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**Global distribution of  
upper tropospheric  
formic acid**

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# Global distribution of upper tropospheric formic acid from the ACE-FTS

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## Abstract

We present the first near global upper tropospheric distribution of formic acid (HCOOH) observed from the space using solar occultation measurements from the Fourier transform spectrometer (FTS) on board the Atmospheric Chemistry Experiment (ACE) satellite. Using a new set of spectroscopic line parameters recently published for formic acid, we have retrieved the concentrations of HCOOH between 5 km and the tropopause for ACE-FTS observations from February 2004 to September 2007. We observe a significant seasonal dependence for the HCOOH concentrations related to vegetation growth and biomass burning. We estimate an emission ratio of  $0.0051 \pm 0.0015$  for HCOOH relative to CO for tropical South American fires using a selected set of data for September 2004. Results from the balloon-borne MkIV Fourier transform spectrometer are also presented and used to validate the ACE measurements.

## 1 Introduction

Formic acid is one of the more abundant organic acids in the atmosphere. As a very soluble species, formic acid is found in the atmosphere as a gas and as a solute in water droplets as well as the formate anion in aerosol particles (Talbot et al., 1988). Formic and acetic acids are responsible for most of the acidity in rain water in remote regions. Formic acid plays an important role in controlling pH-dependent chemical reactions in clouds (Keene and Galloway, 1986, 1988; Jacob, 1986).

Our understanding of the sources and sinks of atmospheric formic acid is still very incomplete (Khare et al., 1999), but sources include direct anthropogenic emissions (e.g. motor exhaust) (Talbot et al., 1988; Kawamura et al., 1985), soil (Sanhueza and Andreae, 1991), biomass burning emissions (Talbot et al., 1988; Coheur et al., 2007), vegetation (Jacob and Wofsy, 1988; Talbot et al., 1990; Schafer et al., 1992), isoprene oxidation (Rasmussen and Khalil, 1988; Keene and Galloway, 1986), olefin ozonolysis (Hatakeyama et al., 1981; Horie et al., 1994), aqueous phase oxidation of formalde-

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hyde (Chameides and Davis, 1983) and gas phase reaction of HCHO with HO<sub>2</sub> as well as some peroxy radical reactions (Atkinson et al., 2006; Su et al., 1979; Madronich and Calvert, 1990). The most important sinks are dry and wet deposition as well as reaction with OH (Sanhueza et al., 1996; Baboukas et al., 2000; Rinsland et al., 2004).

5 As wet deposition is by far the most important sink, the lifetime of the HCOOH in the troposphere is very variable (Hartmann et al., 1991). Radojevic and Harrison (1992) estimate that the lifetime of HCOOH is quite short, ranging from hours to a few days. In the free troposphere, the lifetime of formic acid can be substantially longer because of the relatively slow reaction with OH.

10 Formic acid has been measured in the free troposphere by in situ airborne Fourier transform infrared spectroscopy (FTIR) (Yokelson et al., 1999; Goode et al., 2000) and tunable infrared laser differential absorption spectroscopy (TILDAS) (Herndon et al., 2007). Infrared solar spectra have been used in the ground-based detection of HCOOH by Rinsland et al. (2004) as well as in previous observations by Rinsland et al. (2006 and 2007) and Coheur et al. (2007) using ACE satellite data. Remedios et al. (2007) observed the signature of HCOOH thermal emission using spectra from the MIPAS-B2 balloon instrument, a limb-viewing FTIR.

15 The first-space based observations of HCOOH using ACE data were published by Rinsland et al. (2006). They retrieved formic acid in biomass burning plumes and found strongly enhanced concentrations of up to 2 ppb. From 14 profiles they determined that typical background values are 0.31 ppb in the 110–300 hPa range in the free troposphere for southern middle latitudes. They also calculated an emission factor for HCOOH at tropical middle latitudes of  $1.99 \pm 1.34 \text{ g kg}^{-1}$ . Rinsland et al. used line parameters for the  $\nu_6$  mode of formic acid as provided by HITRAN 2004 (Rothman et al., 2004). In our work, we extend the retrievals to the entire global dataset of ACE measurements using an improved set of formic acid line parameters. We also calculate the emission factor for the same region and dates, and compare our results with Rinsland et al. (2006). We validate our retrievals using observations made with the MkIV balloon-borne FTS.

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## 2 Measurements

The Atmospheric Chemistry Experiment (ACE) is a Canadian satellite that was launched by NASA in August 2003. The primary ACE instrument is a high spectral resolution ( $0.02\text{ cm}^{-1}$ ) Fourier transform spectrometer (FTS) operating from 2.2 to  $13.3\text{ }\mu\text{m}$  ( $750\text{--}4400\text{ cm}^{-1}$ ). Working primarily in solar occultation, the satellite provides altitude profile information (typically 5–100 km) for temperature, pressure, and volume mixing ratios for numerous molecules of atmospheric interest between the latitudes  $85^\circ\text{ N}$  and  $85^\circ\text{ S}$  (Bernath et al., 2005).

The HCOOH retrievals reported in this paper are a research data product. Retrievals for the molecule were not available in the most recent dataset for the ACE-FTS (version 2.2). The retrieval approach used was the same global-fit least-squares approach employed for ACE-FTS version 2.2 processing (Boone et al., 2005). Version 2.2 pressures and temperatures were used in the analysis. The ACE-FTS HCOOH retrievals use the Q-branch of the  $\nu_6$  mode near  $1105\text{ cm}^{-1}$ , with a microwindow of width  $10\text{ cm}^{-1}$  centered at  $1105.6\text{ cm}^{-1}$ . The altitude range for the retrievals extends from 5 to 20 km. Interferers in the spectral window (retrieved simultaneously with HCOOH) are  $\text{H}_2\text{O}$ ,  $\text{H}_2^{18}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ , HDO,  $\text{CO}_2$ ,  $\text{O}_3$ ,  $\text{OO}^{18}\text{O}$ ,  $\text{O}^{18}\text{OO}$ ,  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$ , CFC-12, HCFC-22, and HFC-134a, with separate volume mixing ratio (VMR) profiles retrieved for different isotopologues of a given molecule.

The spectroscopic data for HCOOH used in the retrievals were from Vander Auwera et al. (2007) and Perrin and Vander Auwera (2007). The new line parameters improve the quality of the retrievals, yielding smaller fitting residuals in the least-squares analysis than those achieved using the HCOOH spectroscopic parameters from HITRAN 2004 (Rothman et al., 2005). The line intensities changed by nearly a factor of two compared to the values given in HITRAN 2004. The retrieved formic acid concentrations therefore decrease by nearly a factor of two using the new line parameters. The errors in a single typical VMR profile retrieval are dominated by statistical errors, which are about 50% from 5–10 km in tropical regions and deteriorate at higher altitudes and

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towards the poles.

Almost 12000 occultations (11942) recorded between February 2004 and September 2007 have been considered in our study. They have been filtered using derived meteorological products (DMPs) (Manney et al., 2007) to remove all occultations inside or on the edge of a polar vortex. Occultations in the polar vortices have perturbed profiles because of descent by the cold, isolated air. The high inclination SCISAT orbit ( $74^\circ$  to the equator) (Bernath, 2006) provides a large number of occultations at high latitudes so the potentially perturbed occultations were simply discarded. The occultations were classified using potential vorticity values derived from the Met Office analyses (Swinbank and O'Neill, 1994; Swinbank et al., 2002; Davies et al., 2005) in a similar approach to that adopted by Nassar et al. (2005). The remaining 9178 extravortex occultations were filtered to remove anomalous values (e.g., large negative VMRs) and concentrations with very large estimated errors. The locations of the resulting 8125 occultations are plotted in Fig. 1.

### 3 Validation

The MkIV FTS records solar occultation spectra from a high altitude balloon in the  $650\text{--}5640\text{ cm}^{-1}$  spectral range at a spectral resolution of  $0.01\text{ cm}^{-1}$  (Toon, 1991). MkIV data that were obtained in eight balloon flights carried out from Ft. Sumner, New Mexico ( $34.4^\circ\text{ N}$ ,  $104.2^\circ\text{ W}$ ) have been used to validate the ACE-FTS retrievals. These flights were during the autumn turn-around period when the stratospheric float winds are light enough to permit long durations (15–30 h) at float. The retrieved VMR profiles extend from the cloud tops to the float altitude ( $\sim 38\text{ km}$ ) at 2–3 km vertical resolution. The MkIV retrieval uses the JPL-developed GFIT algorithm as described by Sen et al. (1998). The MkIV analysis used the same HCOOH absorption feature (at  $1107\text{ cm}^{-1}$ ) as ACE, but with a slightly narrower window ( $7\text{ cm}^{-1}$  wide). The spectroscopic parameters used in MkIV retrievals are the same parameters that were used for ACE retrievals from Vander Auwera et al. (2007) and Perrin and Vander Auwera (2007). In Fig. 2 these data are

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plotted along with the ACE-FTS average profile for the September, October, November season for 30° N–54° N and 85° W–115° W (continental USA). The eight MkIV flights were made in September from 1993 to 2007. Very few ACE occultations are near New Mexico so we compare the average ACE profile from the continental USA in the fall season with retrievals from the MkIV flights (Fig. 2). One of the 18 ACE occultations showed enhanced formic acid presumably because of a biomass burning plume and it was excluded from the average. The agreement between ACE average and MkIV profiles was within one standard deviation (Fig. 2).

#### 4 Global distributions, vertical profiles and emission factor

The ACE profiles were averaged in 10° latitude bins for 2005 and for the February 2004 to September 2007 time periods. The averages for 2005 are displayed in Fig. 3 and the numerical values are available in supplementary Tables 1 and 2 (<http://www.atmos-chem-phys-discuss.net/9/12465/2009/acpd-9-12465-2009-supplement.pdf>). Global tropospheric HCOOH distributions observed from space are shown in Figs. 4 and 5. The data are split into four seasons, SON (September, October, November), DJF (December, January, February), MAM (March, April, May) and JJA (June, July, August). Average concentrations for 2005 and for the period February 2004–September 2007 are presented in Figs. 4 and 5, with numerical values in Tables 1 and 2. In these plots the seasonal variations are easy to see. Enhancements of HCOOH concentrations are observed at southern tropical latitudes for the SON biomass burning season and the MAM growing season in the northern hemisphere. High values are also seen in JJA in the northern hemisphere, perhaps associated with boreal fires as well as plant growth. On average the enhanced values are about 300 pptv. The average formic acid profiles (Figs. 2–5) are generally consistent with the very few published aircraft profiles of formic acid. For example, average aircraft profiles at various sites are displayed in the modelling paper by Ito et al. (2007). HCOOH concentrations are higher at lower altitudes and often show a

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sharp decrease with altitude near our lowest measured altitudes of 5–7 km, particularly in tropical regions. These trends at lower altitudes agree with previous studies by Andreae et al. (1988) and Talbot et al. (1992) who reported values in the boundary layer between 0.16 and 2.19 ppbv in tropical regions. Another interesting feature is the observation of a background level of about 10 pptv at high latitudes at 5 km altitude. Figure 6 illustrates this more clearly by showing all observed values at 6.5 km in altitude. A few hot spots with concentrations of up to 590 pptv are present and are likely associated with fire plumes.

We calculate an HCOOH/CO emission ratio for 2004 tropical America fires following the approach follow by Yokelson et al. (1999) and Rinsland et al. (2006). A suitable sample of 14 occultations was used to calculate the background levels of formic acid and carbon monoxide. Using two occultations clearly associated with fires plumes we obtain an emission VMR ratio of  $0.0051 \pm 0.0015$ . This result is in good agreement with the value of  $0.0114 \pm 0.0076$  obtained by Rinsland et al. (2006). As expected from the change in line intensities, our result is about a factor of two lower.

## 5 Summary and Conclusion

The first near global tropospheric distribution of formic acid (HCOOH) has been presented using data from the ACE satellite. 8125 extravortex profiles were used for the period between February 2004 and September 2007. It has been possible to observe seasonal variations, and to relate these variations with the main sources of formic acid: biomass burning and plant growth. Values up to 590 pptv have been observed for individual profiles that are likely associated with biomass burning plumes. Strongly enhanced formic acid concentrations are seen at 5–7 km in the tropics at the lowest altitudes that can be observed by ACE. An emission VMR ratio of  $0.0051 \pm 0.0015$  relative to CO was calculated for biomass burning from tropical South American forests. ACE-FTS observations are in good agreement with similar measurements made by the balloon-borne MkIV FTS. Further work has been started to compare ACE observations

with the predictions of the GEOS-Chem chemical transport model.

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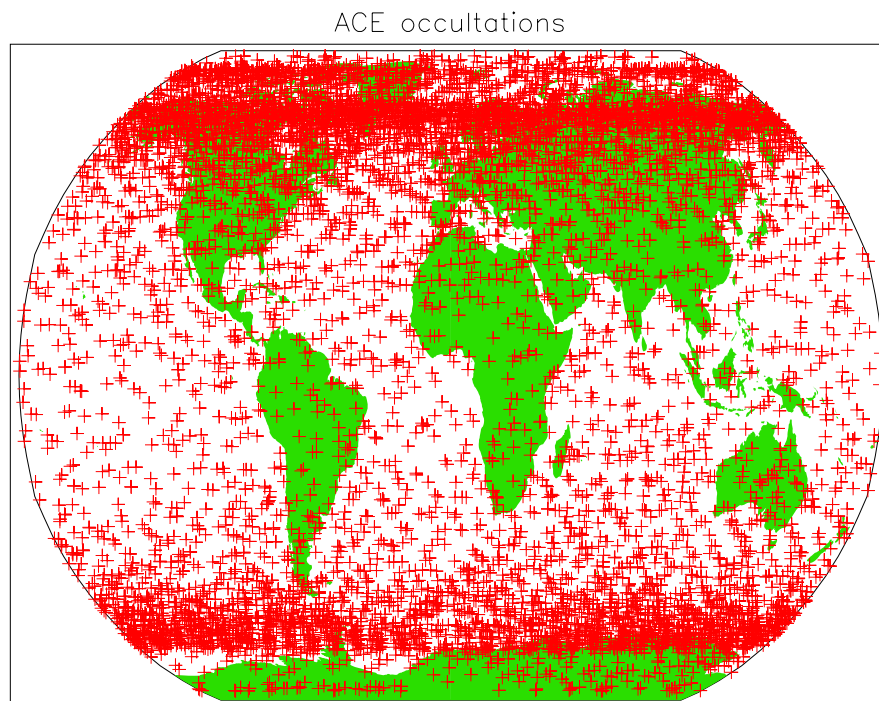
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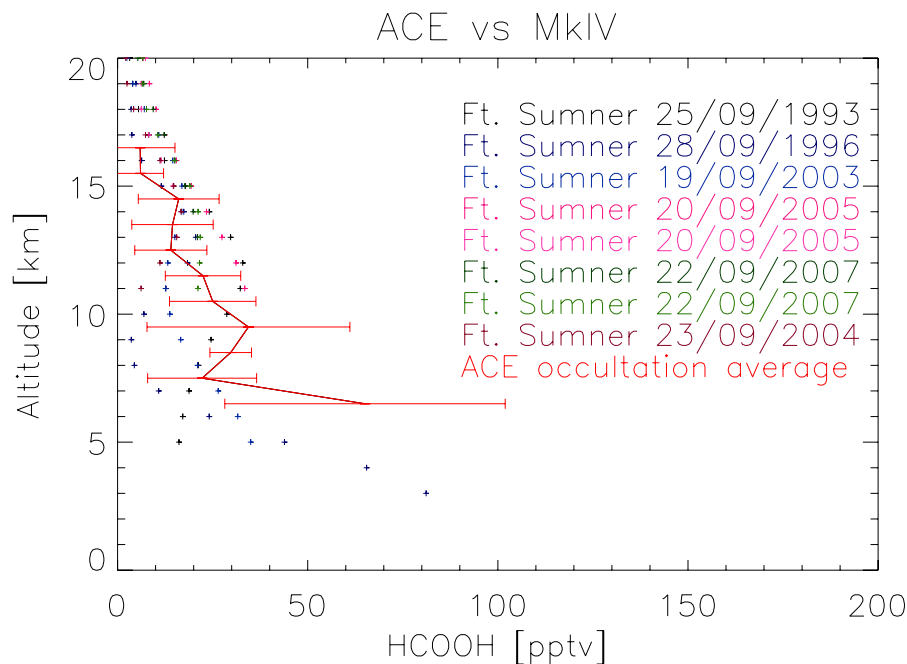


**Fig. 1.** Extravortex occultations for the period February 2004 to September 2007. Each red cross represents the location of an occultation.

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**Fig. 2.** Validation of ACE data using MkIV FTS observations. The individual profiles obtained in balloon flights by MkIV fall within one standard deviation of the ACE occultation average for the same season and geographical region.

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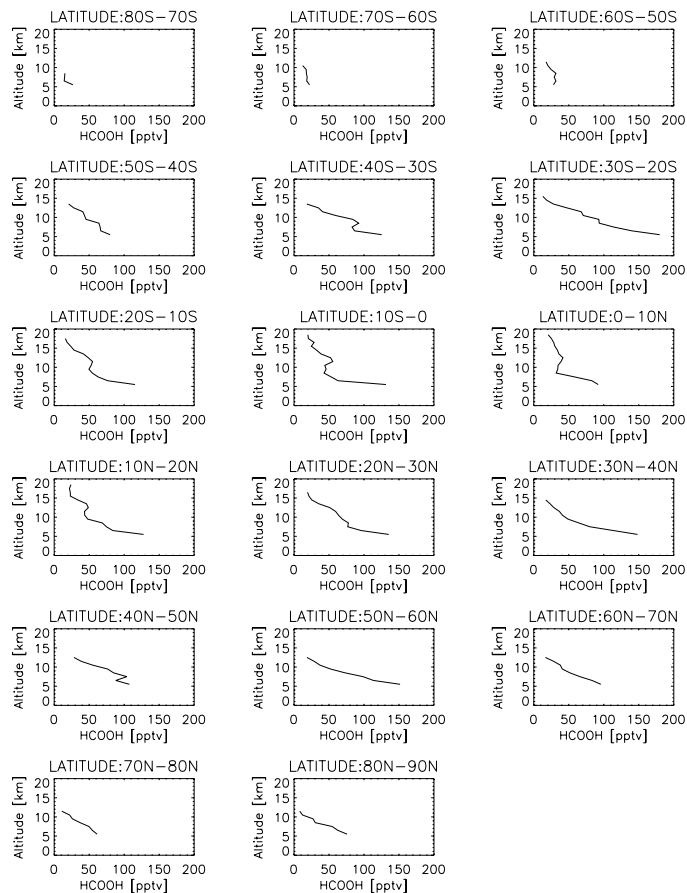
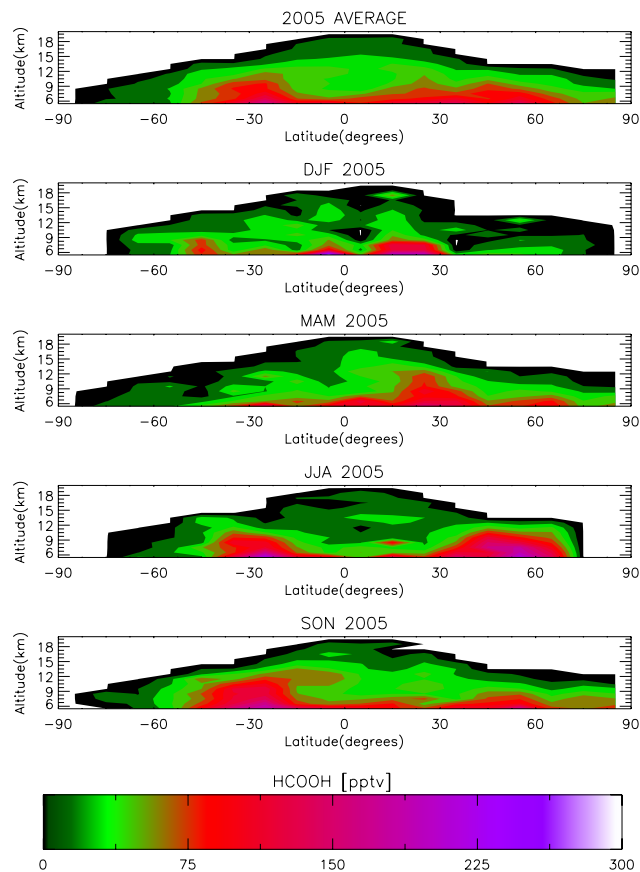


Fig. 3. Average HCOOH profiles for the year 2005 in 10 degree latitude bins.

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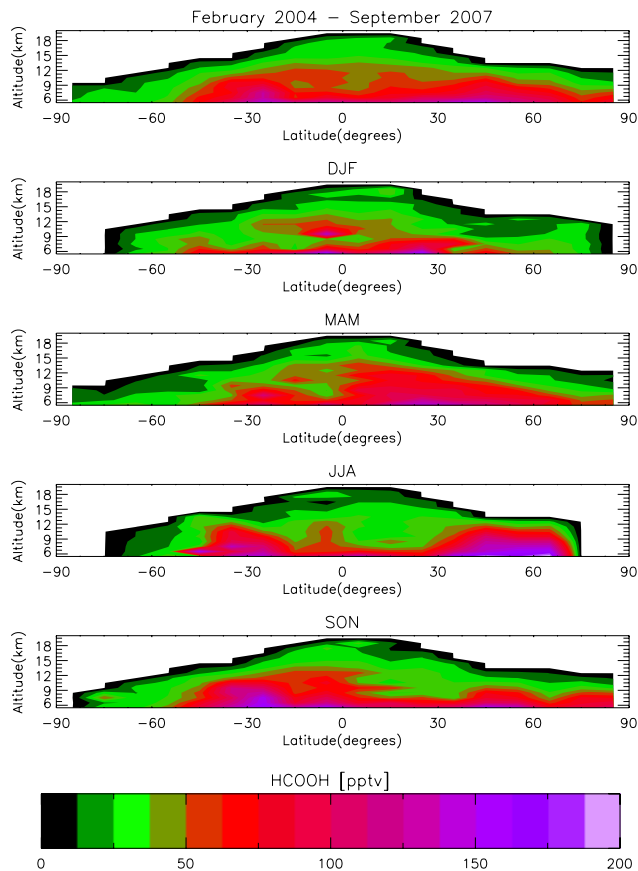
**Fig. 4.** Global HCOOH distribution for the year 2005, showing seasonal variations.

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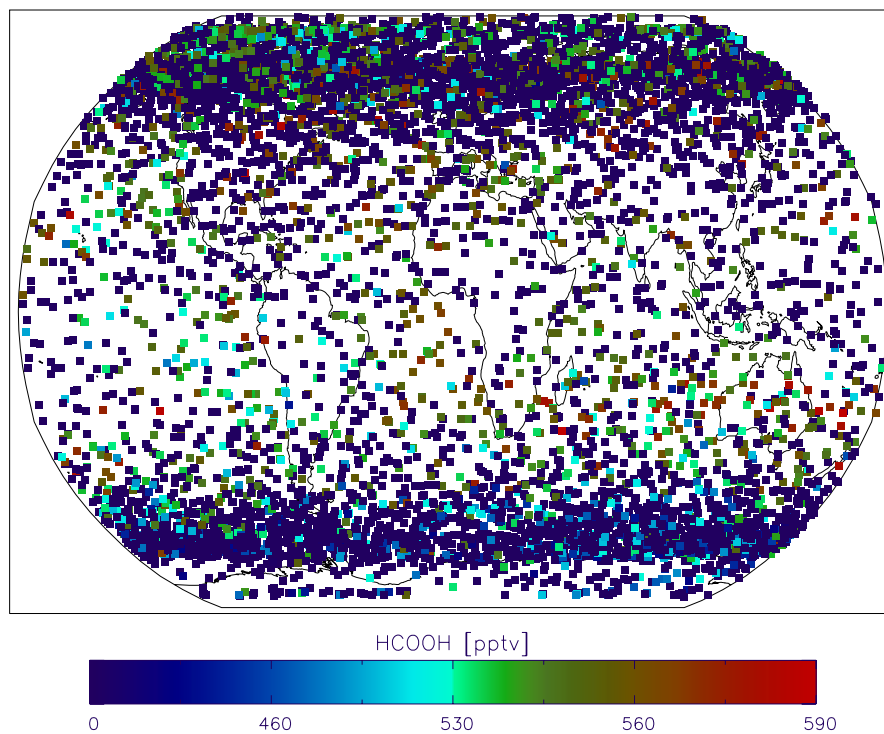


**Fig. 5.** Global HCOOH distribution for the period February 2004 to September 2007.

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**Fig. 6.** HCOOH concentrations at 6.5 km altitude. Hot spots are likely associated with fire plumes.

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