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VOC identification and inter-comparison from laboratory biomass burning using PTR-MS and PIT-MS

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ABSTRACT

Volatile organic compounds (VOCs) emitted from fires of biomass commonly found in the southeast and southwest U.S. were investigated with PTR-MS and PIT-MS, which are capable of fast measurements of a large number of VOCs. Both instruments were calibrated with gas standards and mass dependent calibration curves are determined. The sensitivity of the PIT-MS linearly increases with mass, because the ion trap mass spectrometer used in PIT-MS is more efficient for higher masses, whereas the quadrupole in PTR-MS is most efficient around 70 amu. The identification of VOCs in the complicated mix of the fire emissions was done by gas chromatographic pre separation and inter-comparison with other instrumentation: GC–MS, FTIR, and NI-PT-CIMS. With these state of the art identification methods only 50–75% of the mass detectable by PTR-MS or PIT-MS could be identified. The amount of identified material was dependent on the type of fuel used and the phase of the burns, more can be identified in the flaming stage of the fire. Compounds with masses above 100 amu contributed the largest fraction of the unidentified mass. Emission ratios with CO for all identified and unidentified compounds were determined. Small oxygenated VOCs had the highest emission ratios of the observed compounds.

1. Introduction

Biomass burning is a significant source of atmospheric gases and particles. It occurs naturally in wildfires and is also employed by over half the world population for cooking, land clearing, heating, lighting, and other uses [1]. Although most forest fires are found in tropical regions, fires in boreal forests can have a strong influence on the air quality in the midlatitude Northern Hemisphere. Biomass burning is widely accepted and used in developing nations [2]. In the U.S., prescribed fires are often used to accomplish many beneficial land management objectives such as reducing the danger of larger, more destructive wildfires [3]. However, biomass burning emissions strongly affect regional air quality, and can be transported over large distances to impact regions distant from the source [4–6]. Characterization of smoke emissions produced by the wide range of fuels commonly burned must be performed to understand and manage the effects of biomass burning emissions on regional and global scale atmospheric chemistry and climate.

The most abundant compounds emitted to the atmosphere by biomass burning are carbon dioxide (CO_2) and carbon monoxide (CO); however, there are thousands of additional compounds emitted in smoke plumes. Previous studies have shown that oxygenated volatile organic compounds (OVOCs) account for most of the non-methane organic carbon (NMOC) released from biomass burning [7–11]. Many of these compounds remain poorly characterized due to analytical challenges. Measurements capable of identifying and quantifying the emissions of large numbers of VOCs with a fast time response are necessary to better understand the impact of biomass burning emissions on air quality and climate through ozone and secondary organic aerosol formation.

Proton-transfer-reaction mass spectrometry (PTR-MS) is a widely used technique for online VOC analysis [12] and is a very good tool to study biomass burning emissions, because of its fast time response and ability to measure many VOCs with high sensitivity simultaneously, including OVOCs, aromatics, nitrogen containing compounds, some alkenes and others [12]. Proton-transfer-reaction ion-trap-mass-spectrometry (PIT-MS) is very similar to PTR-MS, but uses an ion trap instead of a quadrupole, which gives the advantage that a whole mass spectrum can be measured in a much shorter time, typically at about 1 Hz [13]. The lower sensitivity of PIT-MS is not a limiting factor for biomass burning experiments, because of the high mixing ratios observed. A disadvantage is that PTR-MS and PIT-MS only determine the mass of the VOCs, which has to be used for the identification, which

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is very challenging in the complicated VOC mix from biomass burning emissions [14]. In this paper we describe the set-up, calibration and inter-comparison for a laboratory fire experiment using PTR-MS and PIT-MS to demonstrate the differences as well as the advantages/disadvantages of both similar techniques. We also identify a large number of important VOCs from biomass burning measured by PTR-MS and PIT-MS using a gas chromatography pre-separation method and inter-comparisons with a comprehensive set of other instruments. We determine the fraction of the mass that still remains unidentified and the emission ratios with CO of a large number of VOCs from the different fuel types, which can be used for example to initialize air quality models.

2. Methods

2.1. Missoula fire lab

The combustion facility at the U.S. Department of Agriculture (USDA) Forest Service, Fire Sciences Laboratory (FSL) in Missoula, MT has a large burn chamber (12.5 m × 12.5 m × 22 m high). Fuels are burned on a $\sim$2 m^2 bed below a 1.6 m diameter exhaust stack with a 3.6 m inverted funnel opening [15,16]. The room is pressurized with temperature and humidity conditioned air, which is vented through the stack, completely entraining any emissions from the fires. A sampling platform surrounds the stack, at a height of 17 m, and the temperature, pressure, trace-gas, and particle measurement equipment was installed here except for the PTR-MS and a gas chromatography mass spectrometer (GC–MS) sampling from an adjacent observation room. Previous work has shown that fire emissions are well mixed in the stack at the height of the sampling platform [7].

Detailed information on each type of fuel burned can be found in Burling et al. [17]. Fuels were collected to represent regional vegetation from the southwestern U.S. and southeastern U.S. and shipped to the FSL. Some pine, spruce and fir samples and an Alaskan duff core sample were also burned in this experiment.

Approximately 5.7 million hectares (17%) of California's vegetation is classified as brush with a significant percentage known as the shrub complex chaparral. Several common species comprise the bulk of plants and were selected as the predominant southwestern biomass fuels for this study: chamise (*Adenostoma fasciculatum*), ceanothus (*Ceanothus* spp.), manzanita (*Arctostaphylos* spp.), and scrub oak (*Quercus berberidifolia*). Fuels from the southeastern U.S. representing fuels commonly managed by prescribed burning were collected from Camp Lejeune in North Carolina and Ft. Benning in Georgia. Pocosin is a dense shrub/pine ecosystem that is extremely flammable during drought. The "treated" samples were dominated by larger diameter hardwood species (red maple, red bay and loblolly bay) that had been recently mechanically masticated into small chips. The "one-year rough" and "two-year rough" refer to understory regrowth one and two years after prior burning or treatment and were a mix of herbaceous and grass species. The untreated samples had not undergone any recent mechanical treatment or burning and were mostly understory red and loblolly bay and some red maple species.

2.2. PTR-MS

PTR-MS utilizes proton-transfer reactions of H_3O^+ to detect various atmospheric trace gases, usually as the MH^+ ion. PTR-MS allows for the detection of numerous VOCs with high sensitivity (10–100 pptv detection limit) and fast response time (1–10 s). This technique has been used extensively in aircraft, ground-based and laboratory studies [12,18]. During this study, a PTR-MS was located in an observation room outside the main combustion chamber. Inside the stack an upward facing inlet was used. The sample line consisted of approximately 20 m of unheated ¼″ o.d. PFA Teflon with a flow of 8 slpm. The PTR-MS sub-sampled ($\sim$200 sccm) from this main flow through 1/16″ heated PEEK tubing. Measurements with the PTR-MS and all other online instruments were started several minutes prior to the fire and run continuously until the end of the fire.

2.3. PIT-MS

The instrument is based on the principle of PTR-MS (proton-transfer-reaction mass spectrometry): VOCs are ionized with H_3O^+, but are then detected with an ion trap mass spectrometer, which has the following advantages: (1) the ability to acquire a full mass spectrum in the same time as one mass with a quadrupole, and (2) extended analytical capabilities of identifying VOCs by performing collision-induced dissociation (CID) and ion molecule reactions in the ion trap. The PIT-MS is described in detail elsewhere [13,19,20], but recent improvements to the sensitivity of the instrument will be discussed below.

2.4. GC–PIT-MS

A combination of gas chromatography, which separates compounds by different retention times in a capillary column, and PIT-MS (GC–PIT-MS) is applied to investigate which compounds contribute to the signal at a certain mass. The GC–PIT-MS is identical to the one described by Warneke et al. [21]. During each fire one sample (50–200 ml) was collected and held in a cryo trap at liquid nitrogen temperature and injected into the GC column right after the fire. The effluent of the GC column was measured with the PIT-MS and a chromatogram of all masses between 30 and 240 amu was acquired.

2.5. GC–MS

Non-methane hydrocarbons and oxygenated VOCs were measured by on-line gas chromatography/mass spectrometry (GC–MS) using an automated set-up. A detailed description of the setup is given elsewhere [22,23]. The GC–MS instrument was set up to analyze air samples with 1–5 min acquisition times once per burn. More than 100 VOCs including many oxygenated compounds, hydrocarbons, halocarbons and alkyl nitrates can be identified and quantified with this instrument.

2.6. FTIR

The open path Fourier transform infrared (OP-FTIR) [17] instrument included a Bruker Matrix-M IR Cube spectrometer and a thermally stable open White cell with a path length of 58 m. The White cell was positioned on the sampling platform so that it spanned the stack directly in the rising emissions stream. The spectral resolution was set to 0.67 cm^{-1} and the spectrometer acquired spectra every 1.5 s (four co-added spectra). The acquired spectra were analyzed offline for CO_2, CO, H_2O, N_2O, NO_2, NO, HONO, NH_3, HCl, SO_2, CH_4, CH_3OH, HCHO, HCOOH, C_2H_2, C_2H_4, CH_3COOH, HCN, propylene and furan. Mixing ratios were obtained by multi-component fits to sections of the IR transmission spectra with a synthetic calibration non-linear least-squares method [24,25].

2.7. NI-PT-CIMS

NI-PT-CIMS (Negative Ion Proton Transfer Chemical Ionization Mass Spectrometer) provides gas-phase acid measurements with 1-s time resolution. The fast time response and high sensitivity of NI-PT-CIMS make it ideal for measurements of both organic

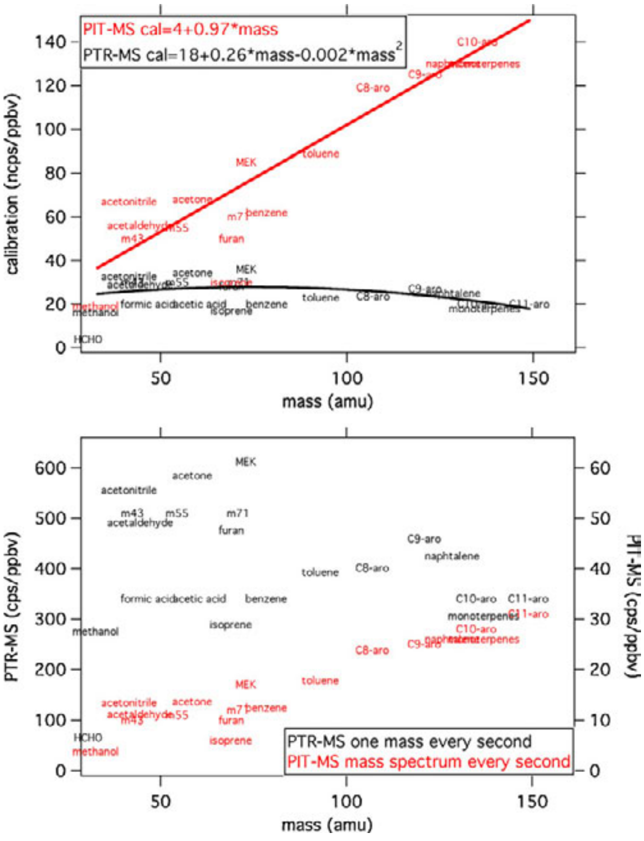

Fig. 1. Calibration factors for PTR-MS and PIT-MS versus mass.

and inorganic acids in rapidly changing conditions such as these biomass burning experiments. A detailed description of NI-PT-CIMS can be found elsewhere [26]. Briefly, NI-PT-CIMS consists of (1) a ^{210}Po source to produce acetate ions ($CH_3C(O)O^-$) from acetic anhydride, (2) a flow tube reactor, in which $CH_3C(O)O^-$ undergoes proton transfer reactions with inorganic and organic acids, (3) a collisional dissociation chamber (CDC) to decluster ions, and (4) a quadrupole mass spectrometer for the detection of both reagent and product ions. All acids with gas-phase acidities higher than that of acetic acid, which is one of the least acidic acids, will undergo the proton transfer reaction and are therefore detectable.

3. PTR-MS and PIT-MS calibrations

Calibrations of the PIT-MS and PTR-MS for all VOCs but formaldehyde were done as described by de Gouw and Warneke [12] using one VOC calibration standard in the field and various calibration standards in the laboratory. Multi-point calibration curves were measured every third day on both instruments and stayed constant throughout the measurement campaign and therefore average calibration values were used. The results are plotted versus the mass of the calibrated VOC in Fig. 1. Only formaldehyde was calibrated as described by Veres et al. [27] using the mobile organic carbon calibrations system (MOCCS) that utilizes a permeation source and a catalytic converter to convert formaldehyde into CO_2 and a LI-COR CO_2 detector for quantification.

In Fig. 1a the calibration factors are normalized to 10^6 cps (counts per second) of H_3O^+ primary ions and are reported as ncps/ppbv [28], which determines the efficiency of product ion production at constant primary ion signal. A clear difference between the two instruments can be seen. Because it is generally more difficult to trap lighter ions in an ion trap, the detection efficiency of the PIT-MS increases with mass over the range of detected compounds in Fig. 1a, whereas the quadrupole of the PTR-MS has a maximum at around 70 amu. The position of this maximum can only be shifted slightly by different instrument setups. The difference in reaction rate coefficient with H_3O^+ for the individual compounds is responsible for the spread around the fitted curves also shown in Fig. 1a.

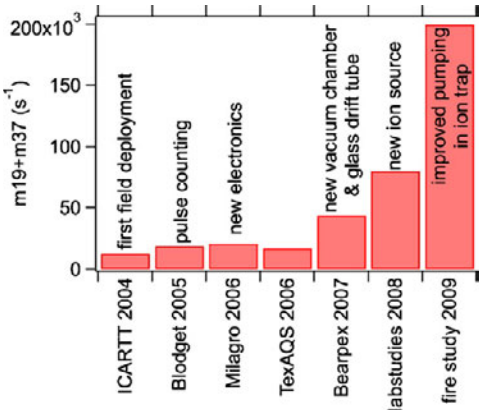

Fig. 2. Average primary ion signal of the PIT-MS during seven measurement campaigns.

In Fig. 1b the calibration factors are shown in cps/ppbv at typical observed primary ion signals, which determines the actual sensitivity of the instruments. The sensitivity of the PTR-MS, even at the larger masses, is about an order of magnitude higher than of the PIT-MS on a 1-s basis. One major difference of the two instruments is that the PIT-MS measures a whole mass spectrum every second, whereas in normal PTR-MS operation mode a number of masses are chosen, which are subsequently measured for usually 1 s. Therefore the time resolution of the PTR-MS is dependent on the chosen number of masses. For example if 10 masses are measured, the order of magnitude difference in sensitivity between the two instruments can be made up for by increasing the trapping time of the PIT-MS to 10 s, so that the actual sensitivity becomes comparable at masses higher than around 150 amu. The calibration factors from Fig. 1 were used for the results presented in this work. For the masses where no gas standard was available the fits shown in Fig. 1 were used. Here it should be noted that the detection limits of both instrument also depend on the instrument backgrounds on the respective masses and not only on the sensitivity. Detection limits can be determined as described by de Gouw and Warneke [12], but are not discussed here, because the mixing ratios measured in the stack before and after each burn determine the background that is subtracted to calculate excess mixing ratios from the fires.

During the campaign the PTR-MS had around 15 × 10^6 cps and the PIT-MS about 0.2 × 10^6 cps H_3O^+ primary ions. The low trapping efficiency especially at lower masses of the ion trap is the reason for part of the difference. The current version of the PIT-MS has undergone several improvements throughout the past 5 years increasing the sensitivity as demonstrated by an increase in detected primary ion count rates. The average primary ion signal for the PIT-MS field experiments is shown in Fig. 2. The improvements are: (1) switching from ion current detection to pulse counting, (2) replacing the original electronics with a fully computer controlled and more stable system, (3) replacing the original vacuum chamber for improved pumping, (4) replacing the standard PTR-MS drift tube with a resistive glass drift tube, and (5) using more efficient pumps on the ion trap chamber. Further improvements of the instrument are certainly possible at this stage and will include phase locking the RF field with the sine wave during the mass scan [13] and changing the waveform of the RF field from a sine wave to a modified square wave to increase the effective trapping time.

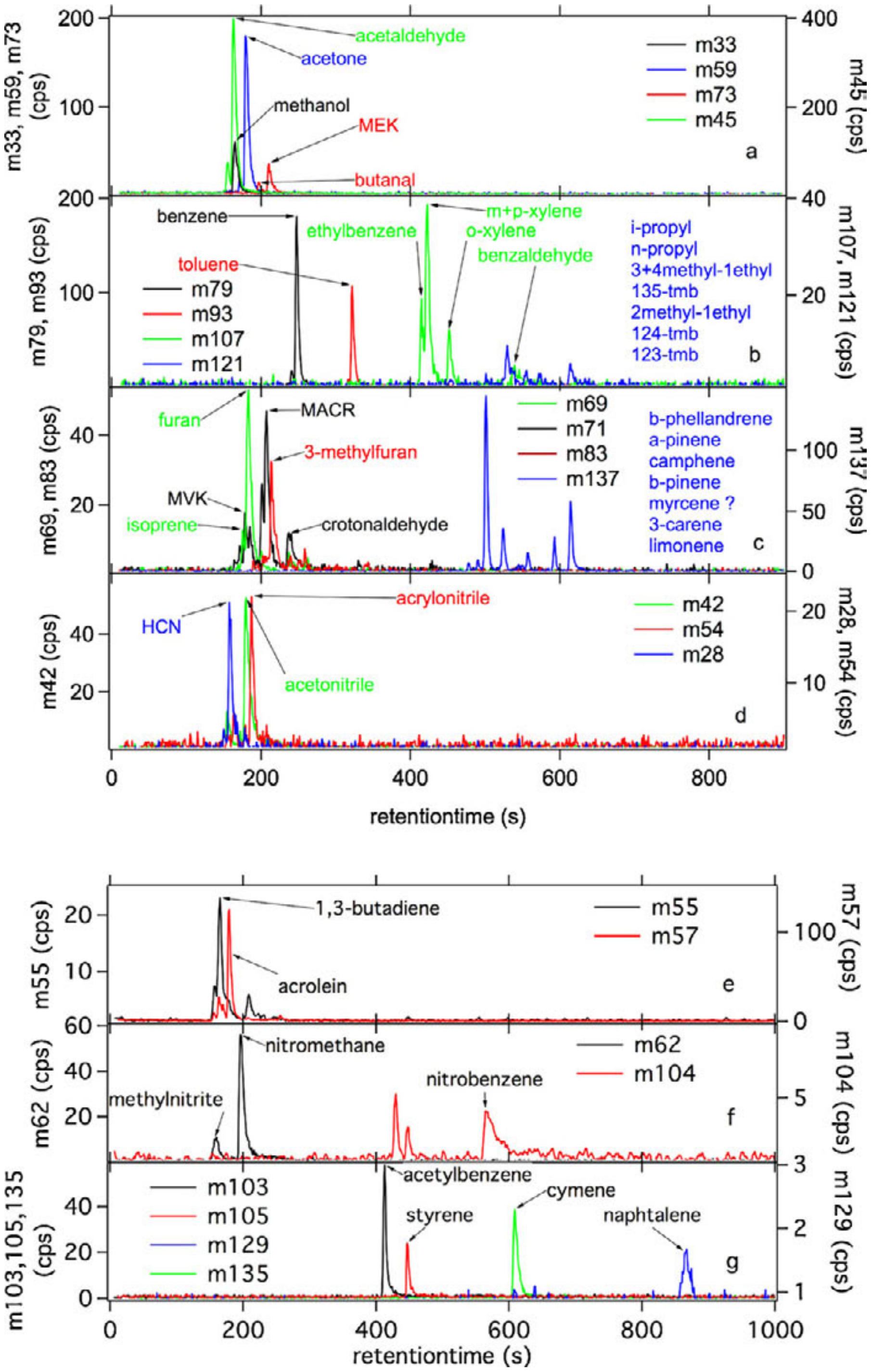

Fig. 3. GC–PIT-MS chromatograms of various masses from fires using pine and spruce needles (a–d) and maritime chaparral (e–g).

4. VOC identification

4.1. GC–PIT-MS

VOCs measured by the PTR-MS and the PIT-MS are identified in this work by their mass, inter-comparisons with other instruments and with GC–PIT-MS [21]. During each fire one sample of 50–150 ml was collected in the cryo trap. The time of the collection was varied through the flaming and smoldering phase of the replicate samples of each fuel type to ensure good VOC identification in both phases of the fires. Typical examples of chromatograms are shown in Fig. 3. The fuel burned in Fig. 3a–d was pine and spruce needles and in Fig. 3e–g maritime chaparral.

Oxygenated VOCs typically measured with PIT-MS and PTR-MS are shown in Fig. 3a. On mass 33 only methanol is detected, whereas on masses 45, 59 and 73 small additional peaks can be seen besides the main compounds on these masses (acetaldehyde, acetone and MEK, respectively). On mass 45 the additional peak is caused by CO_2 [21] that was also trapped in the cryo trap. Propanal and butanal are the small but detectable interferences on masses 59 and 73.

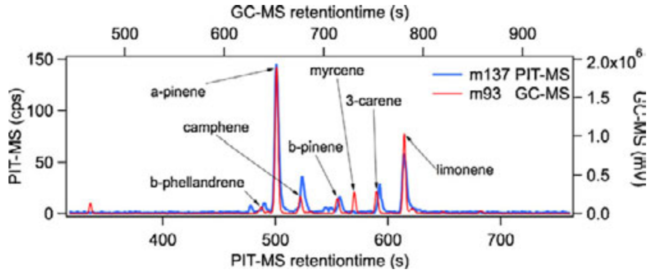

Fig. 4. Chromatograms of mass 137 from the PIT-MS and mass 93 from the GC–MS for the detection of the monoterpenes from a pine and spruce needle burn.

The aromatic compounds regularly detected by PTR-MS and PIT-MS are shown in Fig. 3b. Benzene and toluene have no other interferences and for the C8 and C9 aromatics the sum of the isomers and benzaldehyde are detected as was observed earlier for ambient air [12,21]. Additional aromatic compounds detected during some of the fires are shown in Fig. 3g. Acetylbenzene, styrene, cymene and naphthalene are detected on masses 103, 105, 135 and 129 respectively. A nitrogen containing aromatic compound, nitrobenzene detected on mass 104, was also emitted from some of the fuels burned as shown in Fig. 3f.

Compounds often associated with biogenic emissions are shown in Fig. 3c. Mass 69 in ambient air not influenced by biomass burning or fresh industrial emissions is generally dominated by isoprene [14,21,29]. In biomass burning furan is the dominant compound on this mass as can be seen in Fig. 3c as has been shown previously [14]. Besides MVK and MACR that are usually the main compounds on mass 71, another peak corresponding to crotonaldehyde was detected in most fires. 3-Methylfuran was detected as the dominant compound on mass 83. Various monoterpenes are measured on mass 137 and PTR-MS and PIT-MS are detecting the sum on this mass. A closer look at the PIT-MS chromatogram on mass 137 is shown in Fig. 4 together with a chromatogram from the GC–MS of mass 93, which is used to quantify the monoterpenes. Relatively similar columns are used in both instruments and therefore the dilution order is very similar. The extensive dataset of unambiguously identified compounds from the GC–MS [22] can be used to identify unknown peaks in the GC–PIT-MS in the same way as is shown in Fig. 4 for the monoterpenes.

Chromatograms of nitrogen containing compounds, generally detected on even masses by PTR-MS, are shown in Fig. 3d and f. Acetonitrile, often used as a biomass burning marker in air quality studies [5,30], HCN and acrylonitrile have no interferences on their respective masses. On masses 62 the sum of methylnitrite and nitromethane is measured and on mass 104 the sum of nitrobenzene and two unidentified compounds. In the online measurements mass 104 can therefore not be used as a unique indicator for nitrobenzene.

The chromatograms of mass 55 and 57 show that the measurements of the two air toxics acrolein and 1,3-butadiene have only small interference from unidentified compounds in fire emissions. Many other peaks were found in the chromatograms on various masses similar to the compounds observed by Karl et al. [14] and some of the possible identifications are given in Table 1.

4.2. Inter-comparisons

GC–PIT-MS is an excellent method of determining interferences for the measurement of various compounds, but many “sticky” compounds such as organic acids, that are detectable with PTR-MS and PIT-MS, do not elute from the column. For example on mass 61, where acetic acid is detected, a large signal in the online measurements was seen, but no peaks were detected in the chromatograms. In such cases inter-comparisons with other instruments can be used to determine if various masses are dominated by just one compound or if multiple compounds contribute to the signal at that mass.

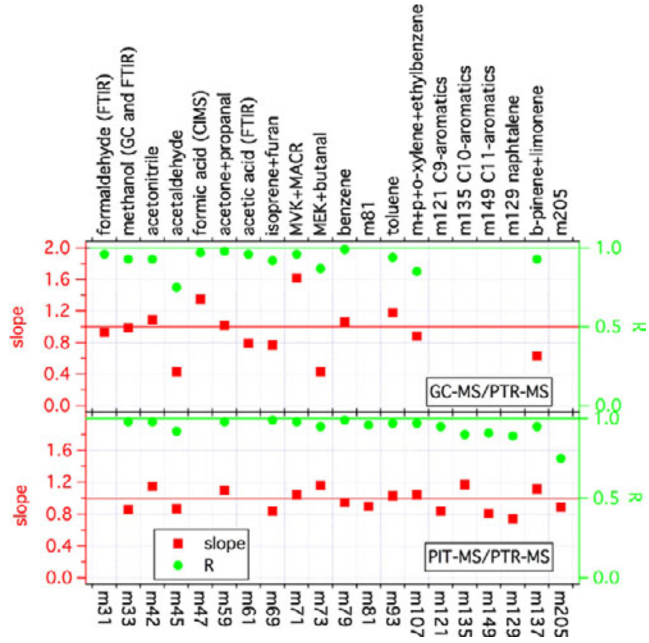

Fig. 5. Slope and *R* coefficient for all possible inter-comparisons between PTR-MS, PIT-MS, GC–MS, FTIR and NI-PT-CIMS.

During the fire campaign many instrument inter-comparisons were possible and the results are summarized in Fig. 5. For all possible inter-comparisons the data from all fires were used and the slope and the *R* coefficient from the scatter plots are shown in Fig. 5. The slopes were determined using an orthogonal distance regression. The lower panel of Fig. 5 shows the inter-comparison of all masses measured by the PTR-MS with the same masses measured by the PIT-MS using the calibration factors as described in Fig. 1. For all masses the agreement is better than 20% and the *R*-coefficient is larger than 0.85 except for mass 205, where the signal was small during most of the fires so that the instrument noise reduced the correlation. For the masses that were dominated by one compound as determined by the GC–PIT-MS and where a calibration standard was available, such a good inter-comparison is certainly expected. For all other masses the good inter-comparison shows that using mass dependent calibration factors for both instruments yields consistent results to within 20%.

The results from the inter-comparisons with the FTIR (formaldehyde, methanol and acetic acid), NI-PT-CIMS (formic acid) and the GC–MS are shown in the upper panel. The individual or the summed compounds are given in the top axis label. For the FTIR and NI-PT-CIMS inter-comparison the data were compared on a 1-s time basis while the PTR-MS data were averaged over the GC–MS sample acquisition time. Most inter-comparisons are within the stated uncertainties of both instruments with some exceptions, where the PTR-MS measured higher signals than is expected from the compounds measured by the GC–MS contributing to the signal at that mass. Mass 45 from the PTR-MS was about a factor of two higher than acetaldehyde from the GC–MS. Some inlet effects [31] and interferences from CO_2 [12] have been reported for acetaldehyde, but the emissions from the fires were so high that these effects are negligible. Acetaldehyde inter-comparisons between the PTR-MS or PIT-MS and the GC–MS have shown good agreements in previous field campaigns in ambient air [12,32] and calibration issues of a factor of two seem unlikely. The correlation coefficient

Table 1
Emission ratios of measured VOCs with CO in pptv/ppbv. Data from the PTR-MS, and PIT-MS are given. Only PTR-MS data are shown for masses that were measured with both PTR-MS and PIT-MS. Only the masses in the PIT-MS where significant emissions were observed are given.

PTR-MS	SW average	SE average	Pines spruce	PIT-MS	SW average	SE average	Pines spruce
HCHO (m31)	6.01	11.34	16.64	m86	0.08	0.21	0.24
Methanol (m33)	3.75	9.47	8.49	2,3-Butadione + pentanone (m87)	0.44	1.56	1.59
Acetonitrile (m42)	0.56	1.03	1.05	m88	0.04	0.17	0.12
m43	3.15	5.66	4.46	Ethylacetate + ? (m89)	0.10	0.49	0.41
Acetaldehyde (m45)	2.21	4.93	5.56	m90	0.01	0.05	0.09
Formic acid (m47)	0.77	1.08	1.00	m91	0.04	0.14	0.20
1,3-Butadiene + ? (m55)	0.36	0.68	1.05	m92	0.05	0.09	0.11
Acetone (m59)	0.84	1.93	1.94	m94	0.08	0.17	0.21
Acetic acid (m61)	4.84	13.61	8.19	Phenol	0.28	0.70	1.35
Isoprene + furan (m69)	0.53	1.38	1.57	m96	0.13	0.31	0.41
MVK + MACR + CTA (m71)	0.43	1.08	1.32	Dimethylfurans+ furfurals (m97)	0.68	2.51	2.61
MEK + butanal (m73)	0.41	1.28	1.17	m98	0.12	0.34	0.41
Benzene (m79)	0.86	0.83	2.29	m99	0.28	1.22	1.26
Monoterpenes + others (m81)	0.68	1.39	2.69	m100	0.04	0.20	0.23
Toluene (m93)	0.30	0.48	0.81	m101	0.25	1.17	1.10
C$_8$-aromatics (m107)	0.19	0.35	0.60	m102	0.05	0.15	0.16
C$_9$-aromatics (m121)	0.11	0.32	0.48	Acetylbenzene (m103)	0.16	0.74	0.66
Naphtalene (m129)	0.19	0.46	0.63	Nitrobenzene + ? (m104)	0.14	0.27	0.27
C$_{10}$-aromatics (cymene) (m135)	0.10	0.22	0.33	Styrene (m105)	0.13	0.29	0.40
Monoterpenes (m137)	0.16	0.55	1.25	m109	0.35	0.66	1.20
C$_{11}$-aromatics (m149)	0.07	0.17	0.22	m111	0.22	0.97	1.46
Sesquiterpenes? (m205)	0.02	0.06	0.06	m113	0.19	1.06	1.20
PIT-MS				m115	0.15	0.87	0.85
PIT-MS	SW average	SE average	Pines spruce	m117	0.18	0.73	1.01
Ammonia (m18)		Not quantified		m119	0.191	0.357	0.19
HCN (m28)		Not quantified		m123	0.171	0.560	0.17
m44	0.29	0.48	0.45	m124	0.07	0.16	0.48
m46	0.24	0.47	0.35	m125	0.19	0.81	1.45
Acrylonitrile (m54)	0.07	0.10	0.11	m126	0.02	0.17	0.45
Propanenitrile (m56)	0.08	0.19	0.18	m127	0.17	0.57	0.88
Acrolein + ? (m57)	0.55	1.39	1.56	m131	0.12	0.46	0.65
m58	0.08	0.21	0.21	m133	0.19	0.40	0.76
m60	0.10	0.40	0.34	m139	0.10	0.60	0.98
Nitromethane + metyhlnitrate (m62)	0.12	0.48	0.37	m141	0.09	0.33	0.48
m63	0.04	0.18	0.14	m143	0.17	0.43	0.72
m67	0.05	0.15	0.18	m145	0.10	0.69	0.80
pyrrole (m68)	0.05	0.15	0.20	m147	0.11	0.31	0.58
m70	0.08	0.18	0.18	m151	0.09	0.35	0.65
m72	0.05	0.17	0.21	m153	0.11	0.40	0.83
m74	0.07	0.25	0.25	m155	0.07	0.25	0.43
Methylacetate + hydroxyacetone (m75)	0.38	1.47	1.68	m157	0.08	0.24	0.45
m76	0.04	0.10	0.15	m159	0.04	0.14	0.34
m77	0.04	0.14	0.15	m161	0.04	0.15	0.32
m80	0.09	0.15	0.18	m163	0.05	0.21	0.33
m82	0.08	0.19	0.22	m165	0.02	0.19	0.39
Methylfuran (m83)	0.31	1.03	1.17	m167	0.01	0.08	0.32
m84	0.09	0.27	0.29	m169	0.04	0.17	0.35
m85	0.37	1.39	1.56	m171	0.03	0.09	0.21

for the scatter plot is also low ($R = 0.75$), and it is therefore likely that for biomass burning another compound (or compounds) contribute to the signal at mass 45 not detectable by GC–MS, FTIR or NI-PT-CIMS. The same is likely for mass 73 (methyl ethyl ketone (MEK), n- and iso-butanal), where another compound seems to contribute. β-Pinene and limonene are compared with mass 137 and cannot explain all of the signal (a-pinene and camphene will make up the rest and we will add those once Jessica has time to integrate the chromatograms). The formic acid comparison showed that the PTR-MS was 38% higher than the NI-PT-CIMS [33]. The PTR-MS was not calibrated for formic acid during the campaign and it was found afterwards in laboratory calibrations that the PTR-MS likely was too high by about 30%. Formaldehyde was calibrated using the MOCCS system [27] at the typical humidity observed during the fires and no humidity corrections were applied for the measurements here, even though formaldehyde detection by PTR-MS is strongly humidity dependent [34]. The comparison with the FTIR is excellent (slope = 0.93 and $R = 0.96$) proving that mass 31 has limited interferences from other compounds besides formaldehyde and that the calibration method using the MOCCS performs well.

4.3. *Identified versus unidentified*

Typical PIT-MS mass spectra are shown in Fig. 6. The available measured calibration factors and the mass dependent calibration factors from Fig. 1 were used to calculate the mixing ratios shown in Fig. 6. Comparing the smoldering with the flaming stage in Fig. 6 it is clear that in the flaming stage, with a more complete combustion, the emitted VOCs are on average smaller and in the smoldering phase overall more VOCs are emitted. In the pine and spruce needle burn shown in Fig. 6c and d the average mixing ratio in the flaming phase of compounds with masses below 100 amu was 30 ppbv and for compounds with masses between 100 and 200 only 4.5 ppbv (15%), while in the smoldering phase the average mixing ratios were 106 ppbv and 28 ppbv (26%), respectively. It should be mentioned here that the two phases are not clearly separated and are usually mixed as the flame moves over the fuel bed [8].

Using the methods described in the previous chapters, the identified and unidentified compounds are shown in the mass spectra in different colors. Larger masses are more difficult to identify and therefore the identified fraction is higher in the flaming stage. In

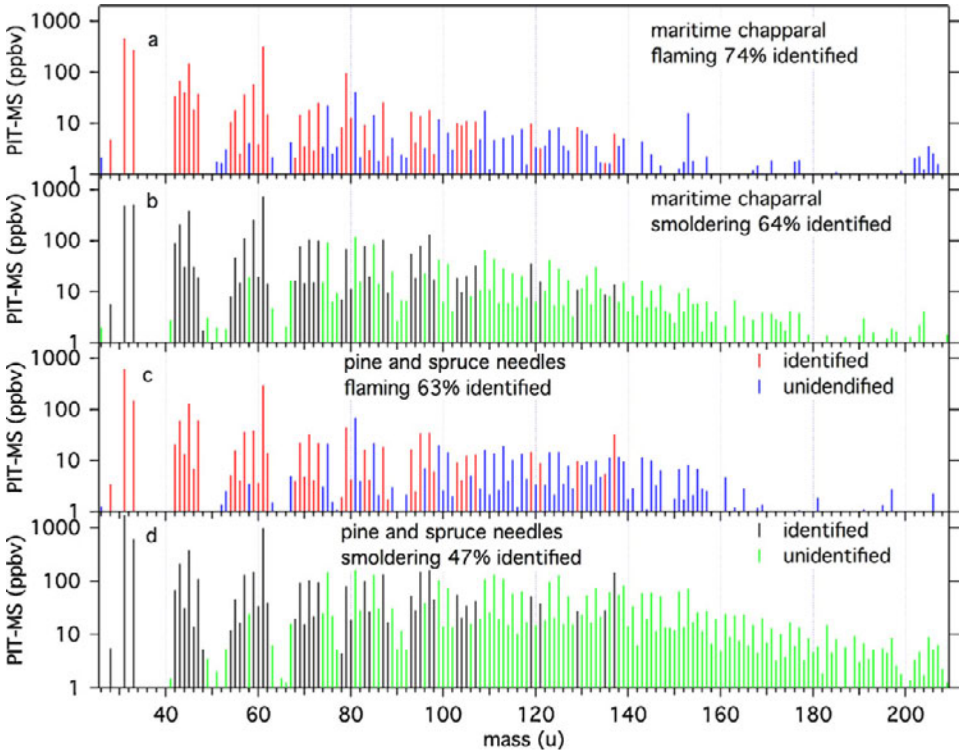

Fig. 6. PIT-MS mass spectra: (a) maritime chaparral during the flaming stage, (b) maritime chaparral during the smoldering phase, (c) pine and spruce needles during the flaming stage, (d) pine and spruce needles during the smoldering phase.

Fig. 6 results from burns using two different fuel types are shown. In the maritime chaparral burns 64–74% of the mass was identified, whereas in the pine and spruce needles burn only 47–63%. Identified fractions of other burns were usually between those values. It should be noted that the percentage values given here are calculated in mass and not in mixing ratios.

5. Emission ratios

Fig. 7 shows the time series of a selected set of VOCs for the same laboratory fire of maritime chaparral, which was a fairly typical burn. The top panel shows CO and CO_2 used to indicate the flaming stage with a strong CO_2 enhancement and the smoldering stage with high CO [8]. CO and CO_2 were measured with the FTIR and the VOCs with the PTR-MS. For benzene and toluene the PIT-MS data are shown as well to again demonstrate the good agreement between the PTR-MS and the PIT-MS.

Excess mixing ratios were integrated over the whole fire to give fire-integrated emission values, only data points corresponding to fire ignition sources were omitted. Fire-integrated molar emission ratios, $ER_{X/CO}$ for species X with CO were calculated by:

$$ER_{X/CO} = \frac{\Delta X}{\Delta CO}, \tag{1}$$

where ΔX and ΔCO are the fire-integrated excess mixing ratios for species X and CO. Emission ratios are usually determined by calculating the slope of the scatter plot of the species X with CO. As can already be seen in Fig. 7, some compounds have very different correlation slopes with flaming stage CO than with smoldering stage CO. Especially in the atmosphere but also in the laboratory fire experiments emissions from both phases are mixed and therefore the fire integrated emission ratios are the most useful quantity.

Emission ratios for all identified compounds and all other masses are listed in Table 1 as averages over southwest and southeast fuels and the deciduous species are shown separately. Some selected emission ratios are shown in Fig. 8 for the individual fuel types. Emission ratios of some compounds measured with the NI-PT-CIMS [33,35] and from the FTIR [17] are also shown. The oxygenated VOCs formaldehyde, acetic acid, methanol, formic acid and acetaldehyde were the compounds with the highest emissions. Most aromatic VOCs with the exception of benzene for some fuel

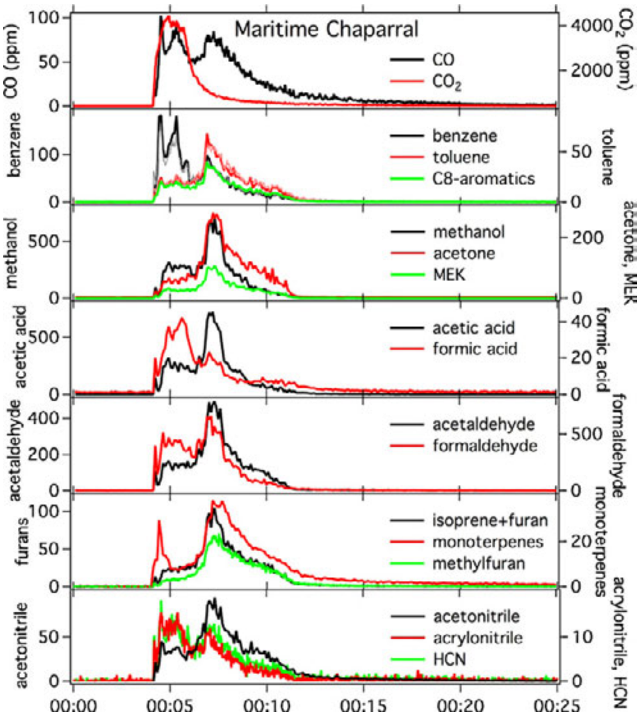

Fig. 7. Time series of various VOCs for a burn of maritime chaparral.

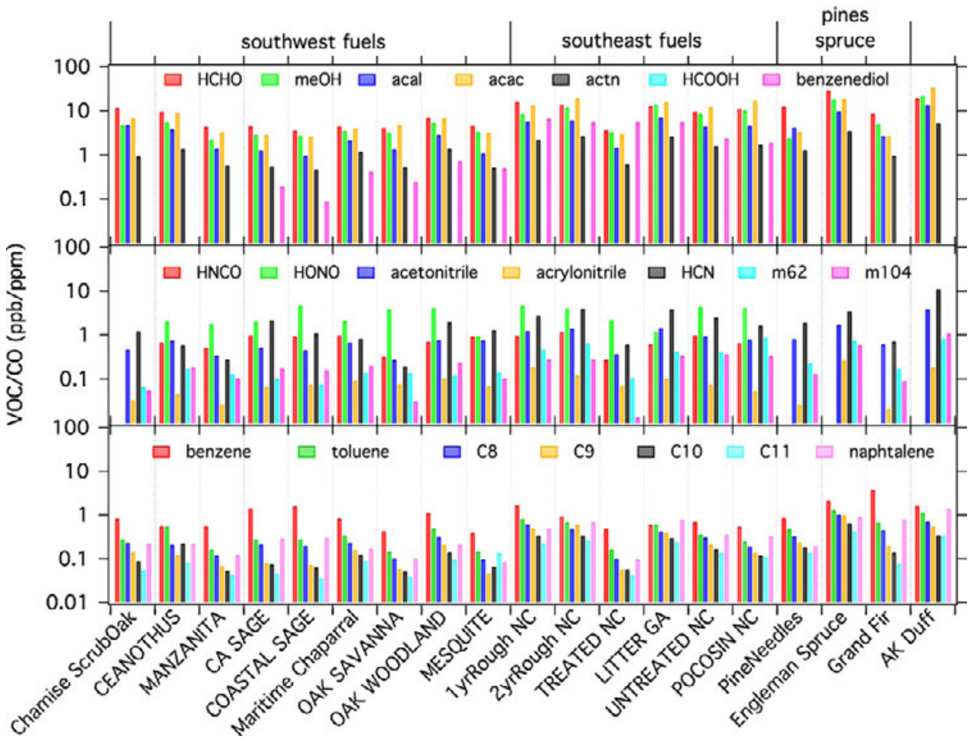

Fig. 8. Emission ratios of selected compounds with CO: (a) oxygenates, (b) nitrogen containing compounds, (c) aromatics. A more detailed description of the fuels is given in the text. meOH (methanol), acal (acetaldehyde), acac (acetic acid), actn (acetone), C8 (sum of C8-aromatics, m107), C9 (sum of C9-aromatics, m121), C10 (sum of C10-aromatics, m135), C11 (sum of C11-aromatics, m149).

types were at least one order of magnitude smaller. The nitrogen containing VOCs are again about one order of magnitude smaller with the exception of HONO. It should be noted here that with the techniques described in this work almost no alkanes or small alkenes can be measured, which will make up a significant part of the emitted mass as well, but the oxygenated VOCs mentioned above are likely the largest emissions from biomass burning [36].

6. Conclusions

A very large number of VOCs are emitted from biomass burning and identification and quantification of such a complicated mix of VOCs is challenging. In this work we investigated VOC emissions of laboratory-generated fires using a PTR-MS and a PIT-MS instrument, which are CIMS techniques that can measure many VOCs simultaneously with a fast time response, but only determine the mass of the compounds for identification. PIT-MS and PTR-MS were calibrated for many compounds and the two instruments compared well for all masses measured with the PTR-MS. Many VOCs emitted from the fires were identified by GC–PIT-MS, a technique that uses a GC column to pre-separate VOCs before measuring them with the PIT-MS. Inter-comparisons with other measurement techniques are used to determine if other compounds that do not elute from the GC such as organic acids contribute to the measured signals on various masses. Unexpected interferences were found for mass 45, which is usually attributed to only acetaldehyde, and mass 73, MEK and butanal.

PIT-MS always measures full mass spectra and the sensitivity is increasing linearly with mass, which makes it a useful tool to investigate the importance of emissions of higher mass compounds from the fires. The identified and unidentified mass fractions of the total PIT-MS signal were determined for the smoldering and the flaming phase of the fires and it was found that in some cases, even with the state-of-the-art techniques used here, only half of the mass was identified. Most of the unidentified mass was from compounds with molecular weights above 100 amu. The large unidentified mass fraction, which is not included in currently models, is certainly important for the production of secondary organic aerosol (SOA). Those unidentified compounds are large and oxygenated VOCs or aromatics and therefore often have a low volatility, which makes it likely that a large fraction of the mass ends up in the aerosol phase after only a few oxidation steps [37].

Emission ratios with CO for all identified and unidentified compounds were determined. Small OVOCs have the highest emission ratios of the observed compounds.

References

[1] P.J. Crutzen, M.O. Andreae, Biomass burning in the tropics – impact on atmospheric chemistry and biogeochemical cycles, Science 250 (4988) (1990) 1669–1678.

[2] D.O. Hall, F. Rosillocalle, J. Woods, Biomass utilization in households and industry – energy use and development, Chemosphere-Global Change Science 29 (5) (1994) 1099–1119.

[3] R.W. Mutch, Fighting fire with prescribed fire – a return to ecosystem health, Journal of Forestry 92 (11) (1994) 31–33.

[4] C. Warneke, R. Bahreini, J. Brioude, C.A. Brock, J.A. De Gouw, D.W. Fahey, K.D. Froyd, J.S. Holloway, A. Middlebrook, L. Miller, S. Montzka, D.M. Murphy, J. Peischl, T.B. Ryerson, J.P. Schwarz, J.R. Spackman, P. Veres, Biomass burning in Siberia and Kazakhstan as the main source for Arctic haze over the Alaskan Arctic in April 2008, Geophysical Research Letters 36 (2009) pL02813.

[5] C. Warneke, K.D. Froyd, J. Brioude, R. Bahreini, C.A. Brock, J. Cozic, J.A. de Gouw, D.W. Fahey, R. Ferrare, J.S. Holloway, A.M. Middlebrook, L. Miller, S. Montzka, J.P. Schwarz, H. Sodemann, J.R. Spackman, A. Stohl, An important contribution to springtime Arctic aerosol from biomass burning in Russia, Geophysical Research Letters 37 (2010).

[6] C. Warneke, J.A. de Gouw, A. Stohl, O.R. Cooper, P.D. Goldan, W.C. Kuster, J.S. Holloway, E.J. Williams, B.M. Lerner, S.A. McKeen, M. Trainer, F.C. Fehsenfeld, E.L. Atlas, S.G. Donnelly, V. Stroud, A. Lueb, S. Kato, Biomass burning and anthropogenic sources of CO over New England in the summer 2004, Journal of Geophysical Research 111 (D23) (2006).

[7] T.J. Christian, B. Kleiss, R.J. Yokelson, R. Holzinger, P.J. Crutzen, W.M. Hao, T. Shirai, D.R. Blake, Comprehensive laboratory measurements of biomass-burning emissions: 2. First intercomparison of open-path FTIR, PTR-MS, and GC–MS/FID/ECD, Journal of Geophysical Research-Atmospheres 109 (D2) (2004) D02311.

[8] R.J. Yokelson, D.W.T. Griffith, D.E. Ward, Open-path Fourier transform infrared studies of large-scale laboratory biomass fires, Journal of Geophysical Research-Atmospheres 101 (D15) (1996) 21067–21080.

[9] R.J. Yokelson, R. Susott, D.E. Ward, J. Reardon, D.W.T. Griffith, Emissions from smoldering combustion of biomass measured by open-path Fourier transform infrared spectroscopy, Journal of Geophysical Research-Atmospheres 102 (D15) (1997) 18865–18877.

[10] T. Karl, A. Guenther, R.J. Yokelson, J. Greenberg, M. Potosnak, D.R. Blake, P. Artaxo, The tropical forest and fire emissions experiment: emission, chemistry, and transport of biogenic volatile organic compounds in the lower atmosphere over Amazonia, Journal of Geophysical Research 112 (2007).

[11] R. Holzinger, C. Warnke, A. Hansel, A. Jordan, W. Lindinger, D.H. Scharffe, G. Schade, P.J. Crutzen, Biomass burning as a source of formaldehyde, acetaldehyde, methanol, acetone, acetonitrile, and hydrogen cyanide, Geophysical Research Letters (1999) 1161–1164.

[12] J. de Gouw, C. Warneke, Measurements of volatile organic compounds in the earths atmosphere using proton-transfer-reaction mass spectrometry, Mass Spectrometry Reviews 26 (2) (2007) 223–257.

[13] C. Warneke, J.A. de Gouw, E.R. Lovejoy, P.C. Murthy, W.C. Kuster, R. Fall, Development of proton-transfer ion trap-mass spectrometry: on-line detection and identification of volatile organic compounds in air, Journal of the American Society for Mass Spectrometry 16 (8) (2005) 1316–1324.

[14] T.G. Karl, T.J. Christian, R.J. Yokelson, P. Artaxo, W.M. Hao, A. Guenther, The Tropical Forest and Fire Emissions Experiment: method evaluation of volatile organic compound emissions measured by PTR-MS, FTIR, and GC from tropical biomass burning, Atmospheric Chemistry and Physics 7 (22) (2007) 5883–5897.

[15] T.J. Christian, B. Kleiss, R.J. Yokelson, R. Holzinger, P.J. Crutzen, W.M. Hao, B.H. Saharjo, D.E. Ward, Comprehensive laboratory measurements of biomass-burning emissions: 1. Emissions from Indonesian, African, and other fuels, Journal of Geophysical Research-Atmospheres 108 (D23) (2003) 4719.

[16] G.R. McMeeking, S.M. Kreidenweis, S. Baker, C.M. Carrico, J.C. Chow, J.L. Collett Jr., W.M. Hao, A.S. Holden, T.W. Kirchstetter, W.C. Malm, H. Moosmoeller, A.P. Sullivan, C.E. Wold, Emissions of trace gases and aerosols during the open combustion of biomass in the laboratory, Journal of Geophysical Research 114 (2009).

[17] I.R. Burling, R.J. Yokelson, D.W.T. Griffith, T.J. Johnson, P. Veres, J.M. Roberts, C. Warneke, S.P. Urbanski, J. Reardon, D.R. Weise, W.M. Hao, J. de Gouw, Laboratory investigation of trace gas and particulate emissions from biomass burning of fuels collected on DoD bases, Atmospheric Chemistry and Physics 10 (22) (2010) 11115–11130.

[18] W. Lindinger, A. Hansel, A. Jordan, On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) – medical applications, food control and environmental research, International Journal of Mass Spectrometry (1998) 191–241.

[19] C. Warneke, S. Rosen, E.R. Lovejoy, J.A. de Gouw, R. Fall, Two additional advantages of proton-transfer ion trap mass spectrometry, Rapid Communications in Mass Spectrometry 18 (1) (2004) 133–134.

[20] C. Warneke, S. Kato, J.A. De Gouw, P.D. Goldan, W.C. Kuster, M. Shao, E.R. Lovejoy, R. Fall, F.C. Fehsenfeld, Online volatile organic compound measurements using a newly developed proton-transfer ion-trap mass spectrometry instrument during New England Air Quality Study – Intercontinental Transport and Chemical Transformation 2004: Performance, intercomparison, and compound identification, Environmental Science & Technology 39 (14) (2005) 5390–5397.

[21] C. Warneke, J.A. De Gouw, W.C. Kuster, P.D. Goldan, R. Fall, Validation of atmospheric VOC measurements by proton-transfer-reaction mass spectrometry using a gas-chromatographic preseparation method, Environmental Science & Technology 37 (11) (2003) 2494–2501.

[22] J.B. Gilman, W.C. Kuster, P.D. Goldan, S.C. Herndon, M.S. Zahniser, S.C. Tucker, W.A. Brewer, B.M. Lerner, E.J. Williams, R.A. Harley, F.C. Fehsenfeld, C. Warneke, J.A. de Gouw, Measurements of volatile organic compounds during the 2006 TexAQS/GoMACCS campaign: industrial influences, regional characteristics, and diurnal dependencies of the OH reactivity, Journal of Geophysical Research-Atmospheres 114 (2009).

[23] P.D Goldan, W.C. Kuster, E.J. Williams, F.C. Fehsenfeld, Non-methane hydrocarbon measurements during the 2002 New England Air Quality study, Journal of Geophysical Research 109 (2004), doi:10.1029/2003JD004455.

[24] D.W.T. Griffith, Synthetic calibration and quantitative analysis of gas-phase FT-IR spectra, Applied Spectroscopy 50 (1) (1996) 59–70.

[25] R.J. Yokelson, T. Karl, P. Artaxo, D.R. Blake, T.J. Christian, D.W.T. Griffith, A. Guenther, W.M. Hao, The tropical forest and fire emissions experiment: overview and airborne fire emission factor measurements, Atmospheric Chemistry and Physics 7 (19) (2007) 5175–5196.

[26] P. Veres, J.M. Roberts, C. Warneke, D. Welsh-Bon, J.M. Zahniser, S. Herndon, R. Fall, J. de Gouw, Development of negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the atmosphere, International Journal of Mass Spectrometry 274 (1–3) (2008) 48–55.

[27] P. Veres, J.B. Gilman, J.M. Roberts, W.C. Kuster, C. Warneke, I.R. Burling, J. de Gouw, Development and validation of a portable gas phase standard generation and calibration system for volatile organic compounds, Atmosphereic Measurements Technology Discuss 3 (1) (2010).

[28] J. de Gouw, C. Warneke, T. Karl, G. Eerdekens, C. van der Veen, R. Fall, Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry, International Journal of Mass Spectrometry 223 (1–3) (2003) 365–382.

[29] C. Warneke, J.A. de Gouw, L. Del Negro, J. Brioude, S. McKeen, H. Stark, W.C. Kuster, P.D. Goldan, M. Trainer, F.C. Fehsenfeld, C. Wiedinmyer, A.B. Guenther, A. Hansel, A. Wisthaler, E. Atlas, J.S. Holloway, T.B. Ryerson, J. Peischl, L.G. Huey, A.T.C. Hanks, Determination of biogenic emissions in the Eastern United States and Texas and comparison with biogenic emission inventories, Journal of Geophysical Research-Atmospheres 115 (2010).

[30] J.A. de Gouw, C. Warneke, D.D. Parrish, J.S. Holloway, M. Trainer, F.C. Fehsenfeld, Emission sources and ocean uptake of acetonitrile (CH_3CN) in the atmosphere, Journal of Geophysical Research 108 (2003), D11.

[31] M.J. Northway, J.A. de Gouw, D.W. Fahey, R.S. Gao, C. Warneke, J.M. Roberts, F. Flocke, Evaluation of the role of heterogeneous oxidation of alkenes in the detection of atmospheric acetaldehyde, Atmospheric Environment 38 (35) (2004) 6017–6028.

[32] J.A. de Gouw, et al., Validation of proton transfer reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England Air Quality Study (NEAQS) in 2002, Journal of Geophysical Research-Atmospheres 108 (D21) (2003).

[33] P. Veres, J.M. Roberts, I.R. Burling, C. Warneke, J. de Gouw, R.J. Yokelson, Measurements of gas-phase inorganic and organic acids from biomass fires by negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS), Journal of Geophysical Research-Atmospheres 115 (2010).

[34] A. Hansel, W. Singer, A. Wisthaler, M. Schwarzmann, W. Lindinger, Energy dependencies of the proton transfer reactions $H_3O^{(+)} + CH_2O$ double left right arrow $CH_2OH^+ + H_2O$, International Journal of Mass Spectrometry 167 (1997) 697–703.

[35] J.M. Roberts, P. Veres, C. Warneke, J.A. Neuman, R.A. Washenfelder, S.S. Brown, M. Baasandorj, J.B. Burkholder, I.R. Burling, T.J. Johnson, R.J. Yokelson, J. de Gouw, Measurement of HONO, HNCO, and other inorganic acids by negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS): application to biomass burning emissions, Atmospheric Measurement Techniques 3 (4) (2010) 981–990.

[36] R.J. Yokelson, T.J. Christian, T.G. Karl, A. Guenther, The tropical forest and fire emissions experiment: laboratory fire measurements and synthesis of campaign data, Atmospheric Chemistry and Physics 8 (16) (2008) 3509–3527.

[37] A.L. Robinson, N.M. Donahue, M.K. Shrivastava, E.A. Weitkamp, A.M. Sage, A.P. Grieshop, T.E. Lane, J.R. Pierce, S.N. Pandis, Rethinking organic aerosols: semivolatile emissions and photochemical aging, Science (2007) 1259–1262.