.041	(0.029)	0.549	(0.329)	0.051	(0.014)
54	0.004	(0.002)	0.018	(0.020)	0.004	(0.002)
55	0.023	(0.012)	0.134	(0.186)	0.024	(0.009)
56	0.002	(0.001)	0.013	(0.009)	0.002	(0.001)
57	0.072	(0.055)	0.492	(0.334)	0.081	(0.039)
58	0.004		0.098		0.005	
59	0.038	(0.030)	0.423	(0.315)	0.043	(0.020)
61	0.301	(0.233)	7.458	(4.987)	0.509	(0.242)
62	0.018	(0.005)	0.282	(0.183)	0.024	(0.002)
69	0.020	(0.015)	0.258	(0.205)	0.028	(0.017)
71	0.035	(0.025)	0.309	(0.243)	0.046	(0.024)
73	0.097	(0.067)	0.728	(0.483)	0.099	(0.036)
75	0.051	(0.086)	1.249	(1.218)	0.091	(0.098)
79	0.034	(0.023)	0.202	(0.114)	0.040	(0.021)
81	0.010	(0.007)	0.151	(0.155)	0.015	(0.011)
83	0.013	(0.011)	0.240	(0.252)	0.022	(0.015)
85	0.034	(0.030)	0.713	(0.510)	0.056	(0.037)
87	0.046	(0.045)	0.763	(0.647)	0.066	(0.051)
89	0.004		0.084		0.007	
93	0.009	(0.007)	0.074	(0.048)	0.012	(0.005)
95	0.011	(0.012)	0.423	(0.361)	0.026	(0.021)
99	0.012	(0.004)	0.486	(0.375)	0.030	(0.005)
101	0.007	(0.007)	0.279	(0.220)	0.014	(0.012)
107	0.007	(0.007)	0.056	(0.035)	0.010	(0.007)
121	0.002	(0.002)	0.116	(0.147)	0.007	(0.008)
Sum[a]					2.487	(1.168)

[a] Sum of all compounds except CO, CO_2 and NO.

Table 5.6. Average MCE and emission factors (g compound/kg fuel) for Miombo.

	Miombo (n=5)					
	EF Flaming		EF Smoldering		EF Total	
MCE	0.994	(0.001)	0.777	(0.016)	0.978	(0.001)
CO	7.16	(2.563)	214.41	(42.898)	26.77	(3.784)
CO_2	1742.24	(4.300)	1368.76	(64.315)	1706.53	(7.799)
NO	1.064	(0.180)	2.538	(0.811)	1.197	(0.174)
CH_4	0.071	(0.018)	2.720	(0.228)	0.365	(0.082)
C_2H_4	0.124	(0.023)	1.078	(0.522)	0.283	(0.083)
C_2H_2	0.040	(0.003)	0.260	(0.118)	0.076	(0.014)
NH_3	0.016	(0.004)	1.353	(0.126)	0.146	(0.041)
HCN	0.059	(0.018)	0.335	(0.128)	0.090	(0.009)
HCHO	0.164	(0.044)	1.661	(0.191)	0.371	(0.073)
HCOOH	0.134	(0.025)	0.771	(0.114)	0.201	(0.020)
mass						
33	0.066	(0.021)	2.118	(0.441)	0.312	(0.124)
42	0.008	(0.002)	0.175	(0.028)	0.027	(0.008)
43	0.053	(0.005)	1.817	(0.227)	0.222	(0.051)
45	0.070	(0.016)	0.951	(0.185)	0.183	(0.054)
54	0.006	(0.002)	0.060	(0.023)	0.014	(0.004)
55	0.025	(0.007)	0.252	(0.153)	0.046	(0.015)
56	0.002	(0.000)	0.043	(0.012)	0.007	(0.002)
57	0.075	(0.018)	0.722	(0.260)	0.165	(0.054)
59	0.035	(0.010)	0.545	(0.120)	0.100	(0.033)
61	0.165	(0.025)	6.406	(0.939)	0.729	(0.204)
69	0.019	(0.005)	0.426	(0.055)	0.066	(0.020)
71	0.033	(0.007)	0.510	(0.121)	0.094	(0.029)
73	0.056	(0.014)	0.683	(0.119)	0.132	(0.038)
75	0.015	(0.003)	1.395	(0.309)	0.132	(0.049)
79	0.025	(0.008)	0.262	(0.062)	0.053	(0.014)
81	0.009	(0.002)	0.188	(0.055)	0.030	(0.011)
83	0.013	(0.003)	0.520	(0.042)	0.064	(0.021)
85	0.020	(0.004)	0.968	(0.094)	0.105	(0.030)
87	0.025	(0.005)	0.743	(0.095)	0.099	(0.035)
93	0.008	(0.002)	0.124	(0.043)	0.023	(0.009)
95	0.007	(0.001)	0.513	(0.051)	0.052	(0.017)
97	0.025	(0.004)	1.465	(0.223)	0.155	(0.032)
101	0.003	(0.000)	0.252	(0.032)	0.026	(0.008)
107	0.006	(0.001)	0.145	(0.035)	0.021	(0.008)
121	0.001	(0.000)	0.103	(0.024)	0.009	(0.003)
Sum[a]					4.399	(1.195)

[a] Sum of all compounds except CO, CO_2 and NO.

Table 5.7. MCE and emission factors (g compound/kg fuel) for Miombo Litter.

	Miombo Litter (n=1)		
	EF Flaming	EF Smoldering	EF Total
MCE	0.979	0.846	0.945
CO	26.272	185.40	67.68
CO_2	1925.251	1651.25	1845.22
NO	2.882	2.219	2.809
CH_4	0.547	4.587	1.915
C_2H_4	0.517	0.735	0.746
C_2H_2	0.165	0.142	0.170
NH_3	0.304	3.565	1.190
HCN	0.073	0.134	0.100
$HCHO$	0.621	0.882	0.703
$HCOOH$	0.364	0.615	0.403
mass			
33	0.379	0.819	0.561
41	0.078	0.129	0.112
42	0.050	0.230	0.113
43	0.302	0.863	0.506
45	0.273	0.397	0.366
47	0.053	0.213	0.095
54	0.032	0.054	0.047
56	0.021	0.029	0.028
57	0.285	0.338	0.401
59	0.115	0.284	0.239
61	1.042	3.394	1.685
69	0.128	0.225	0.190
71	0.171	0.239	0.245
73	0.205	0.425	0.313
75	0.181	0.823	0.348
79	0.071	0.175	0.119
83	0.103	0.272	0.176
85	0.178	0.555	0.299
87	0.147	0.477	0.263
93	0.051	0.086	0.078
95	0.086	0.208	0.133
97	0.227	0.632	0.355
101	0.038	0.172	0.082
107	0.033	0.058	0.050
121	0.017	0.040	0.028
Sum[a]			12.059

[a] Sum of all compounds except CO, CO_2 and NO.

The total MCE of dambo and miombo fires is ~0.98, which indicates that the combustion was clearly dominated by flaming. This is also evident in the total emission factors, which are much more comparable to the flaming than to the smoldering emission factors. All emission factors, except that of CO_2, are higher in the smoldering phase. The EF_{sm}/EF_{fl} ratio in dambo and miombo fires is <5 for compounds that are known to be emitted in significant amounts during both combustion phases, like NO, ethylene, acetylene and HCN. Conversely, for all other compounds the average EF_{sm}/EF_{fl} ratio is 17 in dambo fires (range 1.9 - 60), and 29 in miombo fires (range 2.4 - 90). The highest EF_{sm}/EF_{fl} ratio in the miombo litter fire was 11, but it must to be noted that the flaming MCE of this fire was lower than the flaming MCE of dambo and miombo fires, and therefore the miombo litter emissions were higher in this phase. Also interesting is the fact that the emission factors for the mixed phase (not shown in Table 5.7) of the miombo litter were also particularly high, compared to the emissions of the mixed phase of dambo and miombo fires. For some compounds such as ethylene, acetylene, formaldehyde, mass 57 and mass 71, the influence of the high emissions during the mixed phase had the unusual consequence that the EF_{total} were higher than the EF_{sm} (see Table 5.7).

Beside CO_2 and CO, acetic acid, which represented 80-85% of the signal detected at mass 61 in dambo and miombo fires (the rest was hydroxyacetaldehyde), was the most abundant trace gas emission detected in these fuels. Also methane, NO, methanol (mass 33), formaldehyde, ethylene, ammonia, mass 43 (mainly propene), acetaldehyde (mass 45), mass 97 (furfural, dimethyl furanes), and acetol (mass 75) were among the top fifteen African fire emissions. On average, the sum of emissions (Sum EF_{total}) for miombo fires (4.4 g/kg) was approximately twice as high as for dambo grass (2.5 g/kg), and a little less than half that of miombo litter (11.8 g/kg). This is in good agreement with the composition of the miombo fuel (50:50 mixture of dambo grass and miombo litter).

The high concentration of the lab-fire emissions enabled the measurement of many compounds that were not detected by FTIR or GC-FID in a recent field study of African savanna fires (Sinha *et al.*, 2003; Yokelson *et al.*, 2003a). Including acetaldehyde (m45), phenol (m95), acetol (m75), hydroxyacetaldehyde (m61), MEK (m73), acetone (m59), MVE (m59), furan (m69), benzene (m79), acetonitrile (m42), propenenitrile (m54) and propanenitrile (m56). In that study, which took place in August/September 2000 (SAFARI 2000 dry season) in Southern Africa, the airborne measurements yielded an MCE of 0.941

for a miombo fire, 0.975 for a dambo fire, and ~0.94 was calculated as the average MCE measured for ten savanna fires (Yokelson *et al.*, 2003a). The lab fires burned with a higher MCE_{total} (~0.98) than the field fires in Africa. Since most emitted compounds have a strong linear relationship with MCE (the emission factors of smoldering compounds decrease with increasing MCE), the simple adoption of the lab EF_{total} would underestimate the real EF for compounds emitted during the smoldering phase of real fires.

However, the lab-fire total EF for compounds measured in both experiments, do have a correlation with MCE that is very similar to that of the field-fire EF (Christian *et al.*, 2003). There is overlap between the data sets and similar regression equations were obtained from both data sets for six compounds measured in both studies: methane, acetic acid, methanol, ethylene, benzene and toluene. The average absolute difference between the slopes was 14.6% (Christian *et al.*, 2003). This agreement supports the use of lab-based regression equations, along with field MCE values, to calculate average African emission factors for compounds that were below the detection limits of the instruments employed in the field, or those that were not measured. Table 5.8 lists average emission ratios with respect to CO (CO and NO ratios are with respect to CO_2) and emission factors for compounds emitted from the African biomass laboratory fires. Also given in Table 5.8, the slopes, intercepts and correlation coefficients for regression analyses of the emission factors against MCE, which were used to estimate field average emission factors.

For all compounds listed in Table 5.8 (except CO_2), the emission factor decreases with increasing MCE (indicated by negative slopes). This implies that these species are emitted preferentially during smoldering combustion. The correlation coefficient (R^2) is high for most compounds; however, for those which have a weak correlation with MCE (indicated by a low value of R^2) the emissions are not strongly dependent on the course of combustion process.

Table 5.8. Emission ratios relative to CO (to CO_2 for NO and CO) and total emission factors (from the lab measurements extrapolated to typical MCE values measured in the field for fires of African fuels, sorted in order of decreasing emission factor.

	Laboratory measurements							Calculated	
	Emission Ratio (ER)[a]		Emission Factor (EF)		correlation EF vs MCE[b]			at field MCE (0.94)	
	(ppb/ppm)		(g/kg)		slope	intercept	R^2	EF[b]	ER[b]
MCE	0.98	(0.004)			1.00	0.00	1.00		0.94
CO_2	47619.1	(8230.4)	1713.0	(8.70)	2311.17	-548.51	0.98	1619.36	15062.17
CO	21.42	(3.77)	23.84	(4.10)	-1099.46	1099.71	1.00	68.42	66.39
mass 61[c]	10.52	(4.08)	0.59	(0.25)	-60.08	59.39	0.83	3.03	20.67
NO	0.49	(0.19)	0.91	(0.33)	-51.40	51.19	0.43	2.98	2.70
CH_4	13.88	(7.36)	0.20	(0.13)	-31.21	30.74	0.79	1.47	37.48
mass 33	4.92	(3.91)	0.16	(0.14)	-31.39	30.88	0.66	1.44	18.38
HCHO	10.51	(2.70)	0.27	(0.11)	-22.58	22.37	0.63	1.19	16.19
C_2H_4	7.69	(2.60)	0.19	(0.09)	-22.28	21.99	0.78	1.09	15.96
mass 97	1.17	(0.58)	0.11	(0.06)	-20.37	20.06	0.74	0.95	4.07
mass 43	3.34	(1.75)	0.14	(0.08)	-18.59	18.33	0.72	0.89	8.71
mass 45	3.16	(1.16)	0.13	(0.06)	-14.57	14.39	0.87	0.72	6.73
mass 57	2.09	(0.97)	0.11	(0.06)	-13.71	13.53	0.71	0.67	4.89
mass 75	1.46	(1.24)	0.11	(0.08)	-13.47	13.29	0.37	0.65	3.61
NH3	3.91	(3.70)	0.08	(0.06)	-11.46	11.29	0.48	0.53	12.86
mass 73	1.68	(0.59)	0.11	(0.04)	-9.85	9.75	0.86	0.51	2.90
mass 87	0.93	(0.58)	0.08	(0.05)	-9.69	9.56	0.57	0.47	2.24
mass 85	0.90	(0.48)	0.07	(0.04)	-9.58	9.45	0.71	0.46	2.25
mass 59[d]	1.13	(0.56)	0.09	(0.05)	-9.12	8.99	0.82	0.43	3.07
mass 71	0.93	(0.45)	0.06	(0.04)	-8.53	8.41	0.82	0.41	2.40
HCOOH	4.62	(1.26)	0.18	(0.05)	-4.60	4.68	0.12	0.36	3.24
mass 95	0.41	(0.25)	0.04	(0.02)	-7.12	7.01	0.58	0.33	1.45
mass 69	0.62	(0.35)	0.04	(0.03)	-6.36	6.27	0.81	0.30	1.81
mass 83	0.45	(0.30)	0.04	(0.03)	-6.25	6.15	0.74	0.29	1.45
C_2H_2	2.90	(0.45)	0.06	(0.02)	-3.89	3.87	0.69	0.22	3.48
mass 101	0.18	(0.12)	0.02	(0.01)	-4.36	4.29	0.60	0.20	0.82
HCN	2.40	(0.79)	0.06	(0.02)	-3.83	3.81	0.35	0.21	3.19
mass 79	0.62	(0.28)	0.05	(0.02)	-3.69	3.66	0.49	0.19	1.02
mass 93	0.17	(0.09)	0.02	(0.01)	-3.99	3.93	0.60	0.18	0.81
mass 47	1.24	(0.48)	0.05	(0.01)	-2.28	2.28	0.39	0.14	1.27
mass 55	0.59	(0.33)	0.03	(0.02)	-2.55	2.52	0.30	0.13	1.02
mass 107	0.13	(0.09)	0.01	(0.01)	-2.87	2.82	0.61	0.13	0.51
mass 42	0.35	(0.26)	0.01	(0.01)	-2.53	2.49	0.63	0.12	1.17
mass 81	0.27	(0.15)	0.02	(0.01)	-1.23	1.22	0.19	0.07	0.35
mass 54	0.14	(0.10)	0.01	(0.01)	-1.18	1.17	0.53	0.06	0.43
mass 121	0.07	(0.06)	0.06	(0.01)	-0.76	0.75	0.21	0.04	0.13
mass 56	0.08	(0.05)	0.00	(0.00)	-0.66	0.65	0.53	0.03	0.23
Sum[e]								17.9	184.8

[a] All emission ratios ΔX/ΔCO, except ΔCO/ΔCO_2 and ΔNO/ΔCO_2. Standard deviation in parentheses.

[b] Emission factors calculated using the measured field MCE (0.94); (Yokelson *et al.,* 2003). Emission ratios estimated from this set of EF.

[c] Mass 61 is ~80% acetic acid and ~20% hydroxyacetaldehyde.

[d] Mass 59 is ~66% MVE and ~44% acetone.

[e] Sum excludes CO, CO_2 and NO emissions

5.4.5.1. Comparison of the estimated field emission factors to previous work

The estimated field emission factors (calculated using the field MCE = 0.94) will be compared primarily with the work of Andreae and Merlet (2001), who compiled measured and estimated emission factors for savanna fires and other fuel types, and those of Yokelson *et al*. (2003) and Sinha *et al*. (2003) who reported the SAFARI 2000 results on emissions from African savanna fires. The average emission factors determined for the most important compounds in each study are shown in Figure 5.10. The values are in good agreement for many substances.

CO and CO_2 are the two most abundant emissions from biomass fires. The emission factors for these compounds estimated in this study (EF_{CO2} = 1619 and EF_{CO} = 68 g/kg) are in excellent agreement with the values given by Andreae and Merlet (2001) (EF_{CO2} = 1613 ± 95 and EF_{CO} = 65 ± 20 g/kg). Whereas Yokelson *et al*. (2003) quoted a slightly higher EF_{CO2} (1700 ±60 g/kg), along with a very similar EF_{CO} value (68 ± 30 g/kg).

POVOCs: six of the ten highest emissions from African fires were POVOCs. Almost all of them showed a good correlation with MCE. As noted previously, acetic acid was the major organic emission; the FTIR measurements of acetic acid and hydroxyacetaldehyde account for almost all the signal detected at PTR-MS mass 61. In these fires ~80% of mass 61 was acetic acid and ~20% hydroxyacetaldehyde. Therefore, the estimated acetic acid EF is ~2.42 g/kg ($ER_{CH3COOH}$ 1.65% of CO), which agrees well with Yokelson *et al.* (2003). Andreae and Merlet (2001) estimated an $EF_{CH3C(O)OH}$ (extrapolated from emission ratios to CO) to be a factor 2 lower. Methanol and formaldehyde were the other two major POVOCs emitted by these fires, with EF of 1.44 and 1.19 g/kg respectively (emission ratios are 1.8% and 1.6% of CO respectively). The $EF_{methanol}$ is similar to the EF measured in the field by Yokelson *et al.* (2003) of 1.2 g/kg, and the 1.3 g/kg estimated by Andreae and Merlet (2001).

Mass 59 was mainly methylvinylether (MVE) and acetone. Propanal can be measured with FTIR, but its emission was around the detection limit. For African fires the MVE mixing ratios measured by FTIR was higher than the calculated mixing ratio of mass 59 derived by PTR-MS. Based on former biomass-burning (Holzinger *et al.*, 1999) and other studies (Lindinger *et al.*, 1998; Williams *et al.*, 2001) it was assumed initially that the signal on mass 59 is primarily due to acetone, and consequently the concentration was calculated with the reaction rate that was measured for acetone in the laboratory (Holzinger, *personal* *communication*, 2003). Unfortunately, it was not possible to perform such measurements for MVE, and the concentrations could not be recalculated with the appropriate reaction rate. On the other hand, as explained in section 5.4.2., the quantification of acetone with FTIR is difficult, and in most of the African fires it was below the detection limit. Nevertheless, from the fires during which acetone could be quantified, it was calculated that 66 ± 15% of the mass 59 signal was MVE. This implies that $EF_{acetone}$ = 0.19 g/kg and EF_{MVE} = 0.24 g/kg (Christian *et al.*, 2003). Another interesting feature is that the MVE/(MVE+acetone) ratio has a positive linear correlation with MCE ($R^2 = 0.45$), which indicates that in more efficient fires, the mass 59 signal is probably mainly due to MVE. There are no other field or laboratory measurements of MVE, and only few acetone measurements. The $EF_{acetone}$ value lies below the range (0.25-0.62 g/kg) recommended by Andreae and Merlet (2001), which was based on two available field measurements. The mean value and standard deviation of this range is shown in Figure 5.10. It is also worth comparing the new results with those from an earlier laboratory burning experiment on African fuels, which was performed in the burning facility of the MPI (Jost, 2002; Holzinger *et al.*, in preparation, 2004). The fuel burned in this case was mainly grass, but also branches, shrubs, twigs and litter. The mean MCE from this earlier study was 0.941 (Jost, 2002). Emissions were measured with a PTR-MS and an AP-CIMS (Atmospheric Pressure Chemical Ionization Mass Spectrometer). The mean EF_{mass59} measured by PTR-MS was 0.37 g/kg (Holzinger *et al*, in preparation 2004). The acetone EF range measured by the AP-CIMS was 0.049 – 0.70 g/kg, with an average of 0.16 g/kg (*Jost,* 2002), which represents about 44% of the EF_{mass59}. This is consistent with the findings of this work, namely that less than half of the signal on mass 59 measured in grass-type fires was acetone.

The emission factor of formic acid (EF_{HCOOH} = 0.36 g/kg) lies about a factor two below the Yokelson *et al.* (2003) average (0.62 ± 0.18 g/kg), and the Andreae and Merlet (2001) estimation based on emission ratios to CO (0.7 g/kg). The mean EF of acetaldehyde (mass 45) falls within the error range of the 0.50 ± 0.39 g/kg reported by Andreae and Merlet (2001). The EF of mass 95, which is mainly phenol (EF_{mass95} = 0.33 g/kg) is a factor 100 higher than the Andreae and Merlet (2001) $EF_{phenol\ of}$ 0.003 g/kg, and a factor 3.5 higher than the average EF_{mass95} (0.094 g/kg) given by Holzinger *et al.* (in preparation 2004).

Other important POVOCs emissions, which are not compared in Fig.5.9, include those of masses 97, 75, and 73. The estimated emission factor for mass 97 is 0.95 g/kg; the sum of emission factors of compounds potentially detectable at mass 97 reported by Andreae and Merlet (2001), namely furfural, 2-ethylfuran and the dimethylfurans is 0.24 g/kg, which suggests that there are other unidentified compounds detected at this mass. Acetol (hydroxyacetone, mass 75) is previously unreported in biomass burning emissions. The estimated EF_{acetol} for African fuels is 0.65 g/kg, and the acetol/CO ratio is 0.36%. The EF of mass 73, tentatively identified: 2-butanone (methylethylketone, MEK) and the butanals is 0.51 g/kg, whereas the sum of emission factors of these compounds given by Andreae and Merlet (2001) is 0.31 g/kg. Mass 73 was also reported by Holzinger *et al.* (in preparation 2004) with a lower EF (0.13 g/kg).

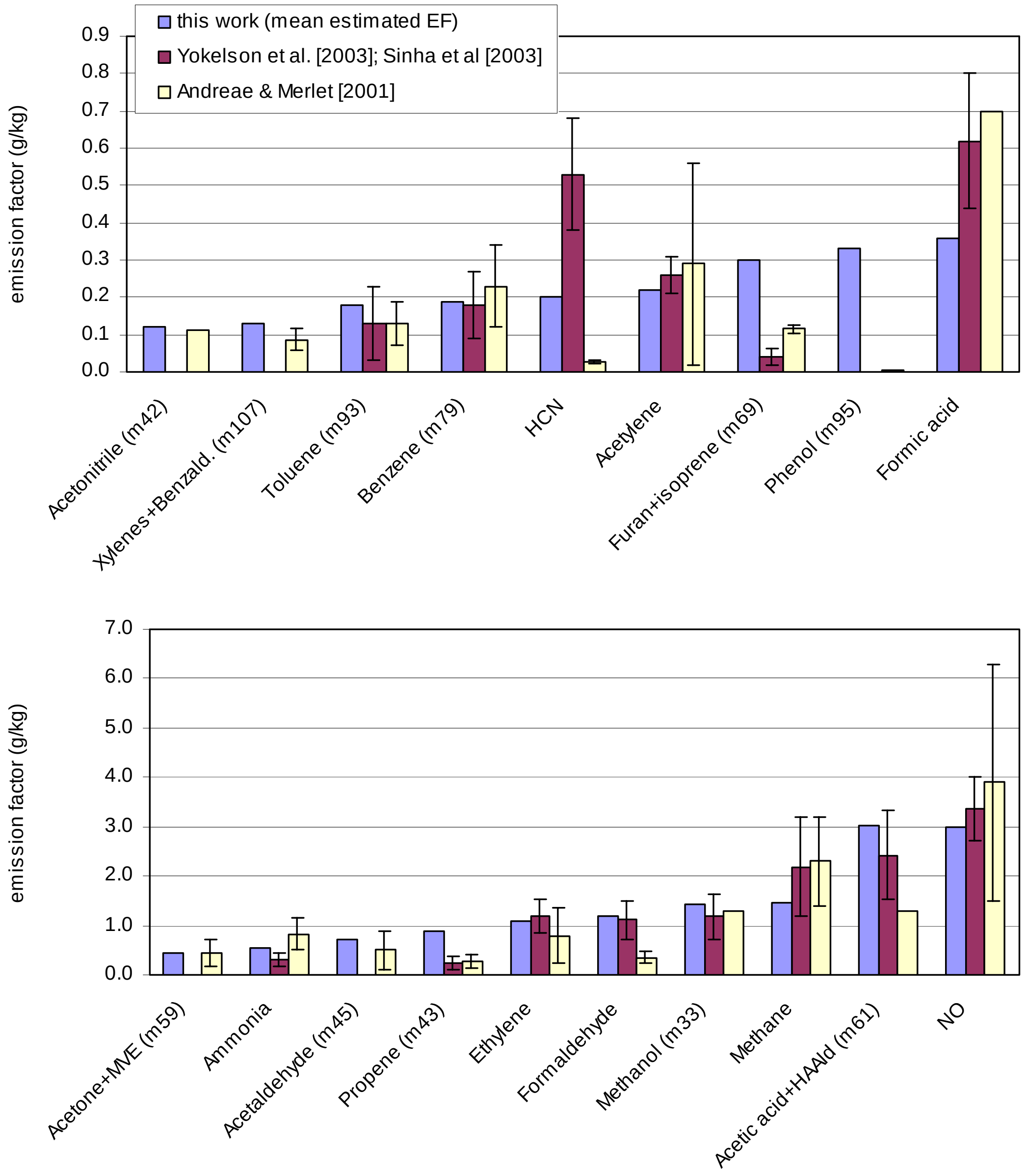


Figure 5.10. Emission factors for important compounds derived from African fuels lab-measurements (this work), burning of savanna in southern Africa (Yokelson *et al.*, 2003; Sinha *et al,*. 2003), and global savanna burning (Andreae and Merlet, 2001).

N-containing compounds: The nitrogen-species emissions are closely linked to the fuels nitrogen content. It is known that the nitrogen content of both living plants and dead plant mater undergoes seasonal changes (Delmas *et al.*, 1995); the fuel burned in this study was collected at the end of the dry season, when the N-content is already very low. The N-content of the dambo grass (0.23%) was comparable to the N-content of dead grass (0.25%) measured in the Kruger Park in South Africa (Lacaux *et al.*, 1996). Miombo had a higher N-content of 0.71%, due to the high N-content of the miombo-litter.

The estimated EF_{NO} of 2.98 g/kg is in the usual range for savannas biomass burning (e.g. the 3.37 ± 0.64 g/kg measured by Yokelson *et al.* (2003), and the Andreae and Merlet (2001) recommendation of 3.9 ± 2.4 g/kg). The NO/CO_2 ratio calculated in the present work was 0.27%.

Ammonia (NH_3) is the second most abundant nitrogen-containing compound emitted by African fuels. The estimated EF_{NH3} of 0.53 g/kg is higher than the (0.28 ± 0.14 g/kg) measured by Yokelson *et al.* (2003) and close to the lower end of the range (0.6 – 1.5 g/kg) given by Andreae and Merlet (2001) which was based on the only previous savanna-fire field measurements in Australia (Hurst *et al.*, 1994a; Hurst *et al.*, 1994b). The emission factor of HCN (0.20 g/kg) differs from the (0.53 ± 0.14 g/kg) reported by Yokelson *et al.* (2003) and the recommended EF by Andreae and Merlet (2001) of 0.025 – 0.031 g/kg for savanna fires, based on the work of *Hurst et al.* (1994a, 1994b). Both Lobert *et al.* (1991) and Yokelson *et al.* (1997) reported that HCN was emitted in highly variable amounts by smoldering combustion of different types of biomass, with an HCN/CO ratio varying from ~0 –5% (the ratio to CO estimated in this study was 0.3%). But despite this high variability, EF_{HCN} has a poor correlation with MCE. This was also observed by Yokelson *et al.* (2003).

The estimated EF for acetonitrile (CH_3CN, mass 42) of 0.12 g/kg agrees well with the value for savannas and grasslands (0.11 g/kg) given by Andreae and Merlet (2001) (also based on the work of Hurst *et al.* (1994a, 1994b)), and is approximately a factor 1.7 higher than that reported by Holzinger *et al.* (in preparation 2004). In a former work of Holzinger *et al.* (1999), a mean CH_3CN/CO ratio of 0.13% (range 0.04 – 0.25%) was reported, which is similar to the estimated ratio to CO in this work (0.117%). The emission factors of propenenitrile (CH_2CHCN, mass 54) and propanenitrile (CH_3CH_2CN, mass 56) of 0.06 and 0.03 g/kg respectively, are 2.5-3 times lower than the 0.024 and 0.013 g/kg determined by Holzinger *et al.* (in preparation 2004), while the ratios to CO (propenenitrile/CO 0.043%;

propanenitrile/CO 0.023%) were found to be very similar to the ratios to CO measured by Lobert *et al.* (1991) (propenenitrile/CO 0.05%; propanenitrile/CO 0.02%).

Methane: The major hydrocarbon emitted is CH_4. Its emission is comparable to that of methanol. The estimated emission factor of this study (1.47 g/kg) is lower than the Yokelson *et al.* (2003) and Andreae and Merlet (2001) mean values (~2.2 g/kg), but taking into account the standard deviations provided by these studies, it is similar.

Unsaturated and aromatic hydrocarbons: The EF of ethylene (1.09 g/kg) and acetylene (0.22 g/kg) are comparable to those reported by *Sinha et al.* (2003) and Andreae and Merlet (2001). The mass 43 (mainly propene) emission factor is about a factor 3.5 higher, but it has to be remembered that other compounds (e.g. cyclopropane) and fragments of propanol (for example) are also detected at mass 43. From the FTIR measurements it was estimated that ~60% ± 28% of the signal of mass 69 was furan, and ~40% was isoprene. Consequently, the estimated EF_{furan} is ~0.18 g/kg, and the $EF_{isoprene}$ ~0.12 g/kg. Both compounds are listed in Andreae and Merlet (2001), although the EF_{furan} is based on a single measurement. The sum of EF ($EF_{furan} + EF_{isoprene} = 0.095 + 0.02$ g/kg) is considerably lower than the EF_{mass69} (0.3 g/kg) derived here. The $EF_{isoprene}$ (0.042 ±0.022 g/kg) reported by Sinha *et al.* (2003) is also almost a factor three lower than that estimated in this study.

The emissions of benzene (mass 79) and toluene (mass 93) are within the emission ranges given by *Sinha et al.* (2003) and Andreae and Merlet (2001). The signal at mass 107 is due to at least these compounds: xylenes, ethylbenzene and benzaldehyde. The estimated $EF_{mass107}$ of this study (0.13 g/kg) is close to the sum of emission factors of these compounds reported by Andreae and Merlet (2001), namely 0.09 ± 0.03 g/kg.

There are 5 compounds with molecular formula C_5H_{10} (protonated mass 71) that were measured by *Sinha et al.* (2003), the sum of emission factors is 0.023 ± 0.015 g/kg. The EF_{mass71} is about a factor 15 higher, but there are also more compounds other than these five alkenes potentially detectable at mass 71, including methyl vinyl ketone (MVK), which was detected by GC/MS in the canister samples taken during some fires of this experiment. Also three compounds with molecular formula C_4H_8 (mass 57) were measured by *Sinha et al.* (2003), with a total EF of 0.064 ± 0.043 g/kg, and six compounds were reported by Andreae and Merlet (2001) with a total EF of 0.245 ± 0.097 g/kg. The measured $EF_{mass\ 57}$ was 0.67, which is still more than a factor 2.5 higher than Andreae and Merlet´s estimate, which therefore suggests that the PTR-MS is detecting more compounds than the already quantified in the literature.

5.4.5.2. Estimated annual emissions from global savanna and grassland fires

Table 5.9. Estimated emissions[a] from savanna and grassland fires worldwide.

		Annual emission	
		Tg compound	Tg Carbon
CO	Carbon monoxide	216.20	92.66
CO_2	Carbon dioxide	5117.19	1395.60
NO	Nitric oxide	9.41	
CH_4	Methane	4.63	3.47
C_2H_4	Ethylene	3.45	2.96
C_2H_2	Acetylene	0.70	0.65
NH_3	Ammonia	1.69	
HCN	Hydrogen cyanide	0.67	
HCHO	Formaldehyde	3.75	1.50
HCOOH	Formic acid	1.15	0.30
Protonated mass			
33	Methanol	4.54	1.70
42	Acetonitrile	0.37	0.22
43	Propene, Cyclopropane; Propanol	2.83	2.43
45	Acetaldehyde	2.29	1.25
54	2-propenenitrile	0.18	0.12
55	1-butyne; 1,2-butadiene; 1,3-butadiene	0.43	0.29
56	Propanenitrile	0.10	0.07
57	butenes; 2-Methyl-1-propene; Acroleine	2.11	1.36
59	Acetone, Methyl vinyl ether	1.37	0.85
61	Acetic acid, Hydroxyacetaldehyde	9.57	3.83
69	Furan; Isoprene	0.95	0.84
71	Dimethyl- (or Ethyl-) cyclopropane; Methylbutenes; Pentenes; 2-methyl-2-propenal; Methyl vinyl ketone; Methacrolein	1.29	1.11
73	2-butanone (Methylethylketone, MEK); Butanal	1.61	1.07
75	Acetol	2.06	1.00
79	Benzene	0.62	0.57
81	$C_4H_4N_2$ (Pyrazine; Diazine; Pyridazine); Cyclohexadiene	0.22	0.20
83	Methylfuran	0.92	0.81
85	C_6-Alkenes	1.46	1.25
87	2,3-butanedione; Pentanone	1.49	1.25
93	Toluene; 1,3,5-cycloheptatriene	0.58	0.53
95	Phenol; $C_5H_6N_2$	1.05	0.94
97	Furfural; Dimethylfuran; Ethylfuran	3.01	2.63
101	Hexanone	0.63	0.53
107	Ethylbenzene; p-xylene; Benzaldehyde	0.42	0.38
121	Ethylmethylbenzenes	0.12	0.11
	TOTAL (excludes CO, CO_2 and inorganic compounds)	**56.2**	**34.2**

[a] Values are given in Tg = 10^{12} g compound (or Carbon) per year.

Table 5.9 provides estimates of emissions from global savanna and grassland fires, which were obtained by multiplying the emission factors that were estimated at the MCE value measured in the field (Table 5.8) by the savanna and grassland biomass burning estimate (3160 Tg/yr) of J. A. Logan and R. Yevich (as cited by Andreae and Merlet, 2001).

The sum of all trace-gas emissions is about 56 Tg/yr, from which 34 Tg correspond to POVOCs, 14 Tg can be attributed to unsaturated hydrocarbons and aromatic compounds, ~5 Tg come from methane, and 3 Tg from N-compounds. The emission of methane is lower than the estimated by Andreae and Merlet (7.4 Tg/yr), which may indicate that it is still biased by overemphasis of flaming combustion, even though the emission factors were corrected by adjusting them to the burning conditions observed in field measurements (i.e. MCE=0.94). On the other hand, the annual estimates for typically smoldering combustion emissions such as CO and acetonitrile (m42), were only 6-12% higher than the values given by Andreae and Merlet (2001).

5.4.6. Emissions from Indonesian fuels

Here we report the first simulations of Indonesian fires. There are no measurements of emissions from field fires to compare with, nevertheless, some comparisons with other biomass fires are possible, and they suggest that the lab fires may be representative. The alang-alang grass, the secondary forest litter (Indo SF Litter) and the semak brush all burned with a lower MCE than the African fuels, and were in the range observed for cerrado (brush and scrub forest), grass and rain-forest fires in Brazil (0.98-0.84) (Ferek *et al.*, 1998). The MCE of the Indonesian peat fire (0.838) was identical to that of peat from Minnesota, and a little above the MCE measured for peat from Alaska, that was burned at the burning facility in Missoula several years ago (Yokelson *et al.*, 1997).

The emission factors for the Indonesian fuels are presented in Tables 5.10-5.13. The emissions of alang-alang grass, Indo SF Litter and semak could be separated into flaming and smoldering emissions, whereas for rice straw and Indo peat this was not possible, and therefore only the total emission factors are given. As for the African fires previously, the emission factors are given in grams per kilogram of dry fuel burned; the values are averages of the same fuel type, followed by the standard deviation in parentheses.

On average, the alang-alang grass burned with a $\mathrm{MCE}_{\mathrm{total}}$ of 0.953, and the mean $\mathrm{EF}_{\mathrm{sm}}/\mathrm{EF}_{\mathrm{fl}}$ ratio was 9.5. The $\mathrm{MCE}_{\mathrm{total}}$ of IndoLitter was 0.901, comparable to that of semak, and the average ratio between flaming and smoldering emissions was also the same as for semak ($\mathrm{EF}_{\mathrm{sm}}/\mathrm{EF}_{\mathrm{fl}}$ ~3), with the exception of ammonia, whose EF was a factor of nine higher during smoldering in the litter fire and up to a hundred times higher in semak fires. The sum of emissions of semak and Indo SF Litter was approximately a factor of ten higher than the sum for alang-alang. The efficiency of the burning is clearly the main driver for these differences.

The rice straw and the peat fires –which burned almost exclusively by smoldering combustion– had the highest emissions. Extremely high acetol (mass 75) emissions were measured from the rice straw fires (21.3 g/kg, or 5.6% of CO). The $\mathrm{EF}_{\mathrm{acetol}}$ of semak and Indo SF Litter were also large (3.3 and 2.3 g/kg, or 1.4% and 0.8% of CO respectively). The acetol emission from rice straw was comparable to the emission factor of mass 61 (26.4 g/kg). Peat, Indo SF Litter and semak had an $\mathrm{EF}_{\mathrm{mass61}}$ between 11 – 13 g/kg. From the FTIR acetic acid and hydroxyacetaldehyde measurements, it was determined that on average 80% of the signal at mass 61 was acetic acid and the remaining 20% was hydroxyacetaldehyde, but this ratio varied from fuel to fuel. The percentages for each fuel are given in the footnotes to Tables 5.10 – 5.14.

Methanol and formaldehyde are among the three most abundant POVOCs emitted by African (e.g. this work, *Yokelson et al.*, 2003) and other fires (e.g. Goode *et al.*, 2000; Bertschi *et al.*, 2003b). Surprisingly, a number of masses with emission factors larger than methanol were detected in the rice straw fires, namely (protonated mass and tentative identification in parentheses) mass 75 (acetol), mass 87 (2, 3-butanedione, pentanone), mass 97 (furfural, dimethylfuran, ethylfuran), mass 45 (acetaldehyde) and mass 99 (C_7-Alkenes).

The ammonia emission from the peat fire was very high (19.9 g/kg; 16% of CO). Yokelson *et al.* (1997) also found comparable emissions from Minnesota peat (15% of CO). The emissions of other N-containing compounds like HCN and acetonitrile, were also large. On the other hand, the emission of a typical flaming compound like NO is relatively low. These results are consistent with the high nitrogen content (see Table 5.1), and the high moisture of this fuel (30.5%, Table 5.4), which favors low fire efficiency and the production and emission of smoldering compounds. Smoldering combustion clearly dominated during the whole course of this fire (MCE=0.838).

Table 5.10. Average MCE and emission factors (g compound/kg fuel) for Alang-Alang, the standard deviation is given in parentheses.

	Alang-Alang (n=4)					
	EF Flaming		EF Smoldering		EF Total	
MCE	0.980	(0.015)	0.822	(0.040)	0.953	(0.008)
CO	18.76	(11.511)	177.02	(55.820)	51.65	(8.695)
CO_2	1685.92	(19.810)	1403.15	(98.651)	1626.74	(18.554)
NO	1.211	(0.738)	0.952	(0.027)	1.131	(0.200)
CH_4	0.345	(0.326)	2.498	(1.247)	0.898	(0.503)
C_2H_4	0.259	(0.223)	0.838	(0.496)	0.465	(0.258)
C_2H_2	0.094	(0.069)	0.154	(0.096)	0.133	(0.044)
NH_3	0.172	(0.230)	2.604	(1.840)	0.696	(0.679)
HCN	0.115	(0.082)	0.223	(0.120)	0.166	(0.029)
HCHO	0.411	(0.231)	1.403	(0.414)	0.570	(0.283)
HCOOH	0.162	(0.091)	0.147	(0.100)	0.152	(0.068)
mass						
33	0.110	(0.090)	1.058	(0.480)	0.351	(0.238)
42	0.036	(0.031)	0.289	(0.130)	0.095	(0.060)
43	0.094	(0.063)	0.758	(0.113)	0.252	(0.119)
45	0.186	(0.143)	0.880	(0.338)	0.381	(0.235)
54	0.023	(0.015)	0.060	(0.021)	0.036	(0.016)
55	0.035	(0.017)	0.089	(0.135)	0.041	(0.029)
56	0.005	(0.002)	0.051	(0.018)	0.017	(0.009)
57	0.151	(0.096)	0.851	(0.339)	0.333	(0.175)
59[a]	0.092	(0.080)	0.534	(0.233)	0.213	(0.137)
61[b]	0.281	(0.122)	3.505	(1.268)	0.989	(0.462)
69[c]	0.040	(0.027)	0.375	(0.159)	0.114	(0.063)
71	0.071	(0.051)	0.515	(0.235)	0.175	(0.094)
73	0.131	(0.061)	0.615	(0.307)	0.247	(0.113)
75	0.060	(0.047)	1.066	(0.435)	0.283	(0.181)
79	0.063	(0.034)	0.181	(0.072)	0.101	(0.034)
81	0.021	(0.013)	0.190	(0.087)	0.059	(0.031)
83	0.025	(0.017)	0.443	(0.237)	0.113	(0.064)
85	0.043	(0.024)	0.625	(0.299)	0.156	(0.073)
87	0.077	(0.046)	0.885	(0.390)	0.248	(0.138)
93	0.023	(0.019)	0.114	(0.058)	0.045	(0.024)
95	0.021	(0.012)	0.671	(0.347)	0.139	(0.067)
97	0.051	(0.023)	1.431	(1.054)	0.283	(0.111)
101	0.008	(0.003)	0.133	(0.055)	0.034	(0.016)
107	0.014	(0.008)	0.145	(0.088)	0.040	(0.019)
121	0.004	(0.003)	0.118	(0.098)	0.024	(0.014)
Sum[d]					7.849	(4.388)

[a] Mass 59 is ~60% acetone, and ~40% MVE.

[b] Mass 61 is ~70% acetic acid and ~30% hydroxyacetaldehyde.

[c] Mass 69 is ~90% furan and ~10% isoprene.

[d] Sum of all compounds except CO, CO_2 and NO.

Table 5.11. Average MCE and emission factors (g compound/kg fuel) for Indonesian Secondary Forest Litter, the standard deviation is given in parentheses.

	Indo SF Litter (n=4)					
	EF Flaming		EF Smoldering		EF Total	
MCE	0.974	(0.001)	0.848	(0.019)	0.901	(0.030)
CO	35.593	(9.777)	160.83	(8.517)	109.445	(31.219)
CO_2	1744.831	(2.816)	1455.436	(47.963)	1572.384	(75.122)
NO	2.298	(0.599)	1.118	(0.307)	1.713	(0.181)
CH_4	1.646	(0.329)	8.031	(1.768)	5.257	(1.946)
C_2H_4	1.697	(0.969)	1.369	(0.461)	1.314	(0.552)
C_2H_2	0.741	(0.612)	0.075	(0.051)	0.222	(0.080)
NH_3	0.512	(0.097)	4.646	(0.352)	2.915	(0.777)
HCN	0.653	(0.464)	0.783	(0.445)	0.708	(0.487)
HCHO	1.549	(0.866)	1.648	(1.125)	1.643	(0.839)
HCOOH	0.411	(0.066)	0.854	(0.676)	0.655	(0.304)
mass						
33	1.205	(0.415)	3.810	(2.720)	3.104	(1.983)
41	0.356	(0.105)	0.597	(0.268)	0.485	(0.235)
42	0.216	(0.050)	0.824	(0.199)	0.585	(0.220)
43	1.047	(0.111)	3.305	(1.742)	2.579	(1.320)
44	0.143		0.139		0.143	
45	1.135	(0.411)	2.410	(1.330)	2.032	(1.040)
46	0.050		0.115		0.077	
49	0.038		0.049		0.050	
53	0.039		0.035		0.033	
54	0.166	(0.077)	0.112	(0.027)	0.123	(0.023)
55	0.246	(0.053)	0.499	(0.212)	0.458	(0.174)
56	0.092	(0.013)	0.193	(0.050)	0.150	(0.047)
57	1.067	(0.357)	1.491	(0.530)	1.327	(0.459)
58	0.059		0.072		0.062	
59[a]	0.629	(0.071)	1.919	(0.642)	1.441	(0.547)
60	0.046	(0.003)	0.302	(0.051)	0.216	(0.081)
61[b]	4.766	(0.155)	17.304	(10.772)	13.660	(7.441)
62	0.264		0.114		0.232	
67	0.110		0.133		0.111	
68	0.157		0.274		0.211	
69[c]	0.563	(0.073)	1.403	(0.380)	1.089	(0.338)
70	0.062		0.123		0.089	
71	0.780	(0.108)	1.445	(0.438)	1.197	(0.362)
73	1.016	(0.228)	2.171	(0.973)	1.815	(0.732)
75	0.791	(0.385)	3.247	(2.415)	2.323	(1.693)
79	0.513	(0.094)	0.482	(0.112)	0.425	(0.072)
80	0.045		0.126		0.073	
81	0.210		0.504	(0.082)	0.363	(0.079)
82	0.100		0.253		0.164	
83	0.511	(0.020)	1.898	(0.554)	1.364	(0.443)
84	0.098		0.167		0.135	
85	0.746	(0.106)	2.756	(0.997)	2.082	(0.748)

Table 5.11. continued

	Indo SF Litter					
	EF Flaming		EF Smoldering		EF Total	
87	0.708	(0.018)	2.252	(0.838)	1.723	(0.620)
89	0.111		0.388		0.236	
91	0.019		0.038		0.027	
93	0.321	(0.015)	0.706	(0.207)	0.504	(0.119)
94	0.035		0.117		0.070	
95	0.363	(0.211)	1.414	(0.419)	0.944	(0.237)
96	0.061		0.214		0.130	
97	1.108	(0.155)	4.019	(1.252)	3.021	(0.984)
99	0.619		1.555		1.029	
101	0.157	(0.083)	1.011	(0.244)	0.693	(0.195)
103	0.230	(0.055)	0.713	(0.239)	0.553	(0.188)
104	0.051		0.183		0.102	
105	0.106		0.254		0.153	
107	0.214	(0.066)	0.407	(0.115)	0.314	(0.073)
109	0.263		1.682		0.805	
111	0.372		1.990		1.021	
113	0.291		1.072		0.602	
115	0.204		0.638		0.374	
117	0.091		0.347		0.202	
118	0.035		0.144		0.076	
119	0.073		0.209		0.118	
121	0.106	(0.052)	0.406	(0.166)	0.265	(0.083)
123	0.144		1.093		0.466	
125	0.178		0.967		0.513	
127	0.079		0.507		0.243	
129	0.125		0.465		0.250	
135	0.071		0.300		0.163	
Sum[d]					65.509	(25.521)

[a] Mass 59 is ~55% acetone, and ~45% MVE.

[b] Mass 61 is ~90% acetic acid and ~10% hydroxyacetaldehyde.

[c] Mass 69 is ~60% furan and ~40% isoprene.

[d] Sum of all compounds except CO, CO_2 and NO.

Table 5.12. Average MCE and emission factors (g compound/kg fuel) for Semak, the standard deviation is given in parentheses.

	Semak (n=4)					
	EF Flaming		EF Smoldering		EF Total	
MCE	0.972	(0.005)	0.855	(0.036)	0.891	(0.012)
CO	33.84	(3.804)	152.96	(15.589)	122.03	(12.81)
CO_2	1714.68	(23.722)	1357.03	(202.888)	1567.02	(35.0)
NO	2.340	(0.760)	1.020	(0.457)	1.619	(0.435)
CH_4	1.704	(0.293)	9.866	(2.415)	6.411	(0.863)
C_2H_4	1.336	(0.359)	2.564	(0.290)	2.332	(0.594)
C_2H_2	0.489	(0.183)	0.321	(0.241)	0.504	(0.264)
NH_3	0.071	(0.099)	7.512	(2.874)	4.953	(2.193)
HCN	0.463	(0.051)	0.905	(0.096)	0.782	(0.101)
HCHO	1.331	(0.097)	2.589	(0.441)	2.489	(0.721)
HCOOH	0.499	(0.033)	1.280	(0.693)	0.922	(0.342)
mass						
33	1.463	(0.670)	4.486	(2.679)	3.301	(1.193)
39	0.120	(0.106)	0.233	(0.279)	0.204	(0.253)
41	0.533	(0.327)	0.852	(0.225)	0.787	(0.074)
42	0.307	(0.092)	1.163	(0.632)	0.857	(0.268)
43	1.452	(0.690)	5.311	(2.027)	3.916	(0.656)
44	0.245	(0.055)	0.302	(0.184)	0.277	(0.103)
45	1.766	(1.295)	3.419	(1.355)	2.794	(0.316)
46	0.146	(0.158)	0.287	(0.013)	0.317	(0.112)
49	0.099		0.072	(0.044)	0.085	(0.018)
53	0.144		0.093	(0.064)	0.100	(0.036)
54	0.278	(0.157)	0.253	(0.130)	0.242	(0.073)
55	0.338	(0.099)	0.625	(0.416)	0.466	(0.266)
56	0.157	(0.088)	0.338	(0.300)	0.249	(0.120)
57	1.500	(0.865)	2.144	(1.100)	1.781	(0.465)
58	0.111		0.073	(0.020)	0.076	(0.013)
59[a]	1.083	(0.735)	2.680	(1.760)	1.975	(0.835)
60	0.080	(0.018)	0.273	(0.304)	0.220	(0.193)
61[b]	5.119	(1.401)	20.572	(18.188)	13.510	(10.964)
62	0.345	(0.030)	0.409	(0.391)	0.359	(0.254)
67	0.287	(0.190)	0.233	(0.088)	0.236	(0.028)
68	0.260	(0.080)	0.581	(0.481)	0.468	(0.278)
69[c]	0.667	(0.101)	2.472	(2.085)	1.672	(1.073)
70	0.109	(0.053)	0.218	(0.205)	0.177	(0.119)
71	1.055	(0.465)	2.152	(1.618)	1.611	(0.884)
73	1.219	(0.635)	2.418	(1.912)	1.795	(1.057)
75	1.233	(0.518)	6.628	(6.865)	4.147	(4.150)
79	0.846	(0.639)	0.718	(0.200)	0.710	(0.093)
80	0.128	(0.072)	0.126	(0.085)	0.122	(0.051)
81	0.419	(0.112)	1.430	(1.303)	0.952	(0.678)
82	0.168	(0.061)	0.382	(0.408)	0.298	(0.247)
83	0.705	(0.215)	3.012	(2.549)	1.971	(1.406)
84	0.120	(0.019)	0.401	(0.383)	0.318	(0.224)
85	1.007	(0.147)	3.941	(3.217)	2.652	(1.775)

Table 5.12. continued

	Semak					
	EF Flaming		EF Smoldering		EF Total	
87	1.174	(0.262)	4.188	(3.897)	2.804	(2.272)
89	0.082	(0.103)	0.587	(0.936)	0.396	(0.601)
91	0.055	(0.032)	0.080	(0.071)	0.071	(0.036)
93	0.433	(0.277)	1.098	(0.844)	0.797	(0.375)
94	0.050	(0.012)	0.121	(0.116)	0.096	(0.070)
95	0.593	(0.120)	2.591	(2.114)	1.685	(1.155)
96	0.089	(0.006)	0.284	(0.338)	0.208	(0.220)
97	1.345	(0.113)	5.721	(5.161)	3.788	(3.024)
99	0.616	(0.069)	2.283	(3.043)	1.661	(1.911)
101	0.233	(0.056)	1.466	(1.477)	0.920	(0.862)
103	0.174	(0.088)	0.621	(0.897)	0.451	(0.615)
104	0.082	(0.003)	0.158	(0.096)	0.134	(0.072)
105	0.185	(0.050)	0.215	(0.147)	0.207	(0.083)
107	0.233	(0.031)	0.651	(0.484)	0.483	(0.245)
109	0.304	(0.042)	1.225	(1.535)	0.889	(0.982)
111	0.353	(0.069)	1.867	(2.752)	1.321	(1.823)
113	0.347	(0.129)	1.561	(2.145)	1.101	(1.367)
115	0.092	(0.092)	0.648	(0.995)	0.451	(0.656)
117	0.113	(0.030)	0.540	(0.811)	0.386	(0.557)
118	0.028	(0.013)	0.156	(0.225)	0.110	(0.148)
119	0.107	(0.059)	0.143	(0.123)	0.121	(0.076)
121	0.117	(0.022)	0.941	(0.977)	0.579	(0.507)
123	0.090	(0.051)	0.633	(0.880)	0.452	(0.582)
125	0.158	(0.087)	1.130	(1.770)	0.767	(1.147)
127	0.069		0.462	(0.689)	0.325	(0.456)
129	0.119	(0.020)	0.371	(0.537)	0.278	(0.367)
135	0.062	(0.062)	0.187	(0.261)	0.136	(0.163)
Sum[d]					87.655	(53.723)

[a] Mass 59 is ~70% acetone and ~30% MVE.

[b] Mass 61 is ~75% acetic acid and 2~5% hydroxyacetaldehyde.

[c] Mass 69 is ~50% furan and ~50% isoprene.

[d] Sum of all compounds except CO, CO_2 and NO.

Table 5.13. Average MCE and total emission factors (g compound/kg fuel) for Rice Straw and Indonesian Peat, the standard deviation is given in parentheses.

Cmpd/mass	**Rice straw (n=3)**		**Indo Peat (n=1)**	***mass***	**Rice straw**		**Indo Peat**
MCE	0.811	(0.046)	0.838				
CO	179.87	(39.765)	215.42	*80*	0.267		2.003
CO2	1215.52	(96.573)	1745.29	*81*	2.720	(0.616)	0.648
NO	0.618	(0.396)	1.00	*82*	0.936		0.355
CH4	9.589	(2.015)	20.80	*83*	5.162	(1.384)	2.163
C2H4	2.841	(0.859)	2.570	*84*	0.842		0.633
C2H2	0.470	(0.131)	0.060	*85*	5.986	(1.516)	2.184
NH3	4.100	(1.238)	19.92	*86*	0.538		0.325
HCN	0.870	(0.190)	8.110	*87*	10.52	(2.570)	2.075
HCHO	3.169	(0.882)	1.400	*89*	3.457		0.519
HCOOH	2.122	(0.259)	0.790	*91*	0.180		0.086
33	6.067	(1.775)	8.234	*93*	1.075	(0.348)	1.552
39	0.122		0.069	*94*	0.277		0.796
41	1.617	(0.429)	0.950	*95*	4.337	(1.275)	3.365
42	1.194	(0.355)	4.912	*96*	0.745		0.512
43	5.352	(1.207)	3.714	*97*	8.574	(2.525)	6.135
44			0.600	*99*	6.559		1.490
45	7.046	(1.587)	3.266	*101*	2.447	(0.773)	0.975
46	0.487		0.388	*103*	1.427	(0.739)	0.575
47	0.805	(0.204)	0.297	*104*	0.289		2.181
54	0.191	(0.013)	0.378	*105*	0.455		0.837
55			0.517	*107*	0.876	(0.306)	0.975
56	0.352	(0.015)	0.355	*109*	3.687		1.136
57	3.217	(1.114)	2.481	*111*	5.290		1.018
59[a]	5.014	(0.847)	2.601	*113*	4.055		1.105
60	0.717	(0.363)	1.404	*115*	1.454		0.926
61[b]	26.40	(2.750)	11.04	*117*	2.609		0.349
62	0.578		0.217	*118*	0.405		0.126
67	0.544		0.163	*119*	0.377		0.286
68	1.511		0.407	*121*	1.731	(0.754)	0.670
69[c]	3.625	(1.084)	1.049	*123*	2.623		1.323
70	0.536		0.511	*125*	3.654		2.385
71	4.234	(1.219)	0.751	*127*	1.663		0.778
73	5.116	(0.839)	2.255	*129*	0.790		1.312
75	21.34	(5.154)	2.210	*135*	0.696		0.315
79	0.874	(0.201)	3.188				
Sum[d]					206.80		147.72

[a] Percentages for acetone and MVE in mass 59 are respectively ~90% and ~10% for rice straw and ~70% and ~30% for peat.

[b] Percentages for acetic acid and hydroxyacetaldehyde in mass 61 are respectively~80% and ~20% for rice straw and ~93% and ~7% for peat.

[c] Percentages for furan and isoprene in mass 69 are respectively ~20% and ~80% for rice straw and ~88% and ~12% for peat.

[d] Sum of all compounds except CO, CO_2 and NO.

The estimation of average emission factors and/or annual mean emissions from Indonesian fires is difficult, since there are some major uncertainties regarding the total area burned, the biomass loading and the ecosystem or biomass-type that burned (Levine, 2000). The Indonesia and Malaysia region is characterized by infrequent and large burning events that coincide with major El Niño/Southern Oscillation (ENSO)-induced droughts (Ropelewski and Halpert, 1987). The 1997-1998 fires in Indonesia, Malaysia and Papua New Guinea, was one of the largest biomass burning events of the twentieth century, and in spite of the extensive use of remote sensing techniques, there is a wide range of estimates for the total area burned in Indonesia: a report from the Asian Development Bank (ADB, 1999) provides a general estimate of 9.7 million ha, while other studies suggest that 4–13 million ha were affected in Kalimantan and Sumatra alone (Liew *et al.*, 1998; Fuller and Fulk, 2001). A few studies describe the land cover types that burned in Kalimantan and Sumatra (Liew *et al.*, 1998; UNDAC, 1998; Siegert *et al.*, 2001; Page *et al.*, 2002), and there are disagreements especially concerning the estimates of peat burned.

As mentioned above, the 1997/98 event was particularly extensive and severe, and therefore, not only the area burned is not a representative average for all years, but the distribution of the burned biomass types may also be different than the average distribution of fuels that burn in Indonesia. In addition, the large quantities of biomass that are burned as domestic fuel (Lobert *et al.*, 1999) are not accounted for. Despite these limitations, it is useful to make an estimate of the average emissions for Indonesian fires. The results are presented in Table 5.14, and were calculated weighting the total emission factors and emission ratios of all fuel types equally. The analysis shows several interesting points.

First, it is worth noting that mass 61, mainly acetic acid, was the highest organic emission. Acetol (mass 75) was second, followed by methane, mass 97 and methanol. The EF_{NH3} (3.7 g/kg) was comparable to EF_{CH4} (5.7 g/kg).

Table 5.14 also shows that the average sum of emission factors of Indonesian fires was ~5.3 times as large as those of African fires. In contrast to most of the emissions, the primarily flaming compounds CO_2 and NO had lower emission factors than the African fires. The average EF_{CO2} (1541 g/kg) and EF_{NO} (1.3 g/kg) were low compared to the average estimated African EF_{CO2} (1619 g/kg) and EF_{NO} (2.98 g/kg). All the POVOC emissions were at least 3.5 times higher than those measured from African fuels. Important N-compounds like NH_3, HCN and acetonitrile were also between 4 and 8 times higher.

Table 5.14. Emission ratios relative to CO (and to CO_2 for NO and CO) and emission factors from fires of Indonesian fuels, sorted in order of decreasing emission factor.

Indo fuels	**Emission Ratio**[a] (ppb/ppm)		**Emission Factor** (g/kg)			**Emission Ratio**[a] (ppb/ppm)		**Emission Factor** (g/kg)	
MCE	0.91	(0.03)			mass 103	1.50	(1.04)	0.72	(0.55)
CO_2	10815.08	(6563.2)	1541.46	(175.45)	mass 117	1.25	(1.54)	0.72	(0.99)
CO	117.17	(77.06)	112.44	(44.50)	mass 93	1.81	(1.57)	0.71	(0.58)
mass 61[b]	47.81	(36.20)	12.73	(10.48)	mass 115	1.25	(1.03)	0.68	(0.60)
mass 75	16.83	(22.25)	5.83	(8.29)	mass 79	1.87	(1.29)	0.67	(0.74)
CH_4	75.18	(30.35)	5.66	(3.63)	mass 127	0.96	(0.88)	0.61	(0.62)
NH_3	45.18	(26.57)	3.71	(2.86)	mass 68	1.82	(1.29)	0.59	(0.49)
mass 97	8.32	(6.98)	3.64	(3.41)	mass 121	1.08	(1.24)	0.58	(0.71)
mass 33	22.35	(13.06)	3.34	(2.64)	mass 129	0.81	(0.60)	0.53	(0.49)
mass 87	8.47	(9.11)	3.32	(3.96)	mass 104	0.81	(1.11)	0.50	(0.83)
mass 43	15.49	(8.89)	2.92	(2.01)	mass 60	1.42	(1.09)	0.46	(0.45)
mass 45	14.08	(9.26)	2.83	(2.43)	mass 80	0.95	(1.34)	0.45	(0.76)
mass 85	6.48	(5.44)	2.44	(2.25)	mass 107	0.93	(0.65)	0.43	(0.36)
mass 99	4.99	(4.57)	2.34	(2.41)	mass 84	1.03	(0.59)	0.43	(0.30)
mass 73	6.43	(4.66)	2.06	(1.79)	C_2H_2	3.55	(3.92)	0.42	(0.56)
mass 59[c]	7.25	(5.57)	2.01	(1.75)	mass 82	1.00	(0.71)	0.39	(0.32)
mass 83	5.05	(4.78)	1.90	(1.97)	mass 55	1.68	(1.13)	0.39	(0.32)
mass 111	3.64	(3.56)	1.88	(2.03)	mass 62	1.29	(0.78)	0.35	(0.21)
HCHO	13.28	(5.00)	1.78	(1.12)	mass 105	0.64	(0.31)	0.34	(0.27)
mass 95	3.90	(3.49)	1.68	(1.71)	mass 96	0.70	(0.50)	0.34	(0.28)
C_2H_4	12.89	(4.90)	1.62	(1.00)	mass 46	1.43	(0.54)	0.32	(0.15)
mass 57	6.66	(3.20)	1.62	(1.13)	mass 44	1.55	(0.54)	0.31	(0.18)
mass 71	5.15	(4.25)	1.59	(1.55)	mass 70	0.79	(0.45)	0.28	(0.21)
mass 113	2.80	(2.61)	1.51	(1.53)	mass 135	0.40	(0.32)	0.26	(0.25)
mass 125	2.33	(2.07)	1.48	(1.46)	mass 67	0.83	(0.38)	0.25	(0.15)
mass 69[d]	4.87	(4.13)	1.46	(1.38)	mass 94	0.46	(0.41)	0.24	(0.29)
mass 109	2.69	(2.19)	1.38	(1.29)	mass 119	0.33	(0.16)	0.19	(0.12)
NO	0.81	(0.32)	1.30	(0.58)	mass 56	0.77	(0.54)	0.19	(0.14)
mass 101	2.56	(2.87)	1.09	(1.13)	mass 39	0.91	(1.18)	0.16	(0.19)
mass 123	1.57	(1.34)	0.96	(0.96)	mass 118	0.28	(0.26)	0.16	(0.15)
mass 42	4.59	(3.94)	0.92	(1.15)	mass 54	0.67	(0.33)	0.15	(0.11)
mass 89	2.00	(2.62)	0.90	(1.31)	mass 91	0.19	(0.11)	0.08	(0.06)
mass 41	4.38	(1.82)	0.89	(0.49)	mass 53	0.36	(0.17)	0.08	(0.05)
HCOOH	4.19	(2.27)	0.88	(0.70)	mass 49	0.39	(0.07)	0.07	(0.02)
mass 81	2.50	(2.63)	0.87	(1.03)	mass 58	0.33	(0.07)	0.07	(0.01)
HCN	6.23	(4.54)	0.85	(1.04)					
Sum[e]						406.18	(274.8)	91.21	(83.2)

[a] All emission ratios are $\Delta X/\Delta CO$, except $\Delta CO/\Delta CO_2$ and $\Delta NO/\Delta CO_2$. Standard deviations given in parentheses.

[b] Mass 61 is ~80% acetic acid and ~20% hydroxyacetaldehyde.

[c] Mass 59 is ~70% acetone and ~30% MVE.

[d] Mass 69 is ~55% furan and ~45% isoprene.

[e] Sum excludes CO, CO_2 and NO emissions.

5.4.7. Emissions from other fuels

Table 5.15 shows the emission factors for fir duff, pine needles and fir duff composite, and Northwest Territories (NWT) duff. Duff fires can smolder for several hours or days. In this study the measurements were stopped after 60–140 min (with the exception of fd3a (see table 5.4 for abbreviations) which did not burn well, and was stopped after 26 min). As expected for fires with relatively low MCE values, the emissions of CO_2 and NO were low, and CO emissions were high. The emissions were comparable to those of rice straw and peat, which also burned mainly by smoldering combustion. It is interesting to note the difference in emissions between the NWT duff (nw1) and the other two fuels, fd and pf1. The carbon and nitrogen content in nw1 was higher than in the others, and its MCE was the same as for pf1; nevertheless, all the measured compounds, except CO and CO_2, had a lower emission factor. Bertschi *et al.* (2003a) burned two samples of NWT duff and measured the emissions with FTIR. The latter fires burned with a higher MCE (0.87), although the observed emission factors were similar for all compounds, except EF_{NH3}, which was considerably higher (8.3 g/kg), and the emission factors of HCN and CH_4, which were lower (1.5 and 7.7 g/kg respectively).

The emission factors for Ponderosa pine, German grass and cottonwood are presented in Table 5.16. The large standard deviation of the pine emission factors denotes the high variability observed in these fires. The highest emissions were measured from the pp1 fire, which also had the highest amount of fuel burned by smoldering (47%, in contrast to 4% and 5% in the other two fires) even though the difference in fuel moisture content was not significant (16% to 15%). The reason for this difference was the relatively light fuel loading of the pp1 fire (0.27 kg/m^2) versus the much more compact packing of pp2 and pp3, which had a fuel loading of 2.9 kg/m^2. A very lightly packed or porous fuel bed tends to burn slowly because individual fuel particles are located so far apart that the heat is transferred inefficiently between particles. On the other hand, a very compact fuel bed also burns slowly because airflow among the fuel particles is impeded (Burgan and Rothermel 1984).

The emissions from the German grass listed in Table 5.16 are comparable with the other grass-type fuels burned in this study. Bertschi *et al.* (2003a) also report emissions from a cottonwood log, which burned with a similar MCE to the one burned in this study, and the emission factors for most compounds were comparable. However, it must be noted that the EF of acetic acid and hydroxyacetaldehyde together (7.2 g/kg) was a factor of three lower than the EF of mass 61 measured here.

Table 5.15. Average MCE and total emission factors (g/kg) for Fir Duff, Pine/Fir Duff and NWT Duff.

Cmpd/mass	**Fir Duff**[a]		**Pine/ Fir Duff**	**NWT Duff**	*mass*	**Fir Duff**		**Pine/ Fir Duff**	**NWT Duff**
MCE	0.85	(0.003)	0.79	0.79	*80*	0.27	(0.12)	1.00	
CO	183.0	(2.47)	237.17	282.67	*81*	0.64	(0.30)	2.43	
CO2	1558.4	(22.28)	1370.9	1631.1	*82*			0.81	
NO	1.00	(0.41)	0.38		*83*	2.27	(0.69)	6.33	1.01
CH4	13.67	(6.52)	25.50	11.61	*84*	0.37	(0.08)	0.91	
C2H4	2.41	(0.71)	3.28	0.99	*85*	3.31	(0.86)	7.93	1.20
C2H2	0.05	(0.06)	0.05	0.002	*87*	3.73	(0.92)	6.95	1.02
NH3	6.70	(2.18)	8.23	1.64	*89*	1.32	(0.61)	2.06	
HCN	2.63	(0.53)	2.64	3.82	*91*	0.79	(0.15)	0.23	
HCHO	0.30		1.47	0.78	*93*	0.84	(0.20)	2.46	1.00
HCOOH	2.64	(0.56)	2.82	1.09	*94*	0.12	(0.03)	0.61	
33	7.06	(2.91)	10.21	2.76	*95*	1.00	(0.38)	4.76	1.03
39	14.95	(6.04)	0.08		*96*	0.16	(0.08)	0.86	
41	0.25	(0.40)	1.73	0.47	*97*	4.84	(1.03)	15.50	3.67
42	1.58	(0.31)	1.72	0.66	*99*	1.82	(0.73)	6.80	
43	2.18	(1.37)	6.65	2.07	*101*	1.25	(0.41)	3.50	0.56
45	4.00	(0.47)	5.41	1.43	*103*	1.33	(0.79)	2.20	0.17
46	0.40	(0.12)	0.44		*104*	0.37	(0.06)	0.76	
54	0.14			0.07	*105*	0.79	(0.16)	0.65	
55	0.55			0.61	*107*	0.63	(0.20)	1.55	0.33
56	0.26			0.13	*109*	0.62	(0.47)	4.92	
57	3.83	(2.10)	3.86	1.22	*111*	1.42	(0.79)	8.02	
59	3.44	(0.85)	4.97	2.19	*113*	0.94	(0.39)	5.11	
60	1.00	(0.61)	1.55	0.02	*115*	0.79	(0.30)	3.12	
61	20.80	(5.36)	22.99	7.31	*117*	0.80	(0.35)	2.83	
62	0.40	(0.10)	0.47		*118*	0.11	(0.01)	0.38	
67	0.09	(0.03)	0.34		*119*	0.33	(0.04)	0.52	
68	0.32	(0.16)	0.81		*121*	0.33	(0.13)	1.71	0.26
69	1.81	(0.28)	4.77	1.15	*123*	0.32	(0.20)	2.96	
70	0.26	(0.06)	0.51		*125*	0.89	(0.62)	6.97	
71	1.79	(0.47)	3.72	0.71	*127*	0.51	(0.18)	2.69	
73	7.13	(4.26)	4.81	1.13	*129*	0.43	(0.23)	2.22	
75	6.24	(2.15)	10.45	0.92	*135*	0.20	(0.11)	0.93	
79	4.86	(3.80)	1.66	0.57					
Sum[b]						145.29	(53.99)	241.81	53.64

[a] Number of fires: Fir Duff (3), Pine/Fir Duff (1), NWT Duff (1).

[b] Sum of all compounds except CO, CO$_2$ and NO.

Table 5.16. Average MCE and total emission factors (g/kg) for Ponderosa pine, German grass and Cottonwood.

Cpd/mass	**Pine**[a]		**German Grass**		**Cotton-wood**	*mass*	**Pine**		**German Grass**		**Cotton-wood**
MCE	0.95	(0.03)	0.97	(0.003)	0.88	*75*	0.59	(0.64)	0.35	(0.14)	12.74
CO	65.34	(27.71)	35.83	(3.18)	124.47	*79*	0.58	(0.74)	0.11	(0.02)	1.56
CO2	1792.5	(109.5)	1684.9	(4.28)	1422.5	*80*	0.03	(0.02)			0.14
NO	1.29	(0.25)	2.42	(0.14)	0.46	*81*	0.32	(0.33)	0.06	(0.02)	3.08
CH4	2.37	(2.39)	0.93	(0.30)	13.17	*82*	0.19	(0.12)			0.26
C2H4	0.58	(0.32)	0.36	(0.05)	2.94	*83*	0.78	(0.83)	0.24	(0.03)	3.41
C2H2	0.08	(0.02)	0.07	(0.04)	0.82	*84*	0.07	(0.06)			0.22
NH3	0.57	(0.34)	0.98	(0.42)	0.25	*85*	0.93	(1.20)	0.36	(0.09)	3.23
HCN	0.15	(0.12)	0.26	(0.01)	0.35	*87*	0.85	(1.10)	0.37	(0.08)	8.90
HCHO	0.54	(0.41)	0.45	(0.08))	2.46	*89*	0.25	(0.29)			2.92
HCOOH	0.69	(1.14)	0.07	(0.04)	3.06	*91*	0.10	(0.13)			0.17
33	1.35	(1.92)	0.33	(0.02)	12.17	*93*	0.23	(0.16)	0.09	(0.02)	0.80
39	0.08	(0.11)			0.08	*94*	0.03	(0.02)			0.11
41	0.22	(0.13)			1.08	*95*	0.44	(0.34)	0.14	(0.03)	6.99
42	0.11	(0.07)	0.19	(0.04)	0.08	*96*	0.06	(0.05)			0.54
43	0.43	(0.29)	0.28	(0.02)	4.55	*97*	1.10	(1.28)	0.44	(0.12)	5.19
44	0.07	(0.05)				*99*	0.76	(0.80)			4.21
45	0.65	(0.71)	0.47	(0.01)	2.61	*101*	0.34	(0.46)	0.08	(0.02)	2.52
46	0.14	(0.18)			0.14	*103*	0.42	(0.55)			1.49
49	0.03	(0.04)				*104*	0.05	(0.03)			0.11
53	0.01	(0.01)				*105*	0.10	(0.07)			0.29
54	0.02	(0.004)	0.05	(0.01)		*107*	0.18	(0.12)	0.07	(0.01)	0.62
55	0.10	(0.01)	0.06	(0.04)		*109*	0.44	(0.29)			2.04
56	0.04	(0.04)	0.03	(0.004)		*111*	0.63	(0.55)			3.21
57	0.49	(0.25)	0.35	(0.05)	1.67	*113*	0.33	(0.32)			2.62
58	0.04	(0.03)				*115*	0.22	(0.25)			1.03
59	0.55	(0.59)	0.28	(0.05)	2.80	*117*	0.21	(0.24)			6.63
60	0.08	(0.08)			0.20	*118*					0.42
61	4.69	(7.12)	1.11	(0.40)	21.59	*119*	0.08	(0.06)			0.34
62	0.16	(0.15)			0.46	*121*	0.14	(0.10)	0.04	(0.01)	0.42
67	0.08				0.44	*123*	0.22	(0.12)			1.36
68	0.08	(0.07)			0.12	*125*	0.38	(0.33)			2.42
69	0.49	(0.47)	0.18	(0.03)	2.28	*127*	0.14	(0.15)			1.48
70	0.05	(0.04)			0.14	*129*	0.14	(0.13)			0.98
71	0.48	(0.44)	0.28	(0.04)	3.97	*135*	0.12	(0.09)			0.32
73	0.55	(0.64)	0.42	(0.09)	2.37						
Sum[b]							27.44	(30.19)	9.48	(2.32)	162.55

[a] Number of fires: Pine (3), German Grass (3), Cottonwood (1).

[b] Sum of all compounds except CO, CO_2 and NO.

5.4.8. Proportional emission of VOCs and other gases integrated over the flaming and the smoldering phases

As already mentioned in section 5.2, emissions from the flaming phase are dominated by highly oxidized products, such as CO_2, NO, N_2O and SO_2, whereas the high diversity of emissions, in particular the VOCs, are produced during smoldering combustion. Nevertheless, most compounds that are measured mainly in the smoldering phase are also emitted during flaming, but oxidized by the flames to a greater or lesser extent (Lobert and Warnatz, 1993). The purpose of this section is therefore to quantify the fraction of the total emissions of these compounds that was emitted during the flaming and smoldering combustion of the different fuels. The *relative* emission of some important compounds during flaming and smoldering combustion is presented in Figure 5.11 (African fuels) and Figure 5.12 (Indonesian fuels). In most fires, the transition from flaming to smoldering combustion did not occur rapidly, and a considerable fraction of the emissions was emitted during the mixed phase. To account for the totality of the emissions, the mixed phase was assumed to contribute equally (50:50) to both flaming and smoldering phases.

Flaming combustion consumed approximately 90% of the fuel in dambo and miombo fires, and 80% in the miombo litter fire (Fig. 5.11). In dambo fires, more than half of the total emissions of almost all compounds were actually emitted in the flaming phase (MCE ~0.99). Even for compounds that are normally emitted predominantly during smoldering, like CO or NH_3, the contribution of the smoldering phase to the total emissions was very little. However, the miombo fires, which burned with a little lower average MCE (0.978), present a different picture: more than 50% of the total emissions of most compounds were during smoldering. Some compounds for which the pattern was different, like ethylene (C_2H_4), acetylene (C_2H_2) and benzene (mass 79), were also found to be emitted in significant amounts during both combustion stages in previous studies. Strangely enough, during the miombo litter fire, more than 50% of the total emissions of many substances occurred during flaming, even though the MCE (0.945) was lower than the MCE yielded in dambo and miombo fires (~0.98). Possible causes for this effect are the high emission factors of the flaming and mixed phases during the miombo litter fire, some of which were even higher for the mixed than for the smoldering phase (see section 5.4.5 and Table 5.7), and therefore could have a big influence on the distribution seen at Fig. 5.11.

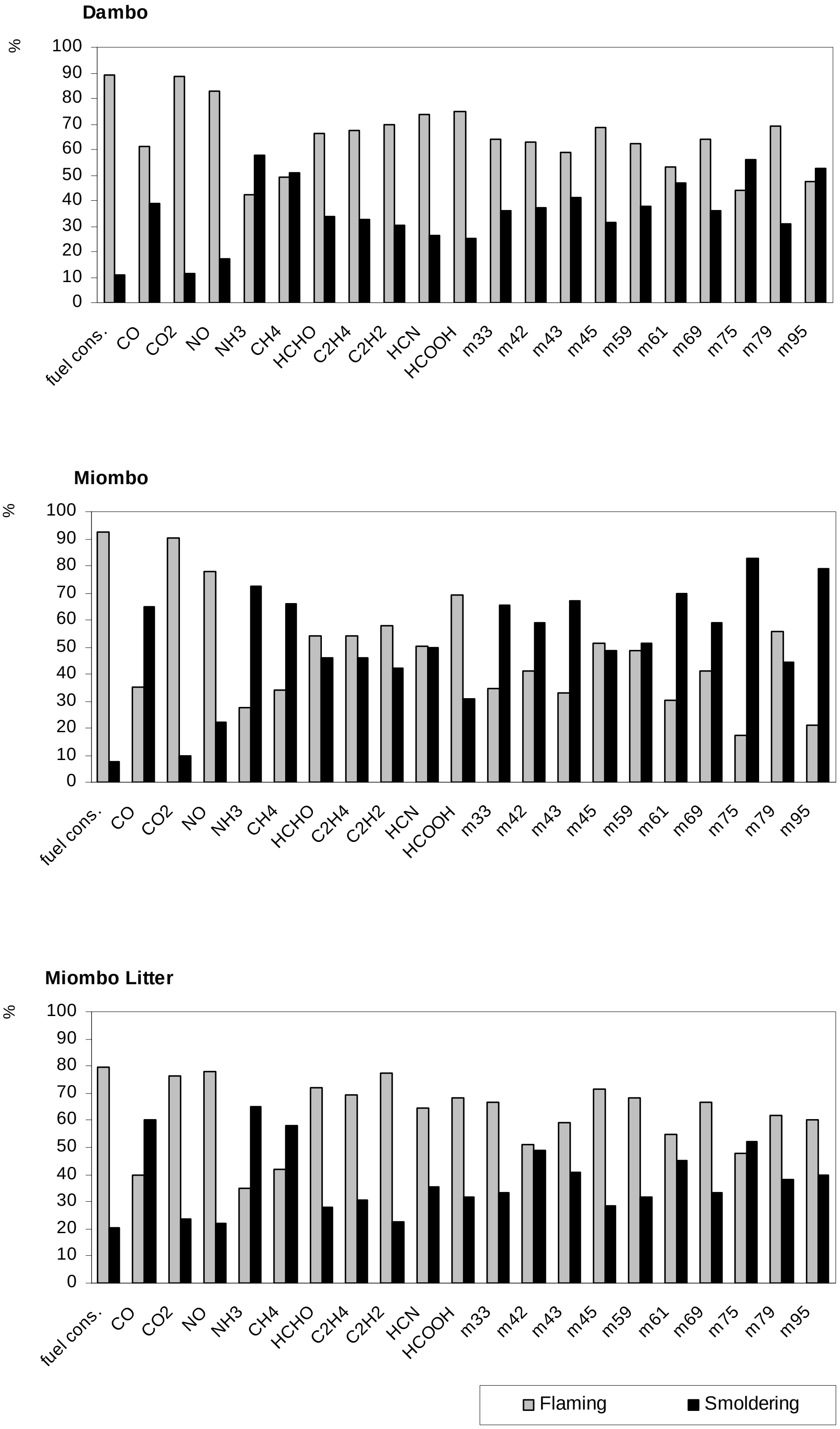


Figure 5.11. Distribution of the emissions of dambo and miombo fires between the burning phases.

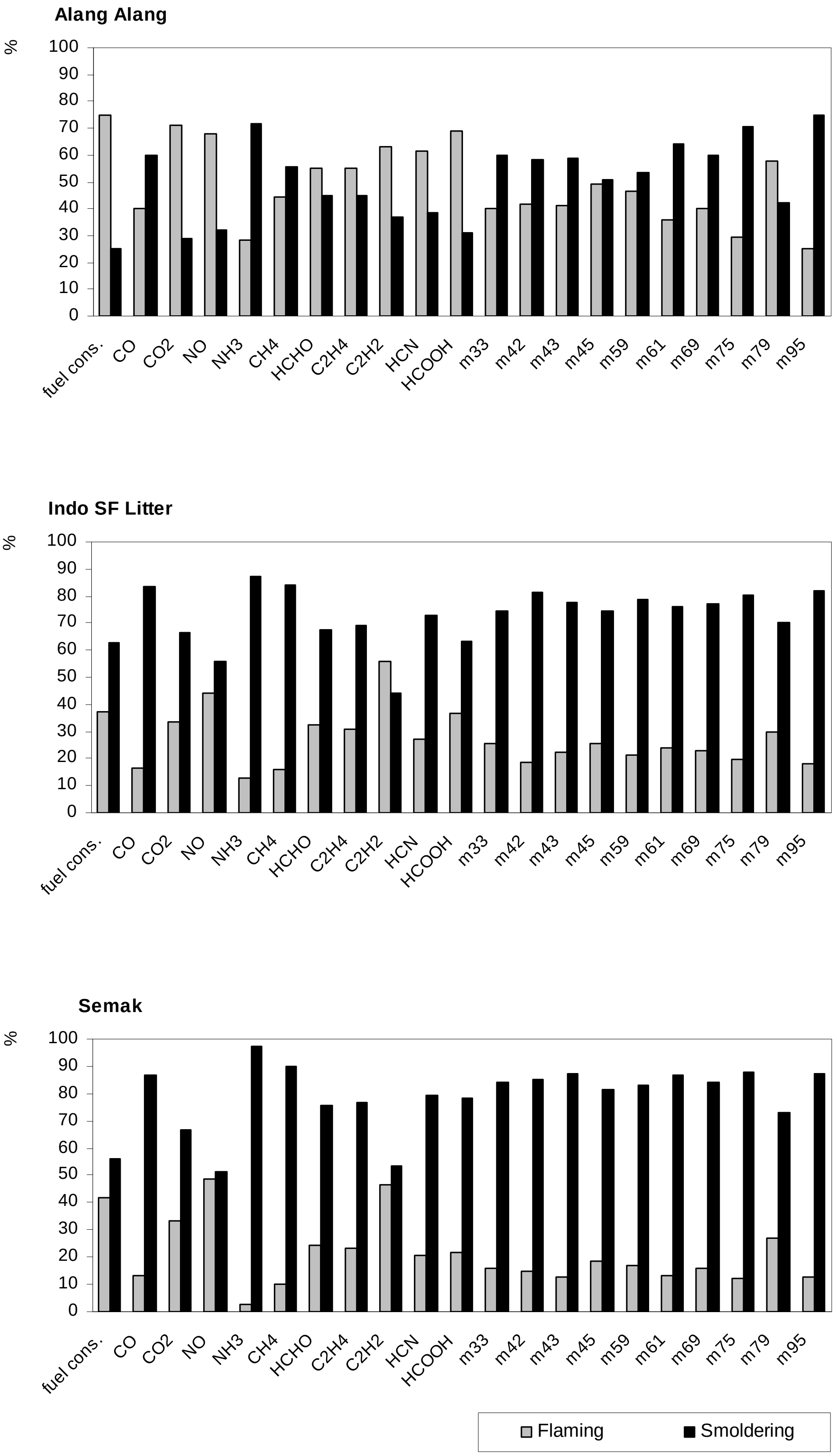


Figure 5.12. Distribution of the emissions of alang-alang, Indo SF litter, and semak fires between the burning phases.

The Alang-alang fires (Fig. 5.12) behaved similarly to the miombo fires. In the other Indonesian fuels, Indo litter and semak, which were at least half-consumed by smoldering, more than 60% of the emissions were produced during smoldering. Exceptions were NO and C_2H_2, whose emissions were almost equally distributed between the two combustion phases

5.4.9. Relative proportion among the main compound groups

The large variability in the amount of trace gases emitted from different fuel types was discussed in the preceding chapters (5.4.5 to 5.4.7). The sum of emission factors of individual compounds was found to range from values lower than 20 g/kg for grass-type fires up to values higher than 200 g/kg fuel burned for rice straw and pine/fir duff fires (Table 5.17). To avoid getting lost in so many individual compounds we formed groups (see Table 5.3) of similar compounds which are: POVOCs, aromatic and unsaturated compounds, nitrogen-containing compounds (other than NO) and methane. In view of the tremendously variable total emission factors, the relative proportions among these groups will be evaluated in this section. The contribution of each group to the sum of emissions, expressed as emission factors (i.e. g/kg) and as percentages is presented in Table 5.17.

Table 5.17 shows that POVOCs accounted for more than half of all emitted trace gases on average (range 36–66%). The average POVOCs emission from African fuels was ~11 g/kg (when extrapolated to typical MCE observed in real fire plumes), this is a factor of two higher than the measured sum of POVOCs during SAFARI 2000 of 5.3 g/kg (Yokelson *et al.*, 2003a), which is not surprising since the number of oxygenated compounds measured in the present study is considerably higher. The highest POVOC emissions were measured from smoldering fires such as rice straw and pine/fir duff. POVOCs have large effects on modeled smoke plume photochemistry (Mason *et al.*, 2001), including net O_3 production and the rates of production of hydrogen peroxide, peroxyacetyl nitrate (PAN) and other longer lived HO_x and NO_x reservoir species.

Aromatic and unsaturated compounds accounted for ~23% of the emissions on average. This corresponds to an EF lower than 5 g/kg for grass-type fires, and ~21 g/kg for Indonesian fuels. The largest emissions were observed from pine/fir duff and rice straw (56 and 45 g/kg respectively), as in the case of the POVOCs.

The emission of N-compounds was extremely variable, depending to a high degree on the nitrogen content of the fuel and the combustion efficiency (see next section). Therefore, African grasses (which burned with high combustion efficiency) and cottonwood (a fuel with very low N-content) showed the lowest emission of nitrogen compounds, around 5%, which represents an EF of less than 2 g/kg. On the other end of the scale we find Indo peat, whose N-content (2.12%) was the highest among the studied fuels, and additionally burned with low combustion efficiency. For this fuel, the nitrogen compounds accounted for 32% of the total emissions, which corresponds to 47 g/kg, about equal to the POVOC emission of this fuel (36%; 52.3 g/kg).

Methane represented 8% of the average total emissions of African and 6% of the Indonesian fire emissions. These percentages correspond respectively to an EF_{CH4} of 1.5 and 5.7 g/kg. The highest CH_4 emissions were observed from the peat and duff fires (11–25 g/kg).

Table 5.17. Proportional contribution of POVOCs, aromatic and unsaturated hydrocarbons, N-containing compounds and methane to the total emission factors[a]

	POVOCs	Aromatic + unsaturated	N-Compounds	CH_4	Sum total EF[b]
African fuels					
Dambo	1.56 (62.8%)	0.63 (25.5%)	0.14 (5.7%)	0.14 (5.5%)	2.49
Miombo	2.60 (59.2%)	1.13 (25.7%)	0.30 (6.8%)	0.37 (8.3%)	4.40
Miombo litter	5.71 (47.4%)	2.88 (24.0%)	1.51 (12.6%)	1.96 (16.3%)	12.06
Average African[c]	10.9 (60.9%)	4.57 (25.5%)	0.99 (5.5%)	1.47 (8.2%)	17.9
Indonesian fuels					
Alang-alang	4.09 (52.1%)	1.82 (23.2%)	1.04 (13.2%)	0.90 (11.4%)	7.85
Indo SF litter	38.6 (58.9%)	14.4 (22.0%)	7.17 (10.9%)	5.26 (8.0%)	65.5
Semak	47.4 (54.1%)	22.1 (25.2%)	11.6 (13.2%)	6.41 (7.3%)	87.7
Rice straw	130.4 (63.0%)	44.7 (21.6%)	21.3 (10.3%)	9.59 (4.6%)	206.8
Indo. peat	53.2 (36.0%)	26.4 (17.8%)	47.2 (32.0%)	20.8 (14.1%)	147.7
Average Indonesian[d]	51.2 (56.1%)	21.4 (23.4%)	12.8 (14.1%)	5.66 (6.2%)	91.2
Other fuels					
Fir duff	72.7 (50.0%)	41.7 (28.7%)	16.2 (11.1%)	13.7 (9.4%)	145.3
Pine/firduff	129.2 (53.4%)	56.3 (23.3%)	29.3 (12.1%)	25.5 (10.5%)	241.8
NWT duff	25.4 (47.4%)	10.2 (19.1%)	6.34 (11.8%)	11.6 (21.6%)	53.6
Pine	15.8 (57.7%)	6.58 (24.0%)	2.53 (9.2%)	2.37 (8.6%)	27.4
German grass	4.89 (51.5%)	2.13 (22.5%)	1.54 (16.2%)	0.93 (9.8%)	9.48
Cottonwood	107.7 (66.2%)	33.9 (20.9%)	7.65 (4.7%)	13.2 (8.1%)	162.6

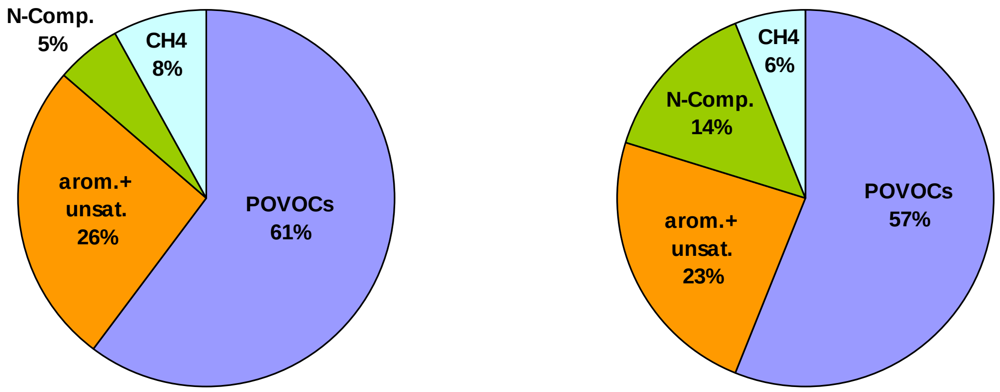
[a] Values are emission factors (g/kg dry matter burned), and expressed as percentages in parentheses.

[b] Sum of total emission factors excludes CO, CO_2 and NO emissions.

[c] Based on estimated emission factors at average MCE measured in the field (0.94).

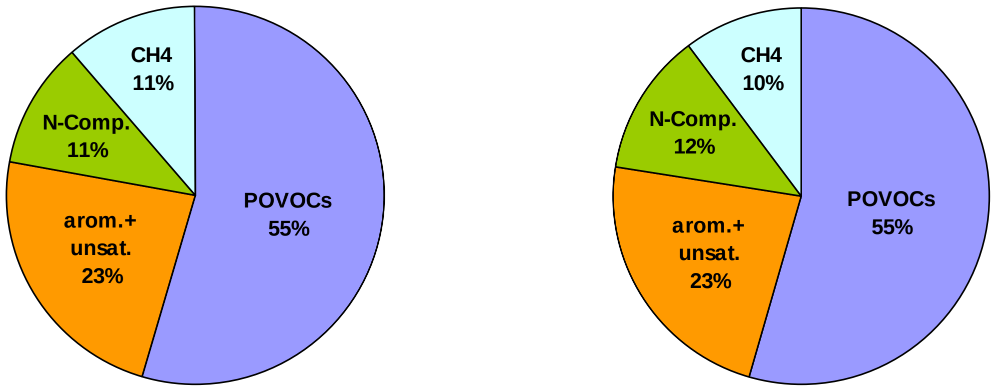
[d] Based on the estimated emission factors of Indonesian fuels of Table 5.14.

A summary of the average proportional contribution of the different compound-types to the total emissions of African, Indonesian and other fuels, as well as an overall average of all fuels is shown in Figure 5.13. In spite of the large differences in emission factors, the emission pattern was similar for all fuels (see also Table 5.17). POVOCs were the most important compound-type emitted by biomass burning, and the highest variability was found in the N-containing compounds.



Average African fuels

Average Indonesian fuels



Average other fuels

Average all fires

Figure 5.13. Average proportional composition of biomass-burning emissions.

5.4.10. Emission mechanisms investigated for acetonitrile

Among the nitrogen-containing compounds, acetonitrile (CH_3CN) is a compound of particular interest, since it can serve as a global tracer for biomass burning, given that its atmospheric production is dominated by biomass burning emissions (Lobert *et al.*, 1990; Holzinger *et al.*, 1999; Bange and Williams, 2000; Holzinger *et al.*, 2001a). The emission of nitrogen-containing compounds is closely related to the fuel nitrogen content and combustion efficiency. Linear relationships with fuel nitrogen content have been found for emissions of NO_x (Clements and McMahon, 1980; Dignon and Penner, 1991; Lacaux *et al.*, 1996), N_2O and propionitrile (Lobert *et al.*, 1991), and other N-VOCs, including acetonitrile (Holzinger *et al.*, in preparation, 2004).

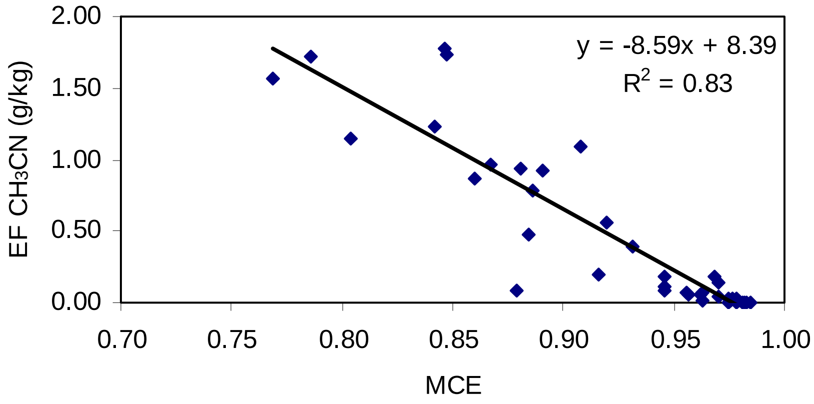


Figure 5.14. Dependence of acetonitrile (CH_3CN) emission factors on the modified combustion efficiency (MCE). All fires, except NWT1 and Indo peat, were included (see text).

Figure 5.14 shows that the emission factor of acetonitrile is strongly anti-correlated with the MCE, i.e. CH_3CN is emitted in much higher quantities during smoldering fires. The $ER_{CH3CN/CO}$ is positively correlated to the nitrogen content of the fuel (Figure 5.15, R^2=0.46), as is the EF_{CH3CN}, albeit more weakly ($R^2 = 0.30$). The high values at 0.67 and 1.05 %N correspond to rice straw and fir duff fires, respectively.

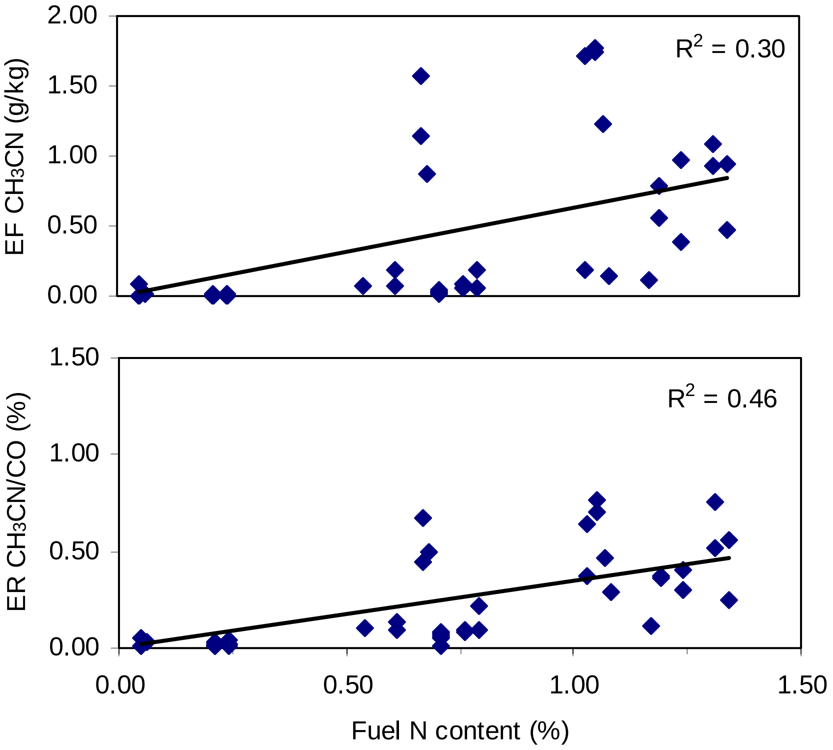


Figure 5.15. Dependence of acetonitrile (CH_3CN) emission factors and emission ratios on the fuel nitrogen content.

Two outliers, the indo peat and NWTduff fires, which had very high N-content and low MCE, were disregarded (also excluded from the correlation in Fig. 5.14). The correlation with the N-content did not change significantly, but the results of the analysis, which is presented next, were improved without these two fires.

With a simple model acetonitrile emission-factors were calculated by using only the linear correlation of EF vs. MCE (Fig. 5.14). The *calculated* EF values plotted against the *measured* EF values are shown in Figure 5.16. The correlation of the calculated EF vs. measured EF was found to be improved when the linear correlation equation was modified to include a factor taking into account the N-content of the fuel. The best fit ($R^2 = 0.93$) was obtained with following equation:

$$calculated\ EF_{CH3CN} = \left(-8.59\,MCE + 8.39\right)\times\left(\frac{\%N}{avg\%N}\right)^{0.7} \qquad (5.7)$$

where *%N* is the N-content of the fuel, *avg %N* the average N-content of all fuels (0.7%), and MCE the modified burning efficiency. The parameters -8.59 and 8.39 have been obtained from the linear fit in Figure 5.14, and *0.7* is an empirical factor which maximizes the correlation between measured and calculated EFs.

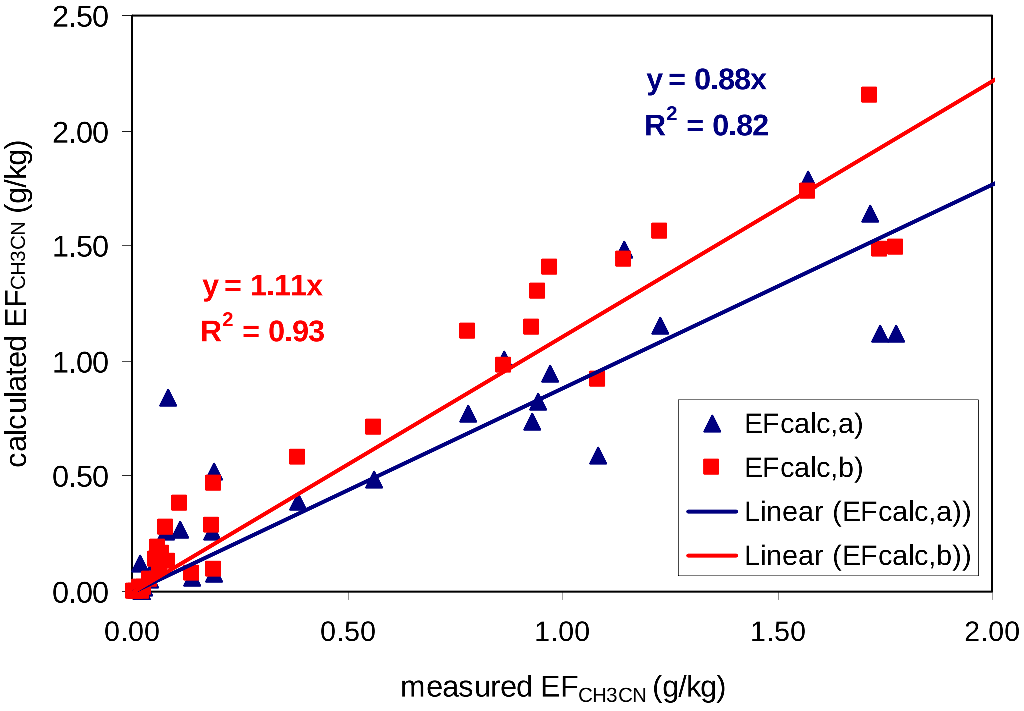


Figure 5.16. Correlation of measured and calculated emission factors of acetonitrile (EF_{CH3CN}). was calculated using (a) correlation with MCE only, and (b) correlation with MCE and N-content of the fuel.

5.5. Summary and conclusion

In this biomass burning study, the trace gas emissions of 44 fires and 15 different biomass types mainly from Africa and Indonesia were analyzed using PTR-MS and OP-FTIR techniques. Around 60 significant mass signals were detected with PTR-MS. Eighteen substances were measured with OP-FTIR, ten of them having proton affinities greater than that of water, and thus a quantitative comparison with the PTR-MS results was possible. Excellent agreement was observed for methanol (mass 33). Reasonable agreement was found for phenol (mass 95) and acetol (mass 75). Two or more contributing compounds were considered for many masses measured with PTR-MS. PTR-MS signal at mass 59 was accounted for –within experimental uncertainty– by the sum of acetone and methylvinylether measured by OP-FTIR. The data suggest that in grass-type fires, acetone accounted for ~40 – 60% of mass 59, and for ~70% in fires which burned with lower efficiency. The signal on mass 61 was accounted for by acetic acid (80%) and hydroxyacetaldehyde (20%), and the signal on mass 69 by the sum of furan (60%) and isoprene (40%).

The average sum of trace gas emissions was estimated to be ~18 g/kg for African fuels at the MCE measured in the field. Six of the ten most important emissions were POVOCs, acetic acid being the major emission, followed by methanol and formaldehyde. The emission of nitrogen-containing compounds (excluding NO) was found to be ~1 g/kg for African fuels. This value, which represents 5% of the total emissions, is low compared to emissions from Indonesian biomass (see below), but not unexpected, since African fuels showed a low N-content. Additionally, these fuels burned mainly with flaming combustion and most N-containing compounds are emitted primarily during the smoldering phase. The emission factor for methane was in the same range as that for methanol, and represented 8% (by weight) of the emissions.

The annual estimates of emissions from global savanna and grassland fires, obtained using the emission factors estimated for African fuels, suggest that the sum of all trace-gas emissions is about 56 Tg/yr, from which 34 Tg correspond to POVOCs (4.5 Tg of which are methanol), 14 Tg can be attributed to unsaturated hydrocarbons and aromatic compounds, around 5 Tg to methane, and 3 Tg to N-compounds.

These were the first lab simulations of Indonesian fires, and there are no field measurements of emission factors or MCE. The relative amount of the different biomass types that on average burn in Indonesia is not known. Therefore, the estimated average emission factors were calculated by weighting all the fuels equally. Acetic acid was the highest organic emission, acetol (mass 75) a compound previously unreported in smoke, was second, followed by methane, mass 97 (a mixture of furfural, dimethylfuran, ethylfuran), and methanol. The relative proportion among individual emissions was similar to that of African fuels, with the exception of N-containing compounds, whose share on the total emissions was on average 14% (compared to 5% for African fuels). This difference was due to the combination of higher N-content, and more smoldering combustion of the fuels. Fires burned with Indonesian fuels had very large NH_3 emissions, e.g. the emission from the single Indonesian peat sample yielded an emission factor of 20 g/kg (16% of CO). The average emission factor of NH_3 is comparable to the emission of methane, and this makes ammonia to the fourth most abundant emission. The sum of total emissions (excluding CO_2, CO and NO) of Indonesian fires was ~91 g/kg. The emission factors of individual compounds were also on average ~5 times as large as those of African fires.

An analysis of the proportion of compound emissions integrated over the flaming and the smoldering phase showed that compounds which are known to be produced more efficiently in the smoldering phase –such as CO and acetonitrile– were also emitted during the flaming phase in considerable amounts. In fires during which approximately 80-90% of the fuel was consumed in the flaming phase, the fraction of *typical* smoldering compounds emitted during the flaming phase ranged between ~30–60%. In other fuels, which were mainly consumed by smoldering, most of these substances were emitted during smoldering, and during flaming only a fraction of 30% or less was emitted.

Despite the big diversity of fuel types burned, and the large differences in emissions measured, the relative proportion among the major emission groups was similar for all fuels: the sum of all measured trace gas emissions was composed on average of 55% POVOCs, 23% aromatic and unsaturated hydrocarbons, 12% N-compounds and 10% methane.

6. Summary

Volatile organic compound (VOC) emissions from tropical savanna grasses and trees, as well as emissions from biomass fires, have been characterized in the course of this work. A proton-transfer-reaction mass spectrometer (PTR-MS) was used for online measurements of VOCs. The detection of VOCs relies on proton-transfer reactions between H_3O^+ primary ions and trace gases with a proton affinity higher that that of water, which is the case for many VOCs and excludes the major components of air.

The biogenic emissions of tropical savanna vegetation were studied in a woodland savanna in Venezuela. Two field campaigns were carried out, the first during the wet season in September/October 1999, and the second in March/April 2000 during the dry season. Three of the most important grass and tree species of the Venezuelan savanna were studied. The emission rates and the controlling variables were determined with a dynamic plant enclosure system, which allowed the measurement of a whole grass tussock or tree sapling.

Most VOC emissions showed a diurnal variation, with highest values at noon and early afternoon, and low or no emissions during the night. In general, the emissions increased exponentially with increasing temperature and solar radiation, but correlated better with temperature. The emission data were therefore normalized to a standard temperature of 30°C, and the *standard emission rates* thus determined allowed for interspecific and seasonal comparisons. The temperature dependence was modeled using the emission algorithm established by Guenther *et al.* (1993). The temperature dependence parameter, β, was in the range 0.08-0.23 K^{-1} for the grass species, and 0.13-0.22 K^{-1} for the tree species. Variations of β were random, with no interspecific or seasonal trend.

Savanna grasses were measured at three developmental stages: mature (in the wet season), and young and dry (in the dry season). The total emission of VOCs from the green (mature and young) grasses was in the range 200-400 ngC/g/h. The oxygenated species methanol (m33), acetaldehyde (m45), acetone (m59) and methyl ethyl ketone (MEK, m73) represented 70-75% of the total, with methanol being the primary emission. The remaining 30% consisted of olefins (propene, m43; butene, m57) and other unidentified species. The total emission of VOCs from the dry grasses was in the range 24-44 ngC/g/h, and methanol accounted for more than half of the total emissions. The standard emission rates of certain VOCs were found to vary by up to a factor of five between plants of the same species, as well as between the different species. Stress to the plant, as well as genetic differences, could be possible explanations for these variations.

Based on the standard emission rates, an estimate of the source strength of savanna grasses for the tropical areas was calculated for methanol, acetone, acetaldehyde and MEK. The annual source of methanol from savanna grasses estimated in this work was between 3-4.4 TgC, which could represent up to 12% of the current estimated global emission from vegetation, which is the main global source of methanol. For acetone, acetaldehyde and MEK, the savannas may contribute up to ~10%, 4% and 30% of the biogenic source, respectively. Nevertheless, these estimates should be considered with care, since the emission inventories of these and other oxygenated VOCs are uncertain; the biogenic sources of many species are particularly poorly quantified.

Two of the three savanna tree species investigated were isoprene emitters, and isoprene was generally also the primary emission of these species, followed by methanol. The highest average isoprene standard emission rate was 23 μgC/g/h, and accounted for ~85% of the carbon emitted from one of these species in the wet season. In the dry season measurements, in contrast, the individuals of this species, whose leaves were still developing, presented much higher methanol than isoprene emissions. The plant-to-plant variation in the standard emission rates was around a factor of three, whereas the interspecific and seasonal/developmental variability was much higher (i.e., more than an order of magnitude). The sum of VOC emissions ranged between 0.6 and 27 μgC/g/h in the wet season, and 0.2 and 5 μgC/g/h in the dry season for all measured tree species.

The biomass burning study comprised the measurement of VOCs and other trace-gas emissions of 44 fires from 15 different fuel types, primarily from Africa and Indonesia, in a combustion laboratory. Fuel types included, among others, grass and litter from African savannas, Indonesian grass, shrub, secondary forest litter, rice straw and peat. In addition to the PTR-MS, the emissions were also measured with an open path Fourier transform spectrometer (OP-FTIR), which measured several gases that cannot be measured with the PTR-MS technique, and ten compounds which have a proton affinity higher than that of water. It was therefore possible to obtain both qualitative support for the PTR-MS mass peak identifications, as well as a quantitative comparison of emissions for many compounds.

The average sum of emissions (excluding CO_2, CO and NO) from African fuels was ~18 g/kg (g of compound per kg dry fuel burned). Six of the ten most important emissions were oxygenated VOCs. Acetic acid was the major emission, followed by methanol and formaldehyde. The emission of methane was of the same order as the methanol emission (~5 g/kg), and the emission of nitrogen-containing compounds was ~1 g/kg. An estimate of the VOC source from biomass burning of savannas and grasslands worldwide suggests that the sum of emissions is about 56 Tg/yr, of which 34 Tg correspond to oxygenated VOCs, 14 Tg to unsaturated and aromatic compounds, 5 Tg to methane and 3 Tg to N-compounds.

The emission factors reported here for Indonesian fuels are the first results of laboratory fires using Indonesian fuels. Since the relative amounts of the different fuels that burn in Indonesia on average is not known, the average emission factors were calculated by weighting all fuels equally. The sum of total emissions of Indonesian fuels was 91 g/kg. Acetic acid was the highest organic emission, followed by acetol (mass 75) a compound not previously reported in smoke, methane, mass 97 (tentatively identified as a mixture of furfural, dimethylfuran, ethylfuran), and methanol. The relative proportion of the different compounds emitted was similar to that of African fuels: 57-61% oxygenated VOCs, 23-26% unsaturated and aromatic compounds and 6-8% methane. The only exception was the group of nitrogen-containing compounds, which accounted for 14% of the total emission from Indonesian fuels, compared to only 5% in African fuels. This difference was caused by a combination of higher nitrogen content and longer smoldering combustion of the Indonesian fuels.

The results of this study show that oxygenated compounds, especially methanol, dominate the emissions of VOC from savanna grasses. For the measured tree saplings, methanol was also an important emission, exceeded only by isoprene. The biomass burning experiments also demonstrate the importance of oxygenated VOCs, which represent about 60% of the total trace-gas emission measured from the burning of African and Indonesian fuels. Acetic acid was the main organic emission from all fuel types, but methanol was also important, especially for the African fuels, for which methanol was in the same emission range as methane, whose emission represented ~8% of the total. Due to the vast area covered by tropical savannas worldwide, the biogenic and biomass burning emission of methanol and other oxygenated compounds may be important for the regional and even global tropospheric chemistry. This study represents a significant improvement to the current biogenic and biomass-burning emission inventories.

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8. Appendices

8.1. List of Abbreviations

A	Leaf area (m^2)
CCN	Cloud condensation nuclei
CH_3CN	Acetonitrile
CH_4	Methane
CI	Chemical ionization
CO	Carbon monoxide
CO_2	Carbon dioxide
dw	dry weight (g)
E	Exchange rates
EI	Electron impact ionization
EF	Emission factor (g of compound/kg dry fuel burned)
ER	Emission ratio (compound X/CO or X/CO2)
GPP	geranyl diphosphate
g_s	Stomatal conductance
H	Henry´s Law constant
H_3O^+	Hydronium ion
HC	Hollow cathode
HCN	Hydrogen cyanide
HO_2	Hydroperoxyl radical
IMR	ion-molecule reactions
IPP	isopentenyl pyrophosphate
LT	Local time
MACR	Methacrolein
MBO	2-Methyl-3-buten-2-ol
MCE	Modified combustion efficiency ([CO2]/ ([CO2]+[CO]))

MEK	Methyl ethyl ketone
MVK	Methyl vinyl ketone
NMHC	Non-Methane Hydrocarbons
NO_3	Nitrate radical
NO_x	Nitrogen oxides, NO + NO_2
NPP	Net Primary Productivity
NMVOCs	Non-methane VOCs
O_3	Ozone
OH	Hydroxyl radical
OP-FTIR	Open-path Fourier Transform infrared Spectroscopy
PAR	Photosynthetically Active Radiation
POVOCs	Partially oxygenated VOCs
ppb	parts per billion, 10^{-9} parts, nmol/mol
ppm	parts per million, 10^{-6} parts, mmol/mol
ppt	parts per trillion, 10^{-12} parts, pmol/mol
PTR-MS	Proton-transfer reaction Mass Spectrometry
Q	airflow through the chamber (L/min)
R·	alkyl (or substituted alkyl) radicals
RO·	alkoxy radicals
RO_2·	alkyl peroxy radicals
sccm	standard cubic centimeters per minute
SD	Standard deviation
SEM	Secondary electron multiplier
SOA	Secondary organic aerosols
Tg	Teragram (10^{12} g)
UTC	Coordinated Universal Time
Vm	molar volume of ideal gas at STP (22.414 L/mol)
VOCs	Volatile Organic Compounds
W	Watt

8.2. List of Figures

8.3. List of Tables

8.4. Appendix to Chapter 3

Table 8.1. Night-time VOC exchange rates [nmol/g/h] from three grass species in the wet and dry season. Data are 10-min averages ± SD of night-time (20:00-5:00) measurements. n.d. means not detected. Some individuals were not measured during the night, and were therefore not included in the table.

	m33	m43	m45	m57	m59	m69	M73
			Wet Season / *Trachypogon plumosus* (mature grass)				
Tp 1	3.7±2.4	-0.4±0.9	-0.8±1.8	-0.3±1.0	2.1±1.6	n.d.	-0.1±0.5
Tp 3	n.d.	-0.2±0.6	-0.2±0.7	n.d.	0.3±0.6	n.d.	n.d.
Tp 4	n.d.	-0.3±1.3	-0.4±1.5	0.2±1.2	0.7±1.2	n.d.	-0.1±0.7
			Dry Season / *Trachypogon plumosus* (young grass)				
Tp 1/y	8.7±6.9	0.4±1.0	-0.1±0.8	n.d.	3.8±3.1	n.d.	0.1±0.4
Tp 2/y	10.8±6.3	0.2±0.6	0.2±0.5	0.2±0.6	1.0±0.6	n.d.	0.1±0.2
Tp 3/y	8.7±5.0	0.2±0.5	-0.1±0.4	-0.1±0.5	2.7±2.2	n.d.	n.d.
Tp 4/y	3.4±2.6	0.1±1.0	-0.1±0.7	1.1±1.0	0.4±0.9	n.d.	0.3±0.4
Tp 5/y	1.4±2.0	0.1±0.5	0.0±0.3	1.5±0.9	0.5±0.5	n.d.	0.6±0.3
			Dry Season / *Trachypogon plumosus* (dry grass)				
Tp 1/d	1.2±0.6	n.d.	-0.1±0.1	n.d.	0.1±0.1	n.d.	n.d.
Tp 2/d	1.0±0.9	-0.2±0.7	-0.3±0.3	0.3±0.8	-0.6±0.3	n.d.	n.d.
			Dry Season / *Axonopus canescens* (dry grass)				
Ac 1/d	1.1±0.8	n.d.	n.d.	0.1±0.2	0.1±0.2	n.d.	n.d.
Ac 2/d	1.2±1.0	-0.7±0.6	-0.2±0.3	n.d.	-0.6±0.3	n.d.	n.d.
Ac 3/d	5.0±1.0	-0.4±0.5	0.0±0.3	0.3±0.3	0.3±0.3	n.d.	n.d.
			Wet Season / *Hyparrhenia rufa* (mature grass)				
Hr 1	2.8±2.2	0.2±1.7	0.9±2.1	0.8±1.7	1.8±1.6	n.d.	0.8±1.0
			Dry Season / *Hyparrhenia rufa* (dry grass)				
Hr 1/d	2.1±0.5	-0.4±0.3	-0.3±0.1	-0.1±0.2	-0.4±0.2	n.d.	n.d.
Hr 2/d	4.2±1.2	-0.5±0.5	-0.2±0.3	0.1±0.3	n.d.	n.d.	n.d.
Hr 3/d	2.4±1.3	-0.6±0.8	-0.6±0.4	-0.2±0.5	-0.8±0.5	n.d.	n.d.

Table 8.2. Net Primary Production (NPP) reported from grasslands and savannas (adapted from House and Hall, 2001)

			Aboveground NPP			Belowground NPP			**Total NPP**	
			(g (dm) /m^2/yr)			(g (dm) /m^2/yr)				Source[a]
Site name	Lat.	Long.	Trees	Grass	**Total**	Trees	Grass	**Total**		
"SAVANNAS"										
Lamto, Côte d'Ivoire	6°13N	5°02 W	633	1450	**2083**	37	633	**670**	**2753**	Menaut & Cesar (1979)
			277	1610	**1887**	23	1040	**1063**	**2950**	
			137	1280	**1417**	13	1330	**1343**	**2760**	
			55	1610	**1665**	5	1900	**1905**	**3570**	
Mokwa, Nigeria	9°18N	5°04E	378							Collins (1977)
Nylsvley, South Africa	24°42S	28°42E	282	157	**439**	187	325	**512**	**951**	Scholes & Walker (1993)
Niono, Senegal	14°18N	6°0W		225						De Ridder et al (1982)
Uttar Pradesh	24°18'N	83°0E	393	617	**1010**	43	618	**662**	**1672**	Pandey & Singh (1992)
Average				**909**						
"GRASSLANDS"										
Towoomba, South Africa	24°50S	28°15E		141						Donaldson et al (1984)
Makaholi, Zimbabwe	19°48S	30°48E		146						Ward & Cleghorn (1964)
Nuanetsi, Zimbabwe	21°24S	30°48E		261						Kelly et al (undated)
Klong Hoi Kong, Thailand	6°0N	100°56 E		1595			625		**2220**	Long et al (1992)
Charleville, Australia	26°24S	146°12 E		520			290		**810**	Christie (1978)
Nairobi, Kenya	1°0N	36°49E		881			431		**1312**	Long et al (1989)
Udaipur, India	25°30N	72°24E		180						Vyas et al (1972)
Jodphur, India	26°18N	73°06E		108						Gupta et al (1972)
Delhi, India	28°54N	77°12E		798						Vashney (1972)
Ejura, Ghana	7°30N	3°30E		870						Greenland & Nye (1959)
Kurukshetra, India	9°58N	76°51E		2500			1131		**3631**	Rajvanshi & Gupta (1985)
Calabozo, Venezuela	8°48N	67°27 W		478			146		**624**	Sarmiento (1984)
Manaus, Brazil	3°20S	60°0W		9418			507		**9925**	Long et al (1989)
Montecillos, Mexico	19°28N	98°28 W		1063			678		**1741**	Long et al (1989)
Lamto, Cote d'Ivoire	6°13N	5°02W		1540			2040		**3580**	Menaut & Cesar (1979)
Average (without Manaus)				**837**						

To be included, studies must have measured NPP over a period of at least a year, and used the sum of positive increments method plus some assessment of losses (turnover and herbivory, or litterfall).

[a] For complete references see House and Hall, (2001)

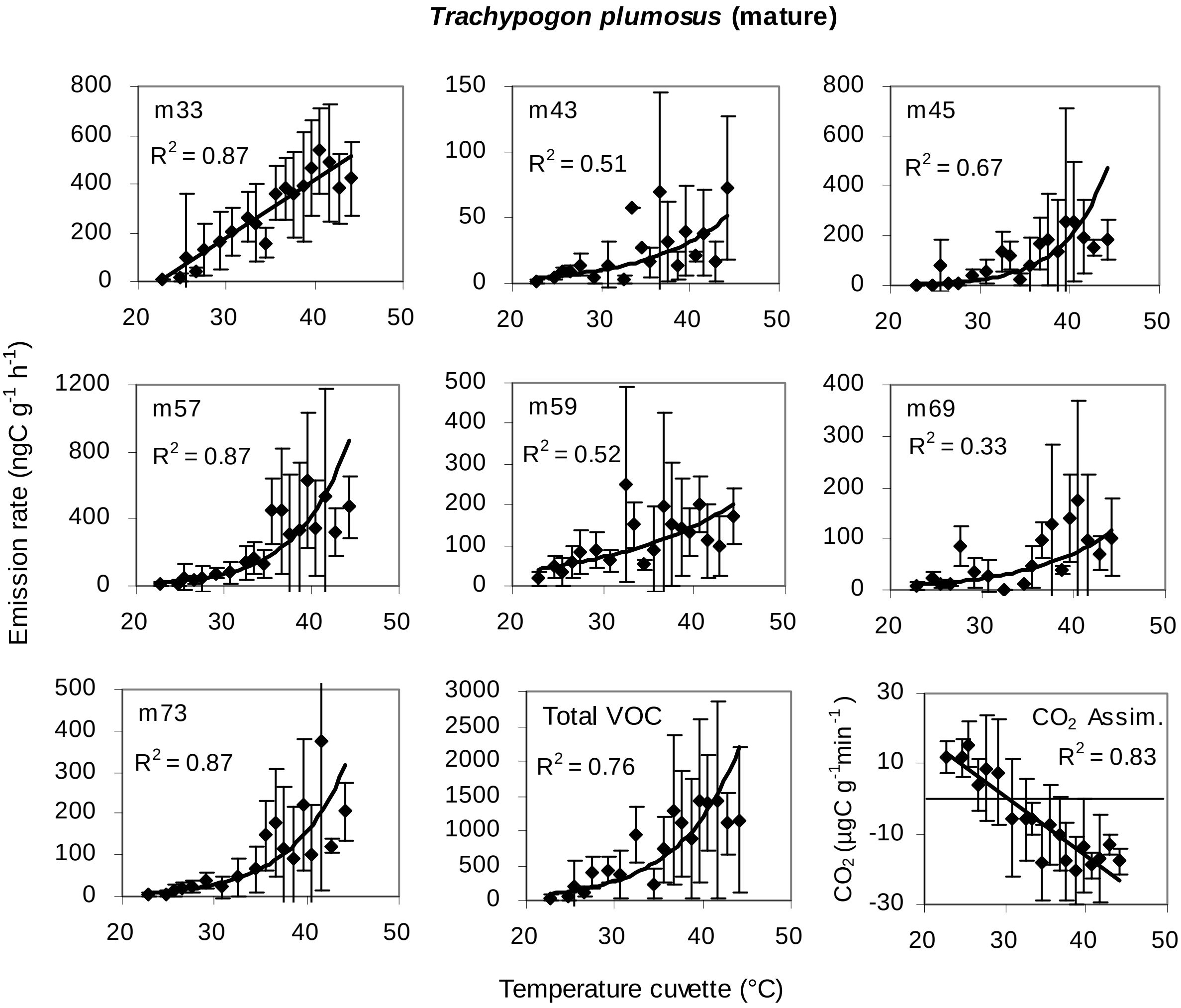
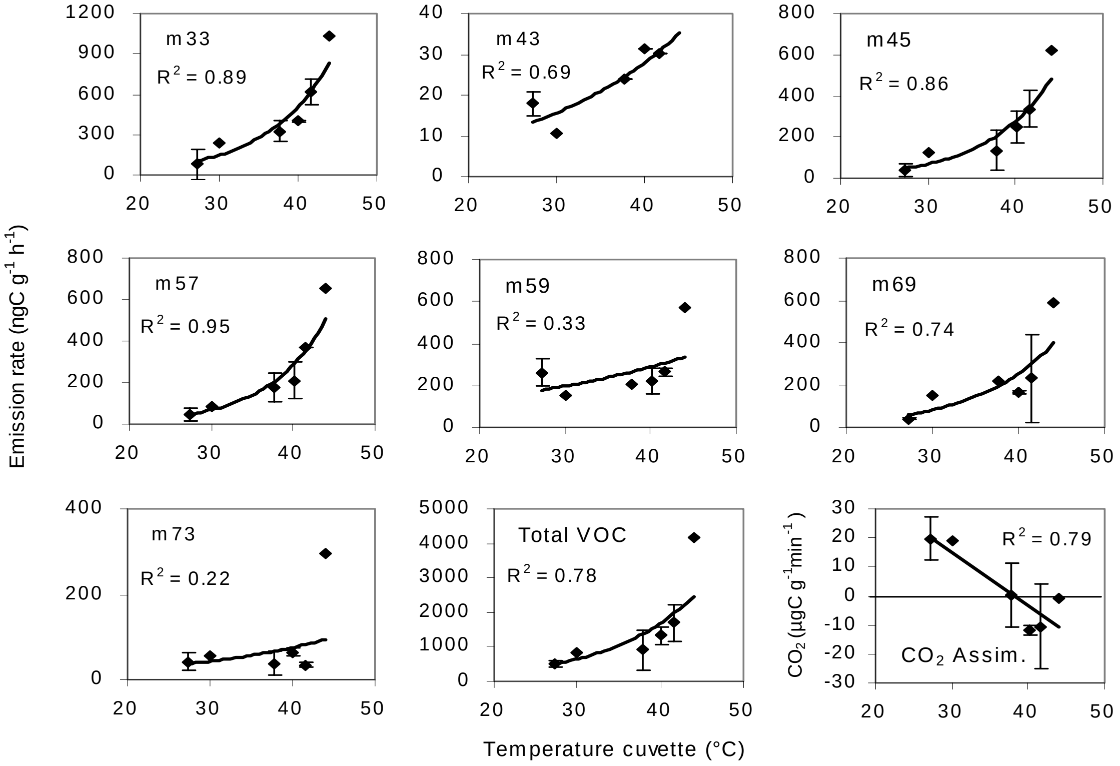


Figure 8.1. Temperature dependence of VOCs emissions from mature *Trachypogon* grasses in the wet season. Error bars represent standard deviation.

***Axonopus canescens* (mature)**



***Axonopus canescens* (dry)**

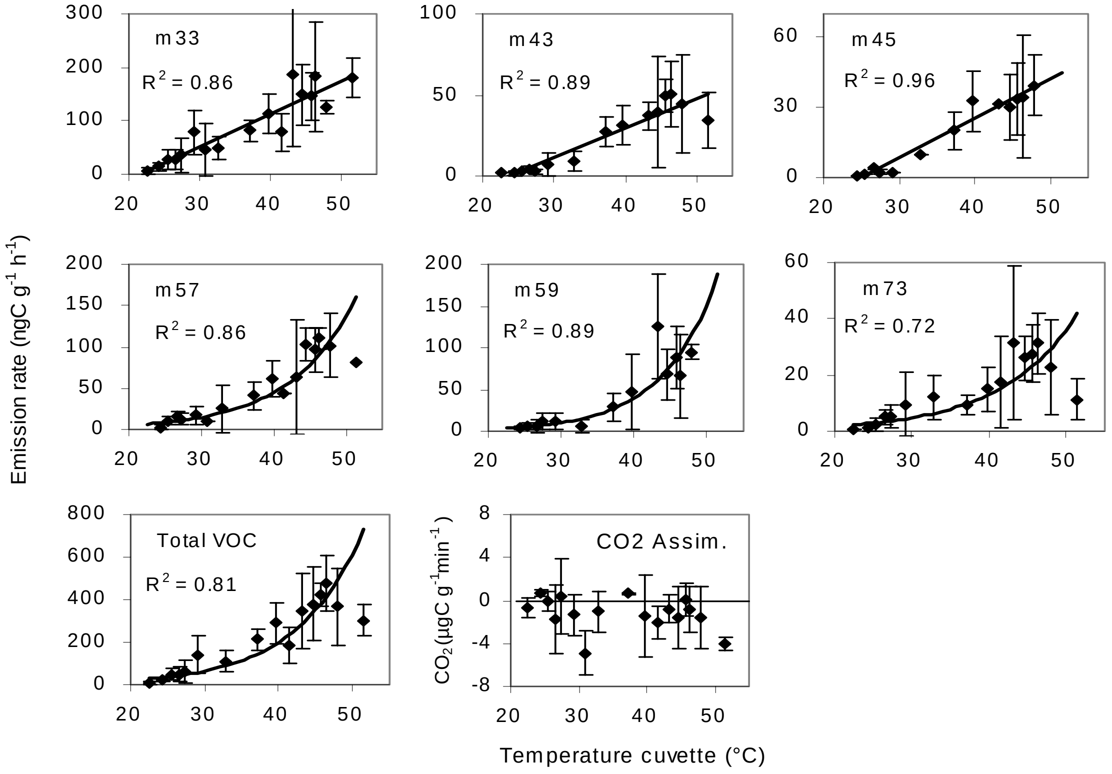


Figure 8.2. Temperature dependence of VOCs emissions from mature (wet season) and dry (dry season) *Axonopus canescens* grasses.

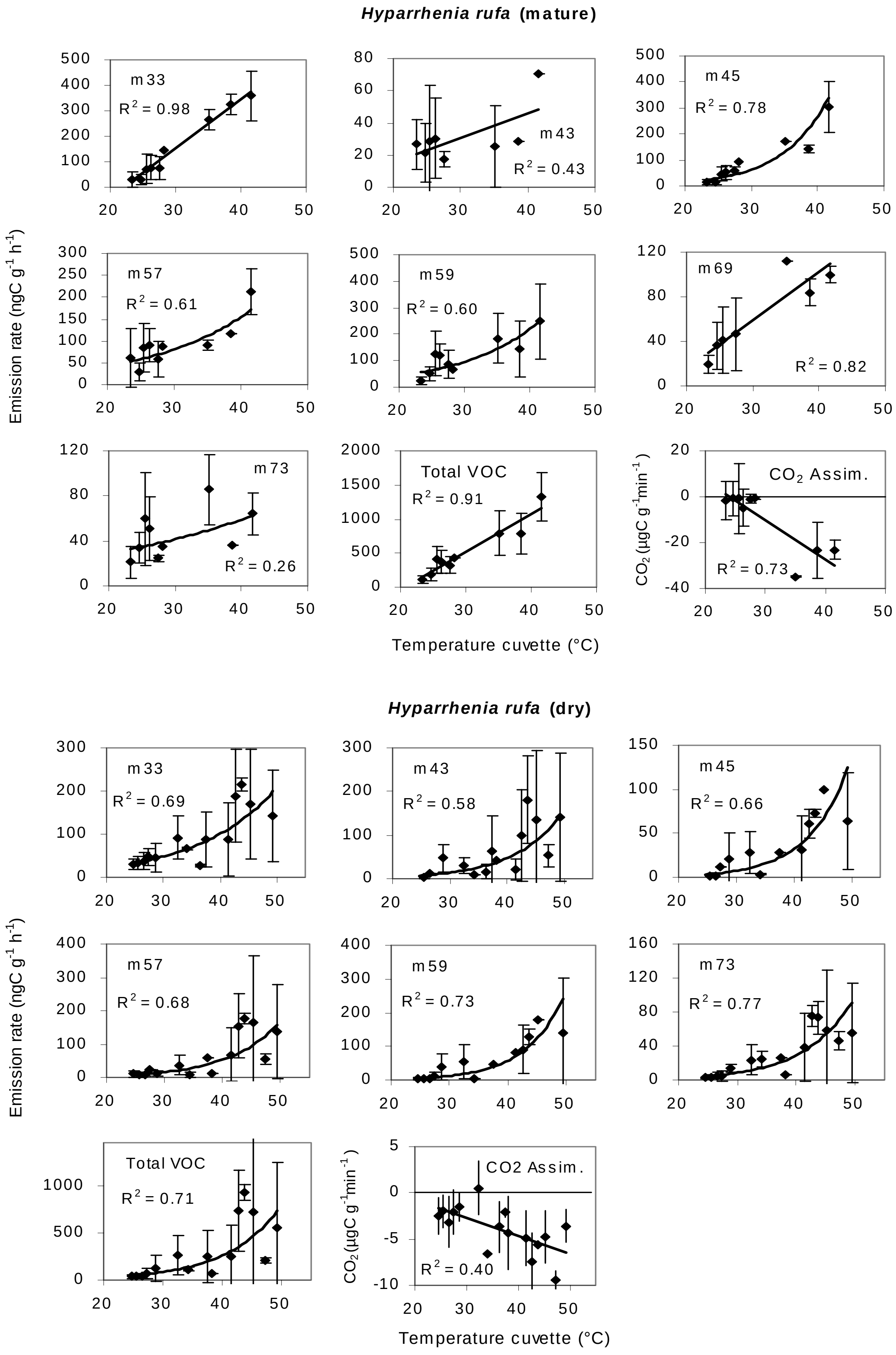


Figure 8.3. Temperature dependence of VOCs emissions from mature (wet season) and dry (dry season) *Hyparrhenia rufa* grasses.

8.5. Appendix to Chapter 4

Table 8.3. Night-time VOC exchange rates [nmol/g/h] from the tree species measured in the wet and dry season. Data are 10-min averages ± SD of night-time (20:00-5:00) measurements. n.d. means not detected. Some individuals were not measured during the night, and were therefore not mentioned in the table.

	m33	m43	m45	m57	m59	m69	m71	m73	m81+m137
Byrsonima crassifolia (wet season)									
Bc 2/ws	n.d.	-0.3±0.6	-0.6±0.8	-0.1±0.6	0.2±0.6	n.d.	n.d.	-2.1±0.7	n.d.
Byrsonima crassifolia (dry season)									
Bc 1/ds	20.0±26.1	0.4±0.3	0.3±0.3	0.6±0.3	0.6±0.4	0.3±0.2	n.d.	0.2±0.2	-0.1±0.0
Bc 2/ds	7.7±9.6	n.d.	-0.1±0.3	0.3±0.2	-0.3±0.8	n.d.	-0.1±0.1	0.1±0.1	n.d.
Bc 3/ds	5.5±9.6	-0.2±2.3	-1.2±1.6	-1.2±1.3	-4.8±5.1	0.1±0.3	-0.4±0.9	-0.2±0.6	-0.2±0.1
Bc 4/ds	28.8±33.9	-0.3±0.2	-0.3±0.4	0.5±0.5	0.4±1.5	0.8±0.2	-0.2±0.2	0.2±0.4	n.d.
Bc 5/ds	32.0±35.1	-0.1±0.3	-0.4±0.3	0.4±0.3	-0.1±0.2	0.1±0.1	-0.1±0.1	0.1±0.1	n.d.
Curatella americana (dry season)									
Ca 1/ds	2.0±1.6	0.2±0.4	n.d.	0.9±0.3	0.1±0.7	0.0±0.1	-0.1±0.1	0.2±0.1	n.d.
Ca 2/ds	1.5±1.3	0.9±2.8	-0.2±1.3	0.3±0.7	-0.1±2.9	0.0±0.4	0.2±0.7	0.4±0.6	n.d.
Cochlospermum vitifolium (dry season)									
Cv 1/ds	151±66	11.6±6.7	14.4±8.3	3.2±3.9	11.3±11.8	2.4±1.7	3.3±3.8	2.2±1.2	1.5±1.1
Cv 2/ds	55.4±62.7	7.3±16.9	-0.7±12.6	1.0±3.9	-2.1±15.9	0.4±1.9	1.4±4.4	1.3±2.3	1.6±1.8

8.6. Appendix to Chapter 5

Table 8.4. Emission ratios relative to CO (ΔX/ΔCO, %) from Alang-Alang, Indo Litter and Indo Peat. Also given is $\Delta CO/\Delta CO_2$.

	Alang Alang			**Indo Litter**			**Indo Peat**	
	Emission Ratio			**Emission Ratio**			**Emission Ratio**	
	average	**SD**		**average**	**SD**		**average**	**SD**
ΔCO/ΔCO2	4.998	0.894	**ΔCO/ΔCO2**	11.067	3.674	**ΔCO/ΔCO2**	13.543	8.328
ΔX/ΔCO			**ΔX/ΔCO**			**ΔX/ΔCO**		
33	0.562	0.314	**33**	2.284	0.938	**33**	2.200	2.146
42	0.121	0.062	**41**	0.291	0.085	**41**	0.234	0.154
43	0.314	0.106	**42**	0.357	0.043	**42**	1.072	0.932
45	0.447	0.220	**43**	1.512	0.406	**43**	0.713	0.799
54	0.036	0.011	**45**	1.128	0.285	**45**	0.643	0.608
55	0.042	0.027	**47**	0.224	0.106	**55**	0.406	0.379
56	0.017	0.006	**54**	0.061	0.012	**57**	0.398	0.343
57	0.311	0.122	**55**	0.212	0.027	**59**	0.510	0.525
59	0.257	0.134	**56**	0.071	0.012	**60**	0.170	0.246
61	0.863	0.279	**57**	0.609	0.109	**61**	1.475	1.673
69	0.088	0.038	**59**	0.855	0.133	**69**	0.146	0.108
71	0.132	0.055	**60**	0.086	0.008	**71**	0.106	0.069
73	0.182	0.066	**61**	5.486	1.680	**73**	0.256	0.278
75	0.199	0.101	**69**	0.411	0.059	**75**	0.237	0.275
79	0.070	0.021	**71**	0.443	0.080	**79**	0.355	0.333
81	0.039	0.016	**73**	0.630	0.108	**83**	0.205	0.249
83	0.073	0.033	**75**	0.812	0.480	**85**	0.191	0.261
85	0.099	0.036	**79**	0.151	0.060	**87**	0.155	0.273
87	0.151	0.065	**83**	0.335	0.131	**93**	0.153	0.129
93	0.026	0.012	**85**	0.570	0.085	**95**	0.270	0.350
95	0.079	0.031	**87**	0.548	0.162	**97**	0.494	0.607
97	0.162	0.067	**93**	0.252	0.243	**101**	0.062	0.111
101	0.018	0.006	**95**	0.230	0.082	**103**	0.037	0.063
107	0.020	0.008	**97**	0.648	0.191	**107**	0.095	0.054
121	0.011	0.006	**101**	0.378	0.432	**121**	0.046	0.049
137	0.003	0.001	**103**	0.155	0.051			
			107	0.083	0.037			
			121	0.062	0.032			
			137	0.051	0.002			

Table 8.5. Emission ratios relative to CO (ΔX/ΔCO, %) from Semak, Rice Straw and Ponderosa pine fuels. Also given is $\Delta CO/\Delta CO_2$.

	Semak			**Rice Straw**			**Pine**	
	Emission Ratios			**Emission Ratios**			**Emission Ratios**	
	average	**SD**		**average**	**SD**		**average**	**SD**
ΔCO/ΔCO2	12.258	1.498	**ΔCO/ΔCO2**	23.195	9.709	**ΔCO/ΔCO2**	5.845	2.880
ΔX/ΔCO			**ΔX/ΔCO**			**ΔX/ΔCO**		
33	2.567	1.086	**33**	1.401	1.590	**33**	1.351	1.613
39	0.123	0.153	**41**	0.483	0.055	**41**	0.196	0.046
41	0.454	0.054	**42**	1.637	1.044	**42**	0.108	0.024
42	0.523	0.211	**43**	1.608	1.094	**43**	0.413	0.102
43	2.290	0.521	**45**	0.934	1.266	**44**	0.053	0.025
44	0.151	0.065	**46**	0.190		**45**	0.534	0.375
45	1.557	0.284	**47**	0.174	0.160	**46**	0.098	0.107
46	0.160	0.049	**54**	0.082	0.032	**47**	0.122	0.170
49	0.040	0.010	**55**	0.315		**49**	0.021	0.023
53	0.043	0.017	**56**	0.473	0.521	**54**	0.017	0.005
54	0.112	0.035	**57**	0.719	0.544	**55**	0.102	0.000
55	0.219	0.138	**59**	2.493	3.225	**56**	0.026	0.016
56	0.116	0.072	**60**	3.145	4.272	**57**	0.365	0.045
57	0.792	0.283	**61**	2.485	3.187	**59**	0.341	0.235
59	1.157	0.555	**62**	0.166		**60**	0.045	0.032
60	0.088	0.083	**67**	0.147		**61**	2.431	3.277
61	5.824	4.711	**68**	0.396		**62**	0.083	0.060
62	0.139	0.106	**69**	0.740	0.170	**68**	0.042	0.024
67	0.084	0.014	**70**	0.136		**69**	0.264	0.150
68	0.165	0.107	**71**	1.645	1.453	**70**	0.024	0.013
69	0.633	0.458	**73**	1.464	1.652	**71**	0.258	0.131
70	0.061	0.044	**75**	1.376	1.701	**73**	0.265	0.219
71	0.582	0.356	**79**	0.512	0.319	**74**	0.023	0.019
73	0.630	0.405	**81**	0.695	0.041	**75**	0.287	0.203
75	1.444	1.443	**82**	0.203		**79**	0.254	0.240
79	0.220	0.021	**83**	0.983	0.367	**81**	0.143	0.096
81	0.307	0.238	**84**	0.178		**82**	0.106	0.097
82	0.088	0.077	**85**	0.785	0.638	**83**	0.316	0.235
83	0.614	0.463	**86**	0.111		**84**	0.027	0.016
84	0.091	0.069	**87**	0.682	0.654	**85**	0.370	0.368
85	0.804	0.576	**89**	0.689		**87**	0.332	0.329
89	0.109	0.168	**93**	0.548	0.438	**89**	0.088	0.088
93	0.220	0.126	**95**	0.588	0.383	**91**	0.035	0.040
95	0.460	0.341	**96**	0.138		**93**	0.098	0.027
96	0.052	0.058	**97**	0.464	0.470	**95**	0.182	0.062
97	1.011	0.835	**99**	1.174		**96**	0.023	0.012
99	0.406	0.485	**101**	0.158	0.082	**97**	0.397	0.325
101	0.237	0.224	**103**	0.113	0.039	**99**	0.246	0.205
103	0.107	0.149	**107**	0.134	0.061	**101**	0.114	0.121
105	0.047	0.021	**109**	0.599		**103**	0.122	0.149
107	0.116	0.069	**111**	0.844		**107**	0.067	0.016
111	0.290	0.409	**113**	0.635		**109**	0.143	0.043
113	0.237	0.302	**115**	0.224		**111**	0.190	0.107
115	0.096	0.142	**117**	0.398		**115**	0.060	0.058
117	0.081	0.119	**121**	1.448	2.233	**117**	0.056	0.055
121	0.105	0.135	**123**	0.377		**121**	0.046	0.014
123	0.089	0.118	**125**	0.517		**123**	0.066	0.010
125	0.150	0.228	**127**	0.232		**125**	0.103	0.056

Table 8.6. Emission ratios relative to CO (ΔX/ΔCO, %) from Dambo and Miombo fuels. Also given is ΔCO/ΔCO$_2$.

	Dambo			**Miombo**	
	Emission Ratios			**Emission Ratios**	
	average	**SD**		**average**	**SD**
ΔCO/ΔCO2	2.015	0.307	**ΔCO/ΔCO2**	2.466	0.361
ΔX/ΔCO			**ΔX/ΔCO**		
33	0.284	0.086	**33**	0.823	0.471
41	0.050	0.017	**42**	0.056	0.029
42	0.021	0.011	**43**	0.446	0.229
43	0.264	0.091	**45**	0.347	0.180
44	0.040	0.011	**47**	0.090	0.047
45	0.297	0.057	**54**	0.021	0.011
47	0.145	0.037	**55**	0.080	0.042
54	0.009	0.004	**56**	0.011	0.006
55	0.046	0.018	**57**	0.247	0.132
56	0.004	0.002	**59**	0.196	0.105
57	0.186	0.068	**61**	1.021	0.525
59	0.114	0.055	**69**	0.082	0.043
61	1.071	0.357	**71**	0.112	0.059
69	0.050	0.025	**73**	0.155	0.081
71	0.081	0.032	**75**	0.150	0.086
73	0.175	0.045	**79**	0.057	0.029
75	0.144	0.149	**81**	0.031	0.018
79	0.065	0.028	**83**	0.066	0.035
81	0.024	0.015	**85**	0.104	0.054
83	0.033	0.019	**87**	0.096	0.053
85	0.081	0.046	**93**	0.021	0.012
87	0.092	0.064	**95**	0.047	0.025
93	0.015	0.006	**97**	0.134	0.065
95	0.032	0.025	**101**	0.021	0.011
97	0.106	0.055	**107**	0.017	0.010
101	0.016	0.014	**121**	0.006	0.003
107	0.010	0.008	**137**	0.002	0.002
121	0.007	0.008			
137	0.001	0.002			