Tropical tape recorder observed in HCN

H. C. Pumphrey,[1] C. Boone,[2] K. A. Walker,[2,3] P. Bernath,[2,4] and N. J. Livesey[5]

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[1] The tropical tape recorder is an effect in which a seasonal cycle in the mixing ratio of a gas is imposed on air entering the stratosphere and is then transported upwards by the Brewer-Dobson circulation. We report the observation of this effect in the mixing ratio of HCN, as measured by two satellite instruments: MLS on Aura and ACE-FTS on SCISAT-1. The cycle does not repeat every year; the data so far suggest that the dominant period is about two years. The reason for this periodicity is not yet fully understood. Comparisons with MODIS fire-count data suggest that it may be connected to inter-annual variations in biomass burning in Indonesia and the surrounding region. **Citation:** Pumphrey, H. C., C. Boone, K. A. Walker, P. Bernath, and N. J. Livesey (2008), Tropical tape recorder observed in HCN, *Geophys. Res. Lett.*, *35*, L05801, doi:10.1029/2007GL032137.

1. Introduction

[2] It has been known for many years that air enters the stratosphere near the equator and that the circulation in the stratosphere is generally upwards at low latitudes. This ascent is steady enough and vertical mixing is slow enough that seasonal variations in the mixing ratio of a gas entering the stratosphere are carried upwards by the air's rising motion. If the gas in question has a long enough chemical lifetime, the seasonal cycle is observable throughout the tropical lower stratosphere. This effect was first observed by *Mote et al.* [1996] in water vapor; the seasonal cycle in this case is imposed by the seasonal cycle in tropopause temperature. *Mote et al.* [1996] described the effect as an "atmospheric tape recorder".

[3] More recently, tape recorders have been observed in CO_2 [*Andrews et al.*, 1999] and in CO [*Schoeberl et al.*, 2006]. The CO_2 tape recorder is driven by seasonal changes in photosynthesis combined with the different biomasses in the Northern and Southern hemispheres. This seasonal variation is familiar from the Keeling curve [*Keeling*, 1998]. The CO tape recorder is driven by the seasonal cycle in biomass burning.

[4] The role of hydrogen cyanide (HCN) as a minor constituent of the atmosphere was first reported in the early 1980s [*Coffey et al.*, 1981]. A compilation of early measurements and modelling work [*Cicerone and Zellner*, 1983] suggests that HCN has sources at the Earth's surface, and sinks in the atmosphere, due to photolysis, and to reactions with OH and $O(^1D)$. The resulting residence time in the atmosphere was estimated at 2.5–5 years. A typical tropospheric mixing ratio is about 0.18 ppbv. More recent studies [*Li et al.*, 2003] suggest a more complex picture in the troposphere, with stronger biomass-burning sources and the ocean as a stronger sink, giving a residence time of 4–5 months.

[5] In the middle atmosphere, HCN is lost slowly due to reactions with OH and $O(^1D)$. As a result, the mixing ratio decreases with both altitude and latitude. The lifetime of HCN in the lower stratosphere is sufficiently long that any seasonal cycle in the tropical upper troposphere should result in a tape recorder signal in the tropical lower stratosphere. In this paper we report two new sets of remotely-sensed data: from MLS on Aura and from ACE-FTS on SCISAT-1. These data allow us, for the first time, to observe a tape recorder signal in HCN mixing ratio in the lower stratosphere.

2. Data

2.1. MLS

[6] The Microwave Limb Sounder (MLS) [*Waters*, 2006] is a small radio telescope. The 1.6 m dish antenna is moved so that its field of view scans across the Earth's limb every 24.7 s. The radiation it receives is converted to a lower frequency in several heterodyne radiometers and analyzed by 32 spectrometers (28 filter banks and 4 digital autocorrelators). Most of the filter banks cover a frequency range centered on a single spectral line of a target molecule. The HCN measurements are derived from band 27, which is centered on the 177 GHz spectral line.

[7] HCN is retrieved by the standard MLS retrieval software [*Livesey et al.*, 2006]. However, the weakness of the signal means that this retrieved product is usable over only the small vertical range between 10 hPa (~32 km) and 1 hPa (~48 km). To obtain HCN mixing ratios over a larger vertical range, we form a weekly zonal mean of the radiances and from these retrieve weekly zonal means of temperature and mixing ratio [*Pumphrey et al.*, 2006]. The resulting data are of usable quality between 68 hPa (~18.7 km) and 0.1 hPa (~64 km). At 100 hPa, retrieval is attempted but the resulting values depend mostly on the a priori. Retrieval is not attempted at pressures greater than 100 hPa. The vertical resolution of the product is 6 km at an altitude of 32 km, degrading to 8 km at 20 km.

2.2. ACE-FTS

[8] The Atmospheric Chemistry Experiment, or ACE, (a.k.a. SCISAT-1) is a Canadian-led satellite mission launched in August 2003 into a circular orbit inclined at 74° to the equator [*Bernath et al.*, 2005]. The primary

[1] School of GeoSciences, University of Edinburgh, Edinburgh, U. K.
[2] Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.
[3] Now at Department of Physics, University of Toronto, Toronto, Ontario, Canada.
[4] Now at Department of Chemistry, University of York, York, England.
[5] NASA Jet Propulsion Laboratory, Pasadena, California, USA.

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instrument is ACE-FTS: a Fourier transform spectrometer with broad spectral coverage in the infrared (750–4400 cm^{-1}) and high spectral resolution (0.02 cm^{-1}) with a maximum optical path difference of 25 cm. Operating in solar occultation, ACE-FTS features a high signal-to-noise ratio but has limited geographical coverage, measuring up to 32 occultations per day. These usually occur in middle and high latitudes; the measurement latitude passes through the tropics eight times in a year. The altitude sampling of the ACE-FTS measurements varies from ~1.5 to 6 km, but the altitude resolution is 3–4 km, limited by the instrument's field of view. The procedure for ACE-FTS retrievals is described by *Boone et al.* [2005]; the data presented here are a development product for which HCN is retrieved over a larger vertical range than the standard v2.2 product. To retrieve HCN, the ACE-FTS retrieval scheme uses 10 microwindows between 1395 and 1460 cm^{-1} and 22 microwindows between 3260 and 3355 cm^{-1}. Near the equator, the majority of retrieved profiles are usable between 68 hPa and 3.8 hPa. All ACE-FTS data shown in this paper are linearly interpolated onto the fixed pressure grid used for MLS retrievals.

3. Results

[9] Figure 1 shows the seasonal cycle of HCN near the equator as measured by both instruments. MLS H_2O and CO are shown for comparison. The strong annual tape recorder signal in H_2O is clearly visible, with bands of wet and dry air leaving the tropical tropopause and rising to about 32 km in approximately 1.8 years. The CO mixing ratio in the troposphere has a semiannual cycle. Between 16 and 20 km this is obscured by an annual cycle due to the strong non-propagating annual signal in the Brewer-Dobson circulation acting on the vertical gradient in CO [*Randel et al.*, 2007; *Schoeberl et al.*, 2007]. Traces of annual tape recorder signal in CO can be seen above 20 km; MLS does not have sufficient vertical resolution to observe any semiannual tape recorder signal which might exist. MLS HCN shows a pattern which rises at a similar speed to the pattern seen in H_2O, but which does not repeat on an annual basis. High mixing ratios are visible at 18 km in mid-2005 and mid-2007, with low values at the same altitude in mid-2004 and 2006. Note that the range of values shown, ±0.02 ppbv, is about ±10% of the total mixing ratio.

[10] ACE-FTS HCN also shows a tape recorder signal with a dominant period of about two years. The timing of the signal appears to be different from the MLS data but this is largely due to the data at the lowest level shown leading the eye astray. We demonstrate this by showing time series of the two data sets at four pressure levels (Figure 2). At 46 hPa the two instruments agree well. At 31 hPa and 21 hPa, MLS is biased high with respect to ACE-FTS, but phasing remains similar. At 68 hPa, the signals are similar, but the MLS data appear to be delayed with respect to the ACE-FTS data. This is because the MLS data at 68 hPa are influenced more by the atmosphere at higher altitudes than by the atmosphere at lower altitudes.

4. Discussion

[11] It is unremarkable that an HCN tape recorder signal exists, given the long photochemical lifetime of the molecule in the lower stratosphere. However, it is remarkable that the dominant period appears to be two years. This is not the same as the behavior of CO, despite both molecules being biomass-burning products. In this section we question the robustness of the measurement and, having concluded that the measurements are not misleading, we suggest possible explanations.

4.1. Vertical Resolution

[12] The tape recorder moves at approximately 9 km/yr, taking approximately 1.8 years to travel from the tropopause to 32 km. Biennial, annual and semiannual cycles at the tropopause become patterns with maxima separated by 18, 9 and 4.5 km respectively. We therefore ask: is the vertical resolution of our measurement sufficient to resolve such patterns? Applying the averaging kernels of the MLS HCN retrieval to sinusoidal profiles with these wavelengths, we concluded that, at 30 km, the measurement filters out almost none of a biennial signal, but 90% of an annual signal. Further experiments with the retrieval formula suggest that by relaxing the smoothing constraint used, an annual signal would be just detectable, at the cost of increased noise. However, re-processing the data set with this configuration revealed no clear annual signal.

[13] ACE-FTS has a vertical resolution almost twice as good as MLS. It should therefore be able to detect an annually varying signal with relative ease. As the data show no sign of such a signal, we conclude that the first impression that one obtains from the data is not misleading: the biennial signal dominates the annual one. Of course, the length of the record is not long enough to establish the signal as consistently biennial.

4.2. Tropical Biomass Burning

[14] As HCN is a product of biomass burning, one hypothesis to explain the observation is that the total amount of biomass burned varies sufficiently from year to year. We test this hypothesis by considering a proxy for the amount of biomass burned: the amount of CO entering the stratosphere. We use MLS measurements at 147 hPa in the 15°S–15°N latitude range for this. The data (Figure 3) have strong annual and semi-annual cycles. but do not show much variation from one year to the next. We therefore fit the data with a statistical model consisting of a mean value, and sinusoidal annual and semi-annual cycles. The residuals from this fit (also shown in Figure 3) show interannual variability that has maxima and minima which occur several months earlier than those seen in HCN at 68 hPa. However, the amplitude of this interannual variability is only about 4.5% of the mean CO mixing ratio. The variability in HCN is closer to 7% of the HCN mixing ratio. We conclude that the inter-annual variability in HCN is only partly explained by the interannual variability in the total amount of tropical biomass burning.

4.3. Indonesian Biomass Burning

[15] It is known from ground-based measurements [*Rinsland et al.*, 2000] that in major El-Nino years such as 1983 and 1998, the HCN mixing ratio in the troposphere can be as much as twice its usual value. In such years there are extensive forest fires in Indonesia and northern Aus-

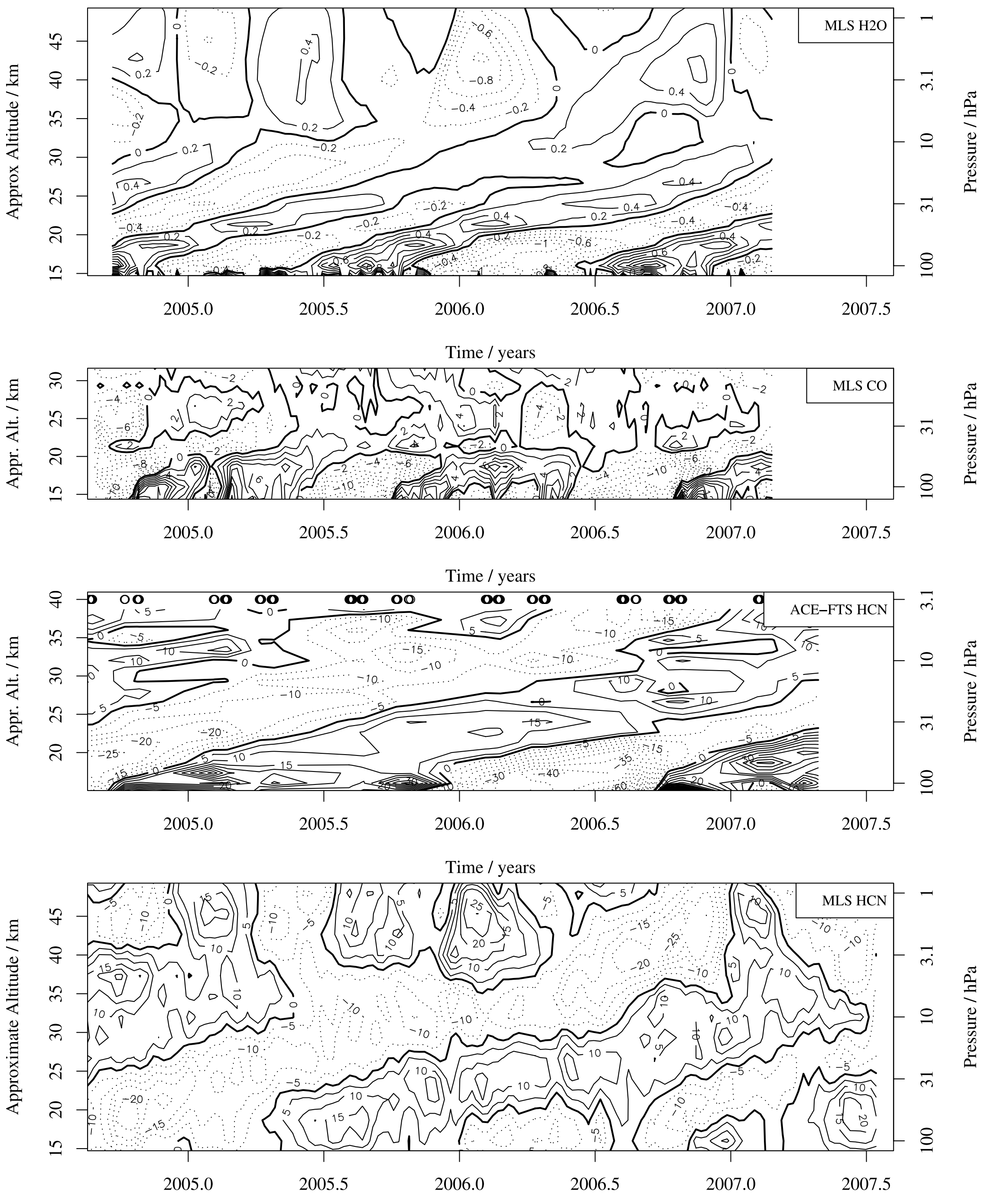

Figure 1. Contour plots of equatorial zonal mean MLS HCN, ACE-FTS HCN, MLS CO, and MLS H_2O. All quantities are differences from the time mean. MLS CO and H_2O data are version 1.5; ACE-FTS data are the research product described in the text. All plots show data within 15° of the equator. Negative contours are dashed, and the zero contour is shown as a heavier line. Contour values are in ppmv for H_2O, ppbv for CO, and pptv for HCN. Circles in the ACE-FTS panel indicate times at which ACE-FTS makes measurements within 15° of the equator. ACE-FTS data are smoothed in time using a Gaussian filter with a width of 30 days.

tralia. These fires burn a high proportion of peat, which produces a higher proportion of HCN than does the burning of other types of biomass [*Christian et al.*, 2003]. We therefore compare the HCN record to an ENSO (El-Nino/Southern Oscillation) index and to the MODIS firecount record in this region.

[16] First, we note that although we have 3 years of MLS data, the tape recorder itself preserves an 18-month record

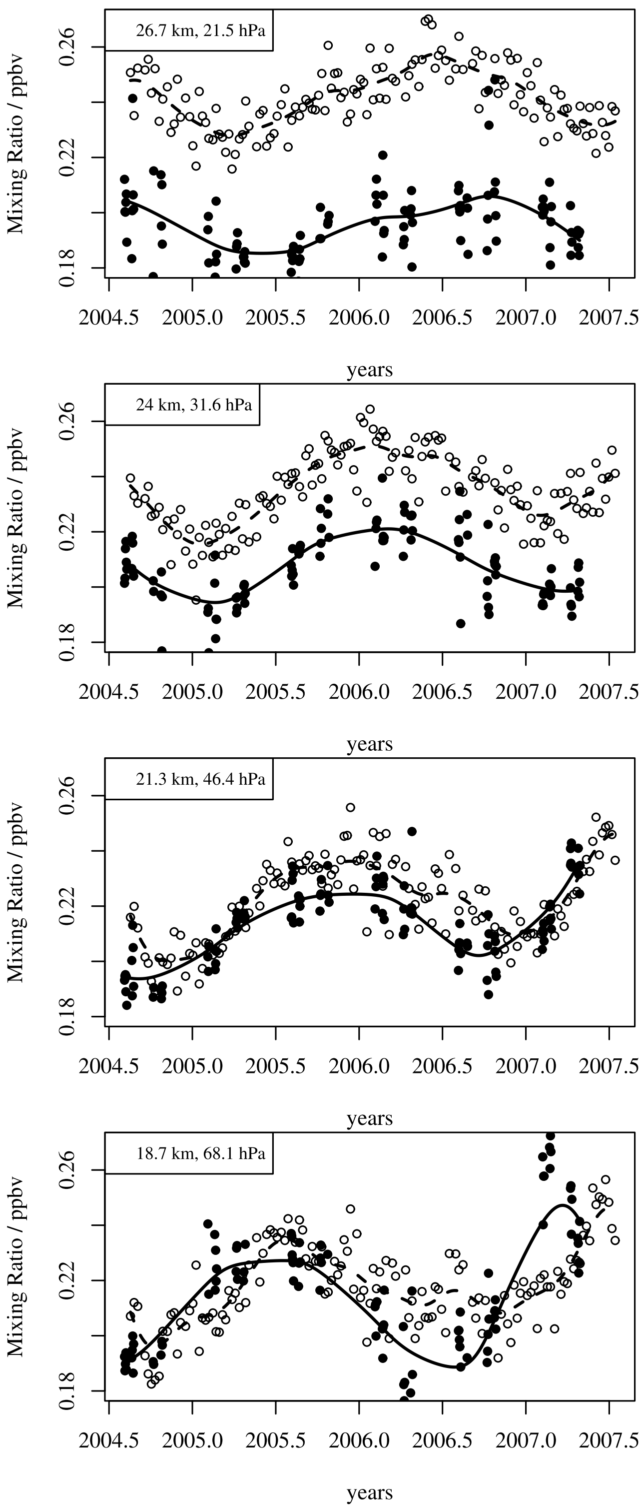

Figure 2. HCN mixing ratio from MLS (open circles, dashed line) and ACE-FTS (solid circles, solid line) at four levels of the MLS retrieval grid. The lines are a local linear fit using the kernel smoothing technique of *Wand and Jones* [1995] with a bandwidth of 0.2 years.

of the entry mixing ratio. We can use the measured values at higher altitudes to re-construct what the mixing ratio would have been at lower levels and at an earlier time. For each level above 68 hPa, we make a linear regression of the 68 hPa data against the data from the higher level at a suitably later time. We then use this statistical model to predict the 68 hPa data at earlier times. We then average the various 68 hPa time series from the higher levels to form a single time series (Figure 4). For comparison, we show the multivariate ENSO index (MEI) [*Wolter and Timlin*, 1993] to give an impression of the state of the ENSO system. Although this index shows variations on a similar time-scale to the HCN data, the correlation is not immediately con-

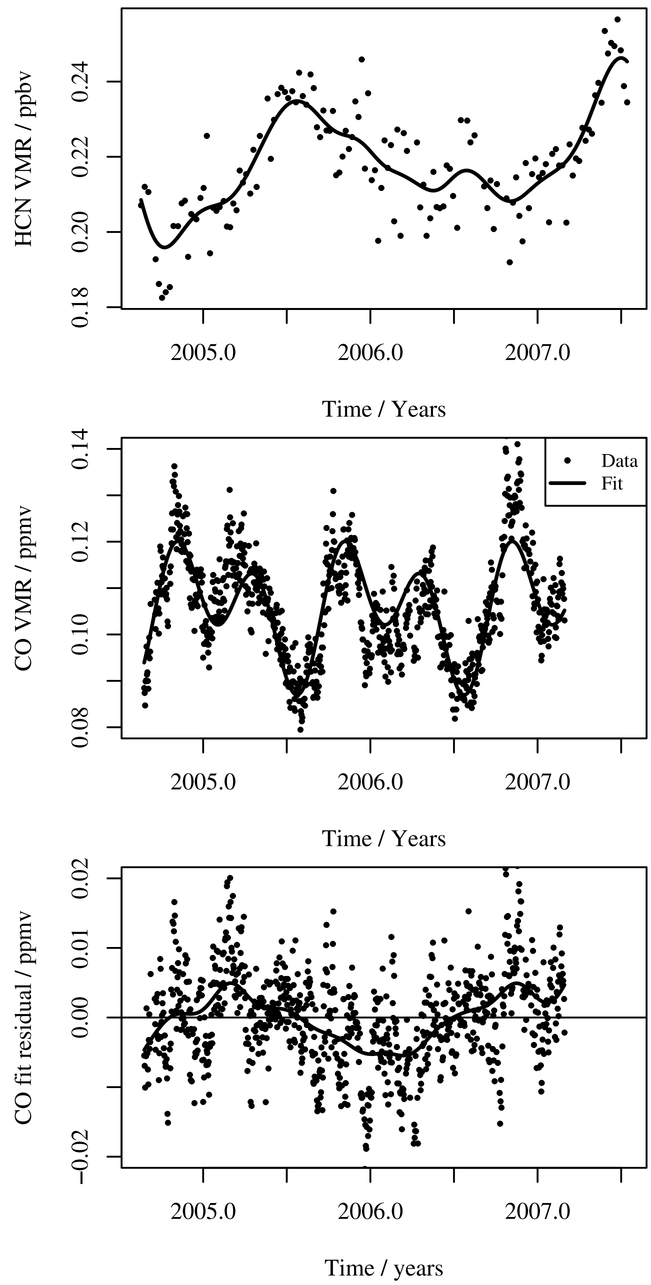

Figure 3. (top) HCN Mixing ratio at 68 hPa. Solid line is a local linear fit using the kernel smoothing technique of *Wand and Jones* [1995] with a bandwidth of 0.2 years. (middle) MLS CO at 147 hPa (dots). Fit assuming only annual and semiannual cycles (solid line). (bottom) Residuals from the fit in the Figure 3 (middle). Solid line is a local linear fit to the residuals.

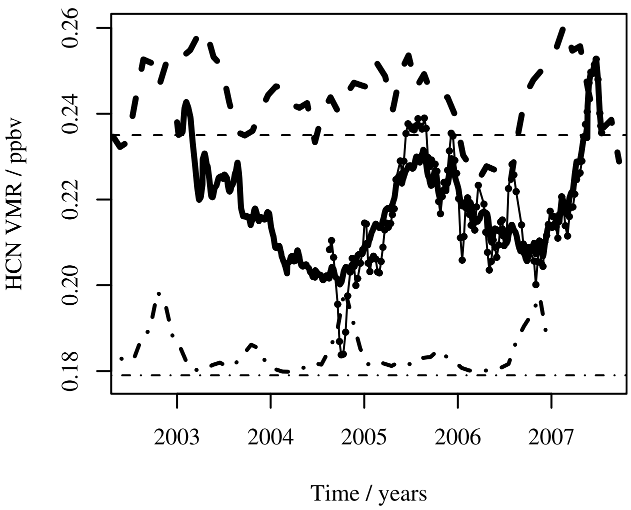

Figure 4. HCN Mixing ratio at 68 hPa derived from MLS data from several altitudes (heavy line). Thin line with dots shows measured data at 68 hPa. Heavy dashed line is the Multivariate ENSO index [*Wolter and Timlin*, 1993] scaled by 0.02; the horizontal light dashed line marks where MEI = 0. Heavy dot-dashed line shows MODIS fire counts over Australia and Indonesia scaled by an arbitrary factor; the horizontal light dot-dashed line marks zero.

vincing. The MODIS firecount data are shown for a region between 40°S and 8°N, and between 90° and 160°E. The firecount time series for this region is unlike that for the tropics as a whole, which is dominated by fires in Africa and South America and which shows only small variations from year to year. Instead, it has strong peaks in late 2002, 2004 and 2006, each occurring a few months before a maximum in the 68 hPa HCN. This correlation does not necessarily imply a causal link, but it is suggestive and provides a clear pointer for more detailed studies.

5. Conclusion

[17] We have presented two new sets of measurements of HCN mixing ratio in the tropical lower stratosphere. We have demonstrated that the two data sets are consistent in regions where both are known to be of good quality. HCN shows a tape recorder effect, with the values entering the stratosphere being preserved and carried upwards by the meridional circulation. Between 2003 and 2007, the HCN mixing ratio of air entering the stratosphere varied by ±10% with a predominant timescale of two years. This behavior is not the same as that shown by CO, which is also a biomass-burning product. However, we note that the total biomass burning in the tropics has a strong semi-annual behavior, leading to a similar behavior in the CO mixing ratio and possibly in the HCN mixing ratio in the tropical troposphere. It therefore seems likely that both HCN and CO have semi-annual tape recorder signals which neither MLS nor ACE-FTS have sufficient vertical resolution to observe.

[18] Forest fires in the Indonesian region emit a higher proportion of HCN than do fires in other tropical regions. They also show a large inter-annual variability, with large peaks occurring a few months before peaks in the mixing ratio of HCN entering the stratosphere. Detailed modelling studies will be required to show whether the Indonesian fires are the main cause of the HCN inter-annual tape recorder.

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P. Bernath, Department of Chemistry, University of York, Heslington, York YO10 5DD, UK. (pfb500@york.ac.uk)

C. Boone, Department of Chemistry, University of Waterloo, 200 University Ave. W, Waterloo, ON, Canada N2L 3G1. (cboone@acebox.uwaterloo.ca)

N. J. Livesey, Jet Propulsion Laboratory, Mail Stop 183-701, 4800 Oak Grove Drive, Pasadena, CA 91109-8099, USA. (nathaniel.j.livesey@jpl.nasa.gov)

H. C. Pumphrey, School of GeoSciences, University of Edinburgh, Edinburgh EH9 3JN, UK. (h.c.pumphrey@ed.ac.uk)

K. A. Walker, Department of Physics, University of Toronto, 60 St. George Street, Toronto, ON, Canada M5S 1A7. (kwalker@atmosp.physics.utoronto.ca)