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**Methanol inside aged
tropical biomass
burning plumes**

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First space-borne measurements of methanol inside aged tropical biomass burning plumes using the ACE-FTS instrument

G. Dufour¹, C. D. Boone², C. P. Rinsland³, and P. F. Bernath²

¹Laboratoire de Météorologie Dynamique/Institut Pierre Simon Laplace, Palaiseau, France

²Department of Chemistry, University of Waterloo, Ontario, Canada

³NASA Langley Research Center, Hampton, VA, USA

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Correspondence to: G. Dufour (gaelle.dufour@lmd.polytechnique.fr)

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First measurements from space of upper tropospheric and lower stratospheric methanol profiles within aged fire plumes are reported. Elevated levels of methanol at 0–45° S from 30 September to 3 November 2004 have been measured by the high resolution infrared spectrometer ACE-FTS onboard the SCISAT satellite. Methanol volume mixing ratios higher than 4000 pptv are detected and are strongly correlated with other fire products such as CO, C₂H₆, and HCN. A sensitivity study of the methanol retrieval, accounting for random and systematic contributions, shows that the retrieved methanol profile is reliable from 8.5 to 16.5 km, with an accuracy of about 20% for measurements inside polluted air masses. The upper tropospheric enhancement ratio of methanol with respect to CO is estimated from the correlation plot between methanol and CO for aged tropical biomass burning plumes. This ratio is in good agreement with the ratio measured in the free troposphere (up to 12 km) by recent aircraft studies and does not suggest any secondary production of methanol by oxidation in aged biomass burning plumes.

1 Introduction

Biomass burning is a major source of anthropogenic air pollution (Crutzen and Andreae, 1990). Intense fires occurring during the dry season of each hemisphere in the tropics are the main source of biomass burning products in the atmosphere on a global scale (Hao and Liu, 1994). In addition to emissions of large quantities of CO₂, CO and aerosols, many other organic compounds are emitted at significant levels (Yokelson et al., 1999; Holzinger et al., 1999; Goode et al., 2000; Andreae and Merlet, 2001). Methanol (CH₃OH) is one of these chemicals.

After methane, methanol is the most abundant organic molecule in the troposphere (Jacob et al., 2005). Typical background concentrations are 400–1000 pptv in clean air in the boundary layer (Lewis et al., 2005) or in the free troposphere (Singh et al., 1995).

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The atmospheric lifetime is about 16 days in the free troposphere (Singh et al., 1995) due primarily to OH oxidation to produce formaldehyde. CH₃OH thus has an important effect on the oxidative capacity of the atmosphere.

5 The primary source of atmospheric methanol is the growth (~60%) and decay (~10%) of plants, with biomass burning providing an additional 10% or so of the budget. The oxidation of methane (and other hydrocarbons) can also produce methanol primarily via the self reaction of the CH₃OO radicals to form CH₃OH and H₂CO, which accounts for another 20%. The direct anthropogenic contribution (e.g., solvent emission) is just a few percent. These numbers are all based on the recent budget of Jacob
10 et al. (2005) and the values have considerable uncertainty, and they differ substantially from previous budgets (Singh et al., 2000; Heikes et al., 2002; Galbally and Kirstine, 2002; von Kuhlmann et al., 2003a, b).

Methanol is involved in HO_x chemistry because the reaction with OH forms the CH₃O and H₂COH radicals, which rapidly react with O₂ to give HO₂ and H₂CO. Formalde-
15 hyde chemistry produces additional HO₂ radicals and CO so methanol is a significant source of both H₂CO and CO (Palmer et al., 2003). The majority of measurements of atmospheric methanol concentrations are performed in surface air (Heikes et al., 2002; Lewis et al., 2005). Recent aircraft campaigns have allowed the measurement of a few methanol profiles in the free troposphere up to 12 km (e.g., Singh et al., 2001, 2004).

20 We report the first methanol profile measurements in the upper troposphere and the lower stratosphere (UTLS) from space. Volume mixing ratios (vmrs) higher than 4000 pptv have been measured by the space-borne instrument ACE-FTS inside biomass burning plumes already detected by this instrument in southern lower to mid-latitudes during October 2004 (Rinsland et al., 2005a). After discussing the reliability
25 of the retrieval, methanol profiles are compared to the corresponding CO profiles and the results are discussed.

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2 ACE-FTS measurements and retrieval

2.1 Evidence of a methanol contribution to the spectra

The Atmospheric Chemistry Experiment (ACE) makes solar occultation measurements and has a global coverage from approximately 85° N to 85° S with a majority of measurements over the Arctic and the Antarctic (Bernath et al., 2005). However, the orbital coverage yields opportunities to study tropical events in the mid and upper troposphere such as biomass burning plumes (Rinsland et al., 2005a) but for limited time spans. The primary ACE instrument is a high resolution (0.02 cm^{-1}) Fourier transform spectrometer (ACE-FTS) operating between 750 and 4400 cm^{-1} . Vertical profiles of temperature, pressure and various atmospheric constituents are retrieved, with a vertical resolution of 3–4 km, from the ACE-FTS spectra recorded at a series of tangent heights using a global fit approach coupled with a Levenberg-Marquardt non-linear least squares method (Boone et al., 2005). Spectroscopic parameters are taken from the HITRAN 2004 line list (Rothman et al., 2005). Molecular absorption lines are fitted in selected microwindows to determine temperature and volume mixing ratio profiles. A set of microwindows is determined for each target species and is optimized to reduce the impact of interfering species, and to retrieve the vertical profile over the broadest possible altitude range. The retrieval algorithm version currently used in the ACE-FTS retrieval process is version 2.2. However, we use a research version of the algorithm, which can include isotopologues as interfering species during the fitting process independently of the main isotopologue, for the methanol retrieval.

The strongest absorption band of methanol in the infrared spectral region is the band at $10\text{ }\mu\text{m}$ (<http://vpl.ipac.caltech.edu/spectra/methanol.htm>). Spectroscopic data of this band have been recently included in the HITRAN database based on the work of Xu et al. (2004). The empirical line list at $10\text{ }\mu\text{m}$ arises mainly from the fundamental CO-stretch mode ν_8 at 1033 cm^{-1} . Methanol is retrieved between 7 and 35 km using a large spectral window ($984.9\text{--}998.7\text{ cm}^{-1}$). Most of the strongest lines in this window

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are lines of the ν_8 and $\nu_8 + \nu_{12} - \nu_{12}$ bands. A small percentage of the lines belong to the $\nu_8 + 2\nu_{12} - 2\nu_{12}$ and ν_7 bands. The main interfering species in the spectral range used are O_3 and its minor isotopologues, CO_2 , H_2O , NH_3 , and C_2H_4 . The isotopologues 1, 2 and 3 (OOO , $OO^{18}O$ and $O^{18}OO$, respectively) of ozone are fitted simultaneously with methanol while the other interfering species are fixed to their previously retrieved values for H_2O (version 2.2) and to their climatological values for CO_2 , NH_3 , and C_2H_4 . The isotopologues 4 and 5 ($OO^{17}O$ and $O^{17}OO$, respectively) of ozone are fixed using the normal isotopic abundances to the values of the main isotope previously retrieved. Data from the same time spans used by Rinsland et al. (2005a) (30 September–6 October 2004 and 26 October–3 November 2004) were analysed. It is worth noting that NH_3 and C_2H_4 are short-lived biomass burning emission products that could then be also enhanced during fire events and that could have significant contribution to the spectrum (Rinsland et al., 2005b). However, Rinsland et al. (2005a) show that the fire plumes detected by ACE-FTS in October 2004 are aged plumes: only relative long-lived species are then detectable. Moreover, we checked that considering climatological vmr values for NH_3 and C_2H_4 does not lead to features in the residuals (observed-calculated) of the spectra. Figure 1 shows the comparison between a simulated spectrum without accounting for the contribution of CH_3OH and the same spectrum including the methanol contribution (the spectrum used corresponds to the spectrum at the maximum of an enhanced profile of methanol). The corresponding residuals (observed – calculated) are also plotted as well as the methanol contribution to the spectrum (shifted down) assuming a vmr value equal to the value retrieved for this spectrum (~ 3900 pptv). The sharp features in the residuals when methanol is not included are similar in position and shape to the methanol contribution to the spectrum. Furthermore, the residuals when methanol is included in the calculated spectrum are reduced substantially (Fig. 1, pink curve), showing a clear contribution due to methanol.

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2.2 Sensitivity of the retrieval to different error sources

ACE-FTS spectra are inverted to vertical profiles of atmospheric state parameters, $\mathbf{x}$, using an iterative nonlinear least squares fitting procedure as described originally by Levenberg (1944) and Marquardt (1963):

$$\mathbf{x}_{i+1} = \mathbf{x}_i + \left(\mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K} + \lambda \mathbf{I} \right)^{-1} \mathbf{K}^T \mathbf{S}_y^{-1} (\mathbf{y} - \mathbf{F}(\mathbf{x}_i, \mathbf{b})), \quad (1)$$

in which $\mathbf{y}$ is the vector of measurements, $\mathbf{F}$ the radiative transfer model, $\mathbf{b}$ the forward model parameter vector, i the iteration number, $\mathbf{K}$ the Jacobian of $\mathbf{F}$ with respect to $\mathbf{x}$, λ is the Levenberg-Marquardt weighting factor and $\mathbf{S}_y$ the error covariance matrix of the measurements that is assumed to be diagonal.

The 1σ statistical error in the case of a Levenberg-Marquardt method is:

$$\sigma_m(x_j) = \sqrt{\left(\mathbf{K}^T \mathbf{S}_y^{-1} \mathbf{K} \right)^{-1}_{jj}} \quad (2)$$

This error that we name “measurement noise error” in Table 1 is the error usually reported by version 2.2. However, considering only the statistical error does not account for systematic errors. To estimate the sensitivity of the methanol retrieval to each uncertain parameter b_j , the retrieval was performed by perturbing each parameter by 1σ of its assumed uncertainty. The error induced in the retrieved profile is:

$$\Delta \mathbf{x}_j = \mathbf{x}(b_j) - \mathbf{x}(b_j + \Delta b_j) \quad (3)$$

Error sources accounting for uncertainties in temperature, tangent altitude pointing, CH_3OH spectroscopic data, instrumental line shape (ILS), and mixing ratios of the main interfering species (CO_2 , H_2O , NH_3 , C_2H_4 and isotopologues 4 and 5 of ozone) are considered. The effects of uncertainties in the baseline of the spectra, spectral shifts and isotopologues 1, 2 and 3 of ozone are not included in this sensitivity study because these parameters are fitted simultaneously with methanol.

Table 1 presents the sensitivity results from the average of the individual results obtained for each enhanced occultation. The total error in the last column is an effective total error as the standard deviations given for each uncertain parameter are the mean of the individual standard deviations of each occultation. Considering the mean standard deviations and the effective total error gives a better representation of the sensitivity of the methanol retrieval to uncertainties rather than considering just a single occultation. We also checked several individual occultations to verify that the average sensitivities were representative of the entire profile, especially near the maximum. The methanol retrieval is mainly sensitive to uncertainties in the tangent height determination, in the temperature and in the spectroscopic data of methanol. Sensitivity to pointing and temperature increases with altitude when CH_3OH vmr decreases whereas sensitivity to spectroscopic data stays constant with respect to altitude (about 13%, as expected). The sensitivity of the retrieval to uncertainties in the ILS and interfering species is less than 1% on average for all the altitudes between 8.5 and 20.5 km. The effective total error deduced is a minimum at the maximum of the profile and represents about 20% of the vmr value and increases with the altitude above the maximum to reach relative values greater than 100% above 16.5 km. The retrieved methanol profiles are thus reliable up to 16.5 km. Above 16.5 km, the reliability of the profiles is poor, but the vmr values retrieved are close to zero as expected.

3 Results and discussion

The ACE-FTS sampled the southern low to mid-latitudes during two time spans, between 30 September (273 in Julian day) and 6 October 2004 (279), and between 25 October (298) and 3 November 2004 (307). The time series obtained for the first of these is plotted in Fig. 2. The latitude of the individual measurements is indicated at the top panel. During the first time period, measurements correspond to sunsets whereas they correspond to sunrises during the second time period. Methanol vmrs as high as (4594 ± 225) pptv at 10.5 km and (2836 ± 461) pptv at 13.5 km are measured

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on 5 October 2004 and on 25 October 2004, respectively. Methanol enhancements decrease between the two time periods corresponding to the decrease in the intensity of the fire season in the Southern Hemisphere. Figure 3 shows the distribution of the ACE occultations in the southern tropical to mid-latitudes for which enhanced methanol levels have been detected during October 2004. These occultations are similar to the occultations for which Rinsland et al. (2005a) show enhancements of other fire products such as CO, HCN and C₂H₆.

Figure 4 shows an example of a methanol profile retrieved from the sunset occultation ss6153 measured on 3 October 2004 at 30.2° S and 56.9° E, and showing the largest enhancement of CO, HCN and C₂H₆ during this period (Rinsland et al., 2005a). Methanol vmr values of about 4000 pptv are measured around the maximum at 10.5 km. The CO profile retrieved for the same occultation is plotted for comparison and the shape is similar. The maximum of the methanol profile is slightly higher than the maximum of the CO profile, but this is likely due to a sampling effect. We also analysed occultations outside the biomass burning plumes for the same time periods (beginning and end of October 2004) and the same latitude band (0–45° S). An example of a background profile is also plotted in Fig. 4 for comparison. It is worth noting that vmr values measured by ACE-FTS for the background cases in the southern low to mid-latitudes agree with values measured from aircraft by Singh et al. (2004) between 8 and 12 km above the Pacific.

Figure 5 shows a correlation plot of methanol versus CO for all of the profiles between 8.5 and 16.5 km measured inside biomass burning plumes during October 2004 in the latitude band 0–45° S. Methanol vmrs and CO vmrs are strongly correlated for measurements inside polluted air masses: the correlation coefficient derived from the plot is 0.91. For comparison, the correlation coefficient deduced from the background measurements performed during the same time period and in the same latitude band is about 0.75. The slope of the linear fit (Fig. 5) for measurements inside biomass burning plumes, defined as $\Delta(\text{CH}_3\text{OH})/\Delta(\text{CO})$, is (16.4 ± 0.5) pptv/ppbv. Since only measurements in polluted air masses are considered, this value can be compared to

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the enhancement ratios reported for example by Singh et al. (2004). They report a mean enhancement ratio of 16 pptv/ppbv in the free troposphere for fire plumes from Southeast Asia measured over the Pacific. Christian et al. (2003) find a mean value of 24 pptv/ppbv for Indonesian fuels. Holzinger et al. (2005) report a higher mean value of 38 pptv/ppbv over the Mediterranean arguing that an aged fire plume was sampled in which secondary production took place. However, Rinsland et al. (2005a) show that fire plumes sampled by ACE-FTS during October 2004 were aged for about 7 days and our value is closer to the value of Singh et al. (2004), who also measured aged plumes. Secondary production of methanol is unlikely in the air masses sampled by the ACE-FTS. It is important to note that until now methanol profiles have been measured only by aircraft in situ and these measurements have all been below 12 km in altitude. The ability of ACE-FTS to retrieve methanol profiles above the tropopause is a significant improvement.

4 Summary and conclusion

In this paper we show the first measurements of upper tropospheric methanol profiles within aged fire plumes from the space-borne infrared spectrometer ACE-FTS. A detailed study of the sensitivity of the methanol retrieval, including random and systematic contributions, implies that the total error is about 20% at the maximum of the profile in the case of enhanced profiles measured inside polluted air masses and the profile is reliable from 8.5 to 16.5 km. We report methanol vmr values higher than 4000 pptv for occultations measured from the tropics to mid-latitudes during October 2004. The correlation between upper tropospheric carbon monoxide and methanol is stronger in polluted air masses than in the background case. The upper tropospheric enhancement ratio with respect to CO deduced from ACE-FTS measurements inside aged biomass burning plumes agrees well with the ratio measured in the free troposphere (up to 12 km) by recent aircraft measurements.

The ability of the ACE-FTS to measure methanol profiles in the UTLS (in the case of

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pollution events here) will lead to further scientific studies. Extending these capabilities to background methanol measurements will allow global mapping of methanol, the second most abundant organic species in the troposphere after methane, and will give better constraints to models used to derive estimates of the global methanol budget.

5 *Acknowledgements.* Funding for ACE is provided by the Canadian Space Agency and the Natural Sciences and Engineering Research Council (NSERC) of Canada. Support was also provided by the NSERC-Bomem-CSA-MSI Industrial Research Chair in Fourier Transform Spectroscopy.

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Table 1. Sensitivity study of the methanol retrieval for measurements inside tropical biomass burning plumes (October 2004)^a.

Altitude km	Mean vmr	Meas. noise	Spectr. Data ^b	Pointing ^c	T ^d	ILS ^e	CO ₂ ^f	H ₂ O ^g	NH ₃ ^h	C ₂ H ₄ ^h	OO ¹⁷ O ⁱ	O ¹⁷ OO ⁱ	Total Error ^j
8.5	1576	319	204	87	51	0.7	5	8	11	6	0.7	0.3	392 (25)
10.5	1767	240	237	102	57	0.6	4	5	6	4	0.6	0.3	357 (20)
12.5	1292	263	169	77	38	0.8	3	3	4	2	0.7	0.2	324 (25)
14.5	749	276	98	55	16	0.8	2	2	1	0.7	0.5	0.3	298 (40)
16.5	296	341	40	48	14	2	2	2	0.5	0.6	0.4	0.4	347 (117)
18.5	214	392	26	39	21	4	2	1	0.8	0.8	1	1	395 (185)
20.5	221	470	33	76	33	10	2	2	0.6	1	3	3	479 (217)

^a The mean methanol vmr values and the errors are in pptv.

^b Based on spectroscopic uncertainty of 15% for methanol as given in the HITRAN2004 database.

^c Based on a tangent height uncertainty of 150 m.

^d Based on a temperature uncertainty of 2 K.

^e Since the ILS is parameterized, uncertainty in the ILS is induced by perturbing the field of view by 5%.

^f Based on an uncertainty of 1%.

^g Based on early validation results (10%) (McHugh et al., 2005).

^h Based on a global uncertainty of 20% (including spectroscopic and climatological uncertainties).

ⁱ Based on a variation of 5% of the vmr values compared to the main isotope.

^j The effective total error (see text) is given in absolute (pptv) and in relative (%) units (numbers in parentheses)

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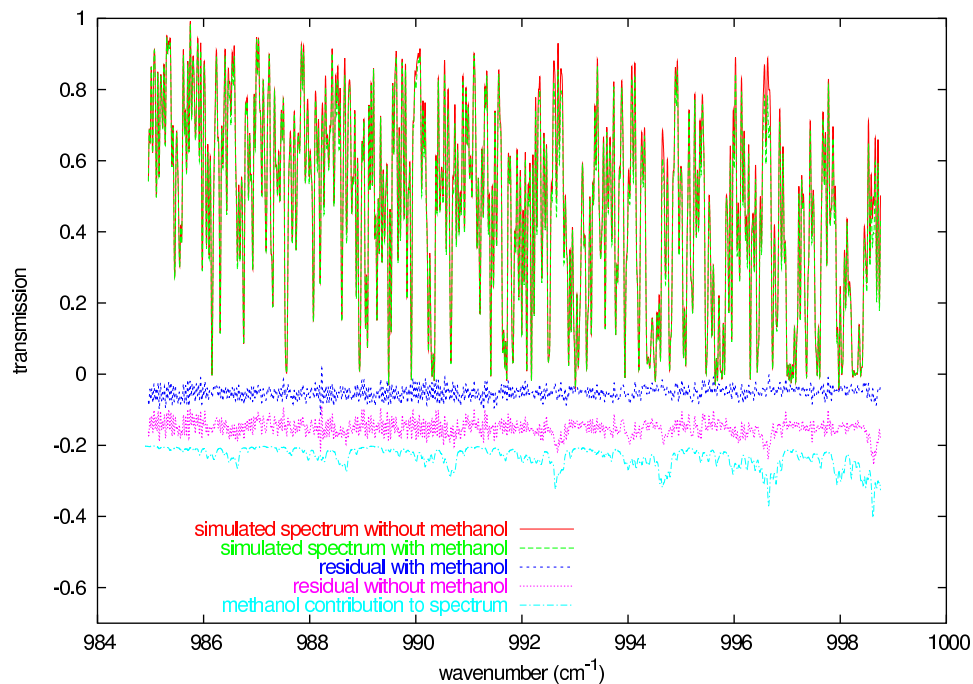


Fig. 1. Simulated spectra with methanol included or excluded in the calculation. The corresponding residuals (observed – calculated) and the computed contribution of CH_3OH to the spectrum using the retrieved vmr are plotted (shifted downwards for clarity).

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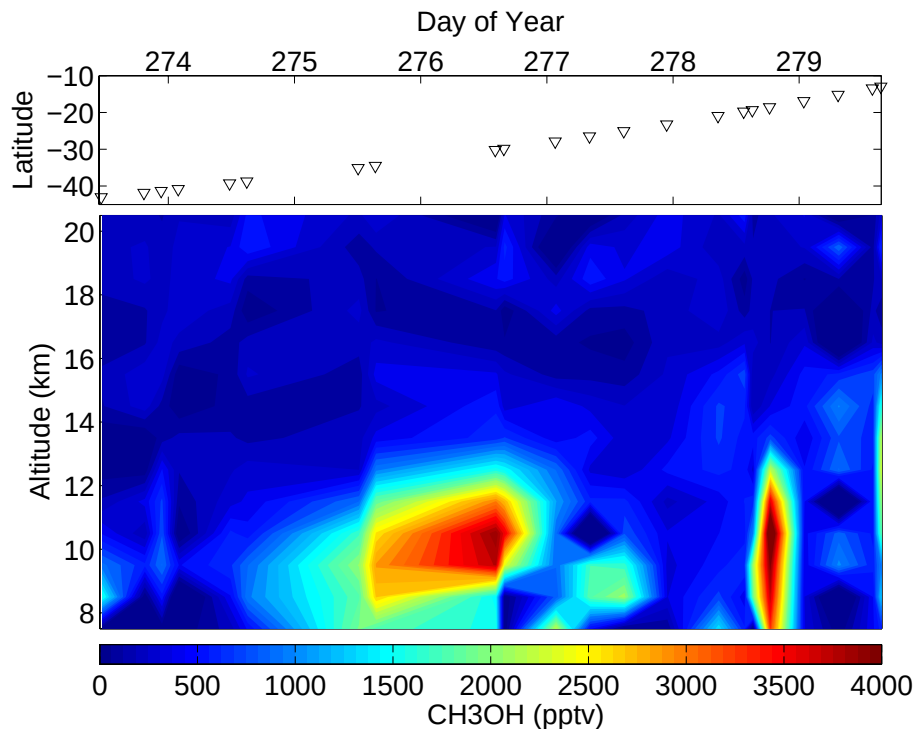


Fig. 2. Time series of ACE-FTS measurements of methanol for sunsets between 30 September (273, Julian day) and 6 October 2004 (279, Julian day). The latitude and the time of each individual measurement are shown at the top of the panel.

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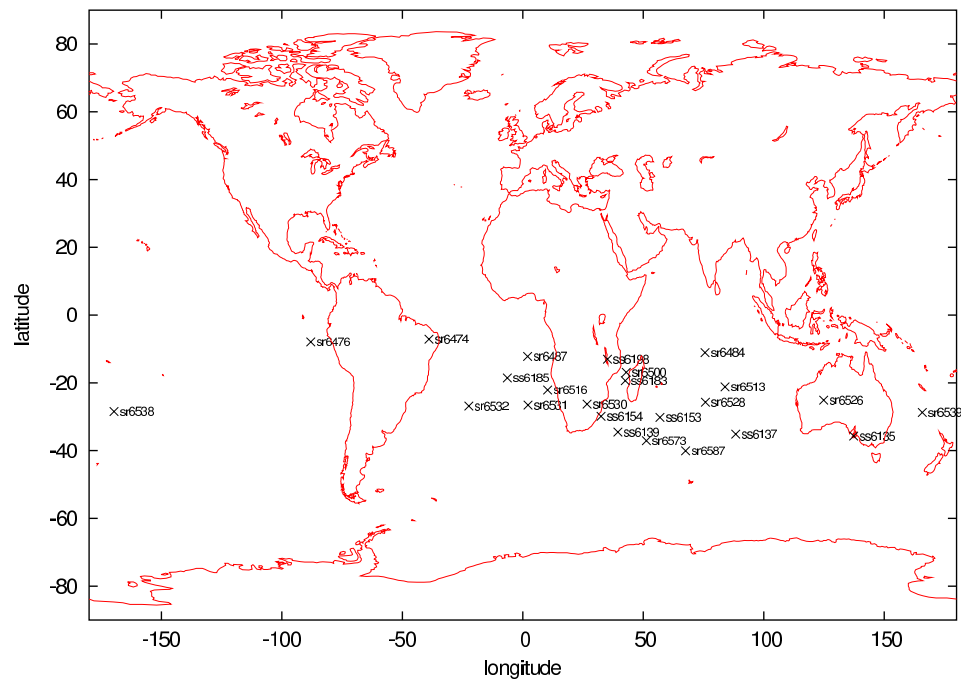


Fig. 3. Location of ACE-FTS occultations showing enhanced levels of methanol during October 2004.

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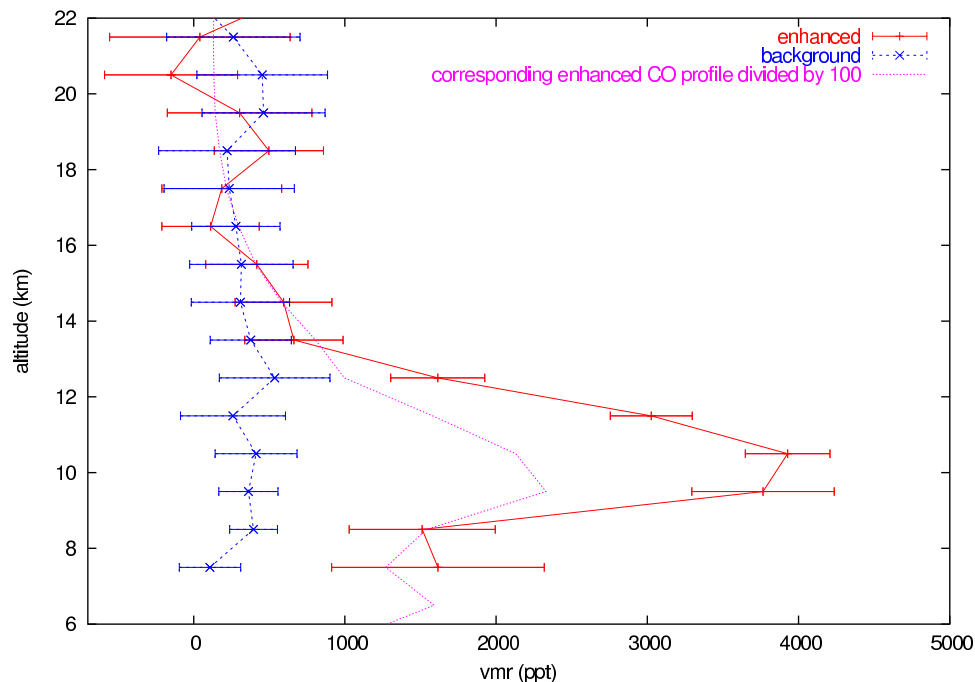


Fig. 4. Enhanced methanol profile retrieved from the sunset occultation ss6153 measured on 3 October 2004 at 30.2° S and 56.9° E. The CO profile retrieved for the same occultation is plotted for comparison as well as an example of background profile of methanol retrieved during the same time period and in the same latitude band. Errors correspond to the 1σ error defined in Eq. (2).

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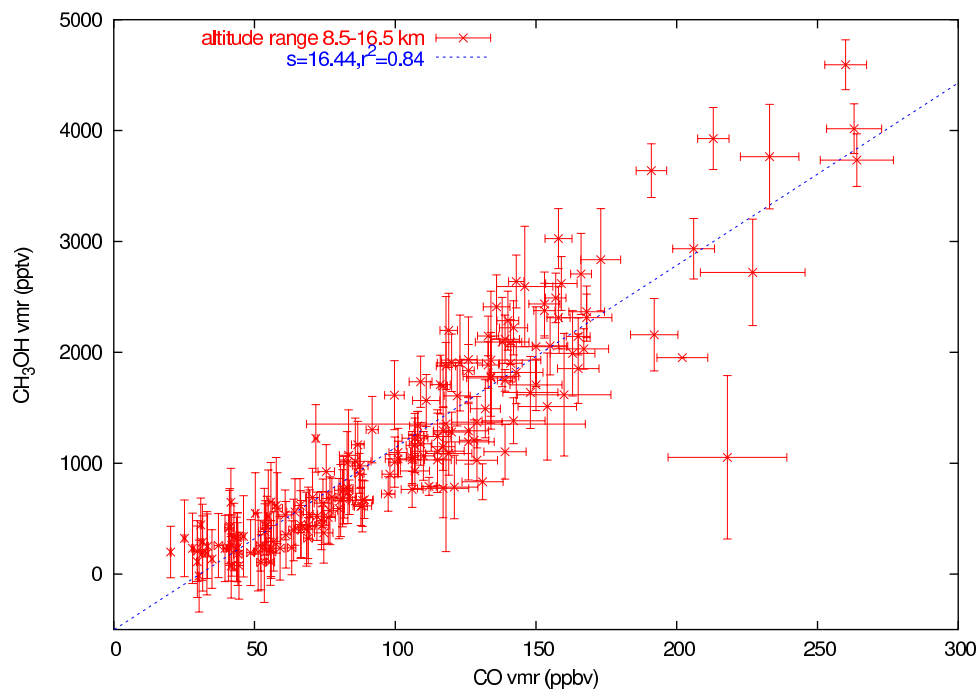


Fig. 5. Correlation plot of methanol and carbon monoxide vmrs measured between 8.5 and 16.5 km inside aged biomass burning plumes from 30 September to 3 November 2004 at 0–45° S latitude and the linear fit results. Errors correspond to the 1 σ error defined in Eq. (2).

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