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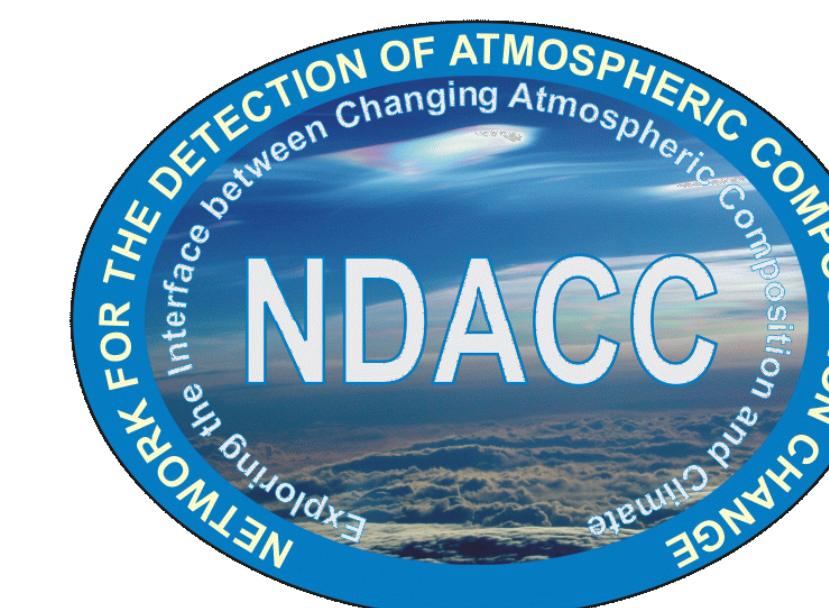


Changes in atmospheric composition discerned from long-term NDACC measurements : Tropospheric gases measured by infrared Fourier transform spectroscopy at Mauna Loa, Hawaii.



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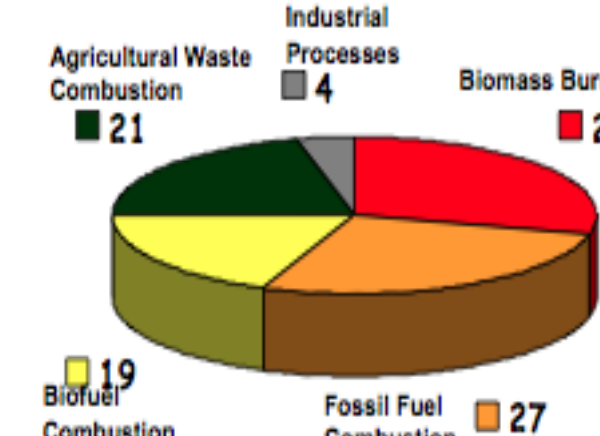
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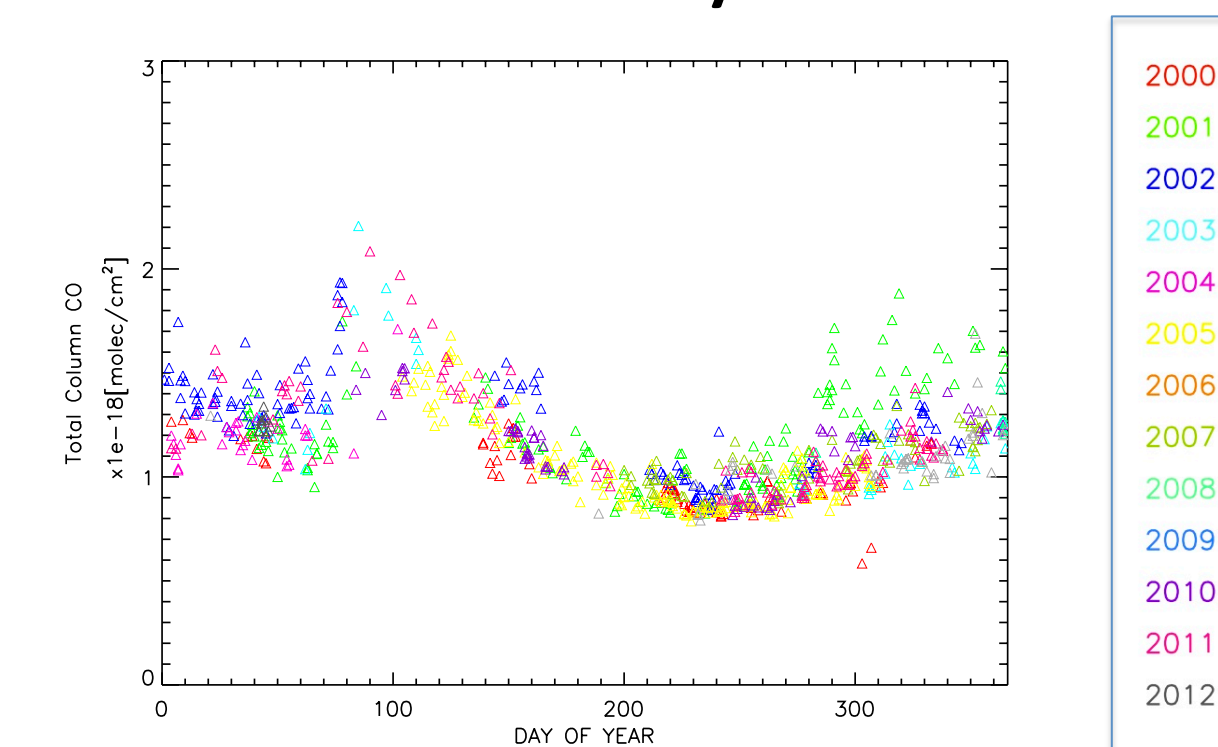
Since 1995 a solar-viewing Fourier transform spectrometer (FTS) has been operated at Mauna Loa, Hawaii (19.54N, 155.58W, 3397 m MSL), as part of the Network for the Detection of Atmospheric Composition Change [NDACC; formerly the Network for the Detection of Stratospheric Change (NDSC)]. Observations have been made, on average, xx days per year, from 1995 to 2009. Semi-autonomous operation of the instrument, including its associated optical, cryogenic, and control systems, is important to acquiring a regular long-term data record. High-spectral-resolution (up to $.0013\text{ cm}^{-1}$), infrared solar-absorption spectra, in the range from 600 cm^{-1} to 4500 cm^{-1} , are acquired routinely in compliance with the specifications set out by the Infrared Working Group of the NDACC. The retrieval methodology employs an optimal estimation technique that produces vertical profiles that are integrated to derive total column amounts. Column and profile data for a number of atmospheric constituents are regularly archived at the NDACC Data Handling Facility. Some tropospheric observations and trends are shown below. [Semi-Autonomous FTS Observation System for Remote Sensing of Stratospheric and Tropospheric Gases. Hannigan J.W., Coffey M.T., Goldman A., *Journal of Atmospheric and Oceanic Technology*: **26**, 1814–1828. DOI: 10.1175/2009JTECHA1230.1. 2009.]

CO

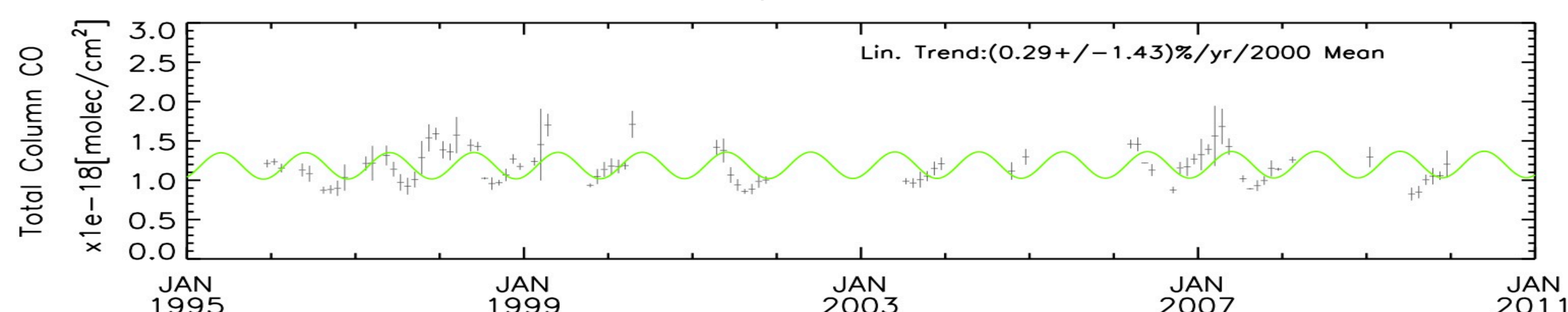
Carbon monoxide is the third most abundant carbon-containing gas in the atmosphere (after CO_2 and CH_4). Sources of CO are fossil-fuel combustion, anthropogenic and biogenic (isoprene, monoterpene, alkene) oxidation of VOCs, oxidation of CH_4 and biomass burning. CO is a precursor of tropospheric O_3 and CO_2 (Net: $\text{CO} + 2\text{O}_2 \rightarrow \text{CO}_2 + \text{O}_3$). The lifetime of CO in the troposphere is about 2 months. The long-term trend in CO at Mauna Loa for the period from 1995 to 2009 is $0.29 \pm 1.43\%$ /year, that is not significant.



Seasonal Cycle

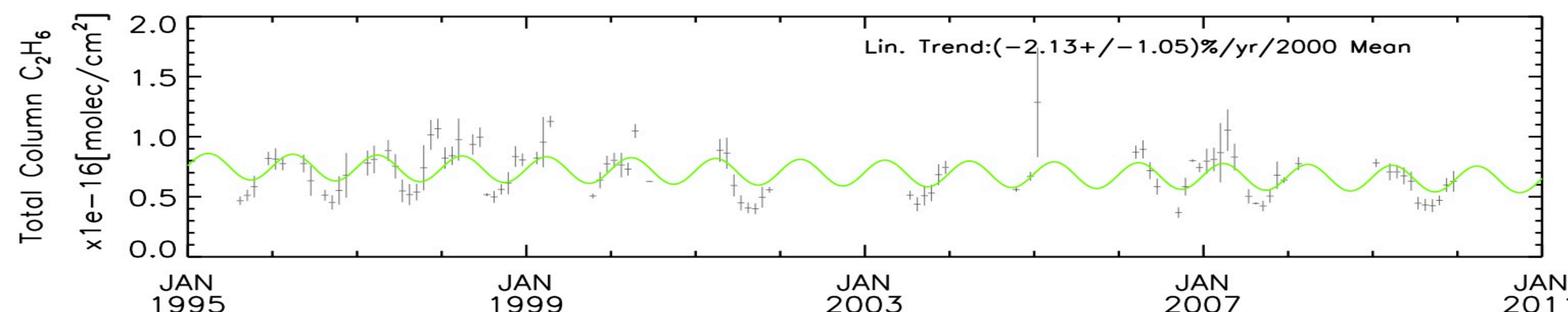
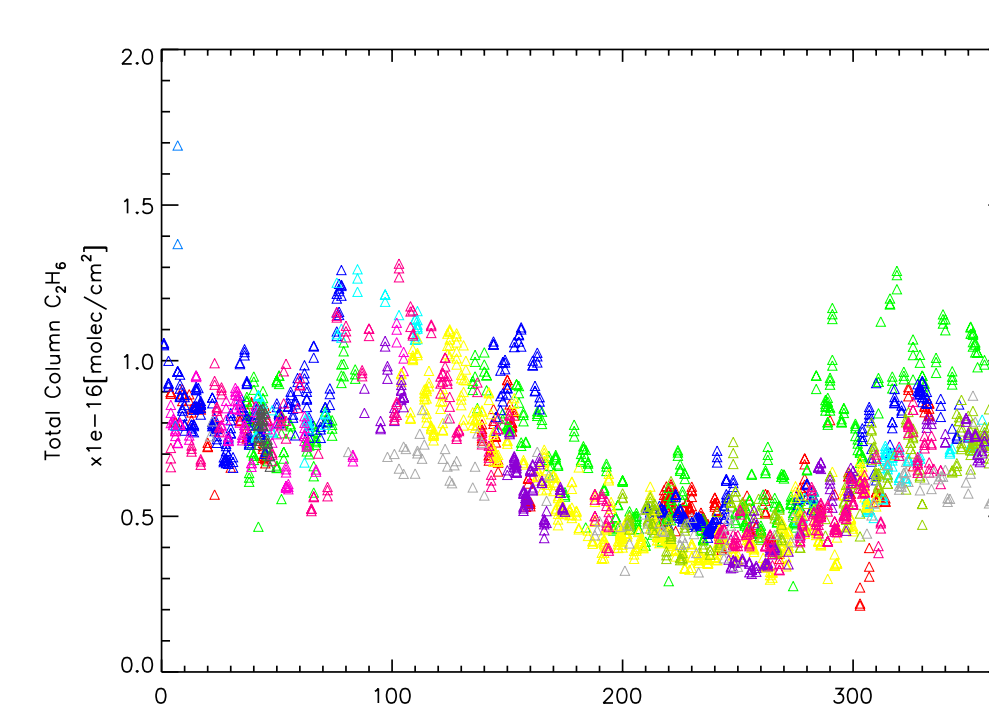


Long-term trend



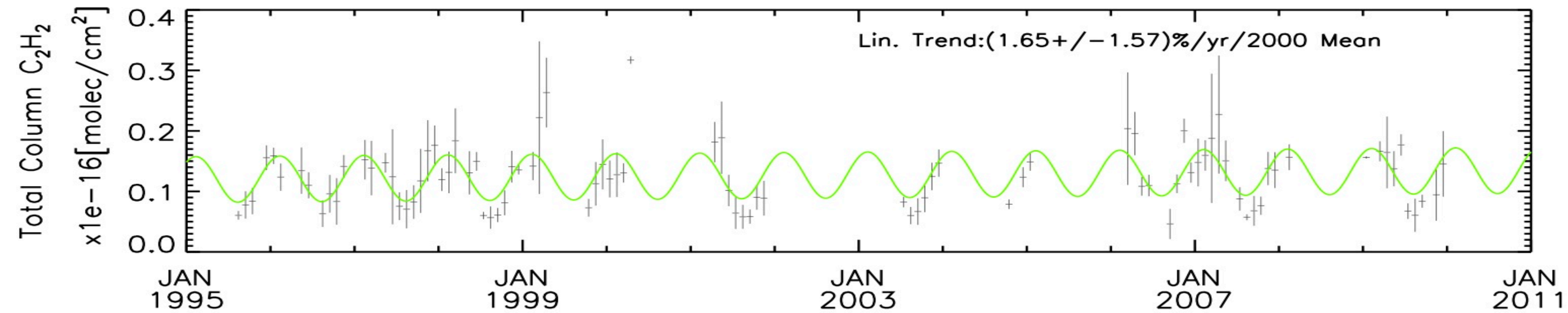
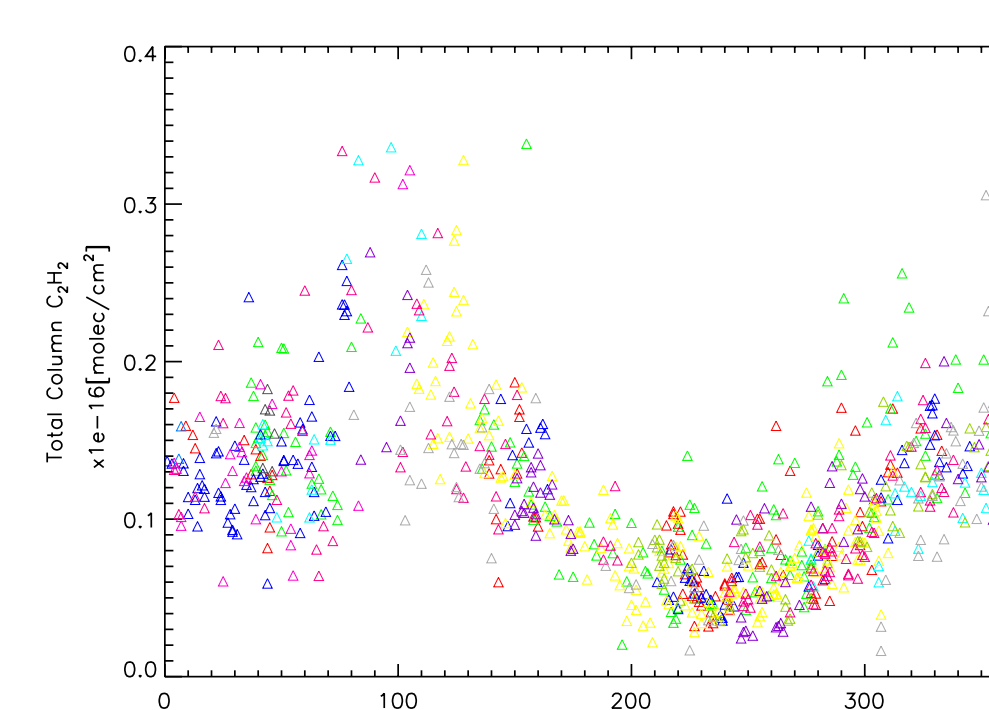
C₂H₆

Ethane is the most abundant non-methane hydrocarbon. It is emitted to the atmosphere through fossil fuel use and production, biofuel use and biomass burning. Like other hydrocarbons it is a precursor of tropospheric O_3 and CO. The main destruction of ethane is by OH oxidation. It has an average lifetime of about 2 months (20 days in summer and 160 days in winter). The seasonal cycle of ethane concentration (and the cycles of CO, C_2H_2) are controlled by the abundance of OH, with maximum ethane in winter and a minimum in summer. At Mauna Loa emission sources and inputs from transport are relatively constant. The long-term trend in C_2H_6 at Mauna Loa for the period from 1995 to 2009 is $-2.13 \pm 1.05\%$ /year.



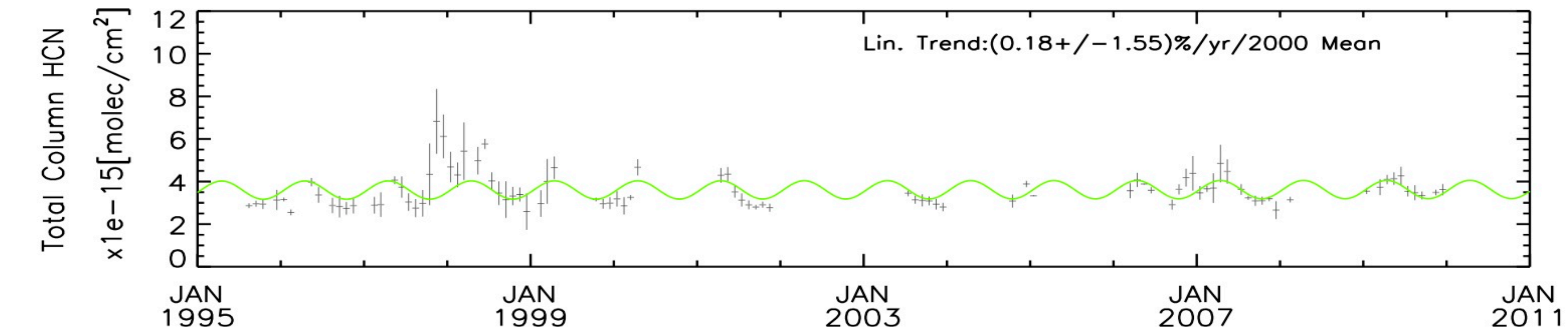
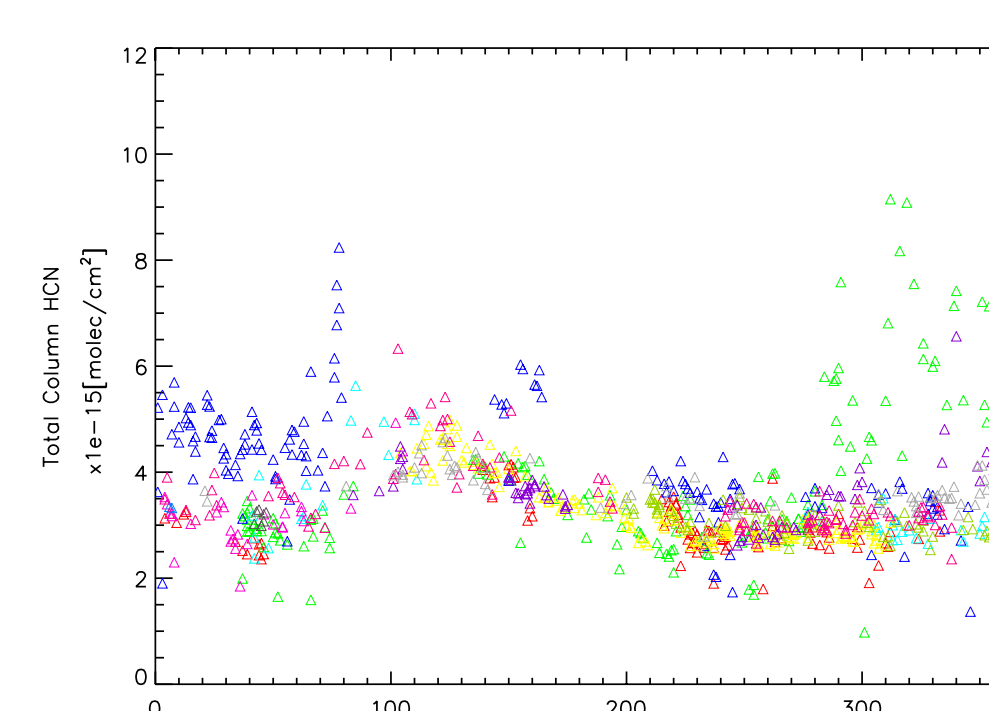
C₂H₂

Acetylene like ethane is a precursor of tropospheric O_3 . Tropospheric sources are through fossil fuel use and production, and biomass burning. The main destruction of acetylene is by OH oxidation. As for CO and C_2H_6 the phase of the seasonal cycle reflects the rate of reaction with OH, the faster the reaction the earlier the peak in winter and the more rapid the decline in spring [Goldstein *et al.*, *JGR*, **100**, 1995]. It has a lifetime of about 1 month. The long-term trend in C_2H_2 at Mauna Loa for the period from 1995 to 2009 is $1.65 \pm 1.57\%$ /year.



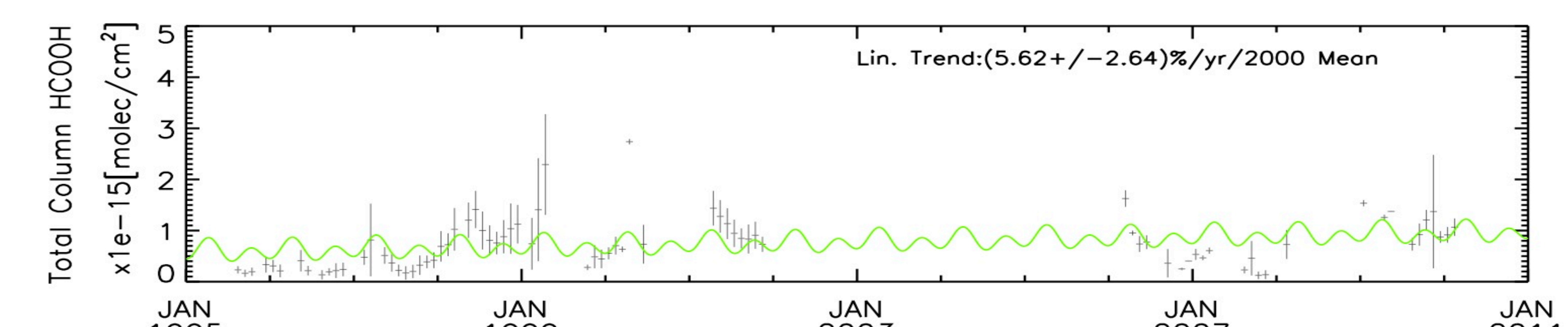
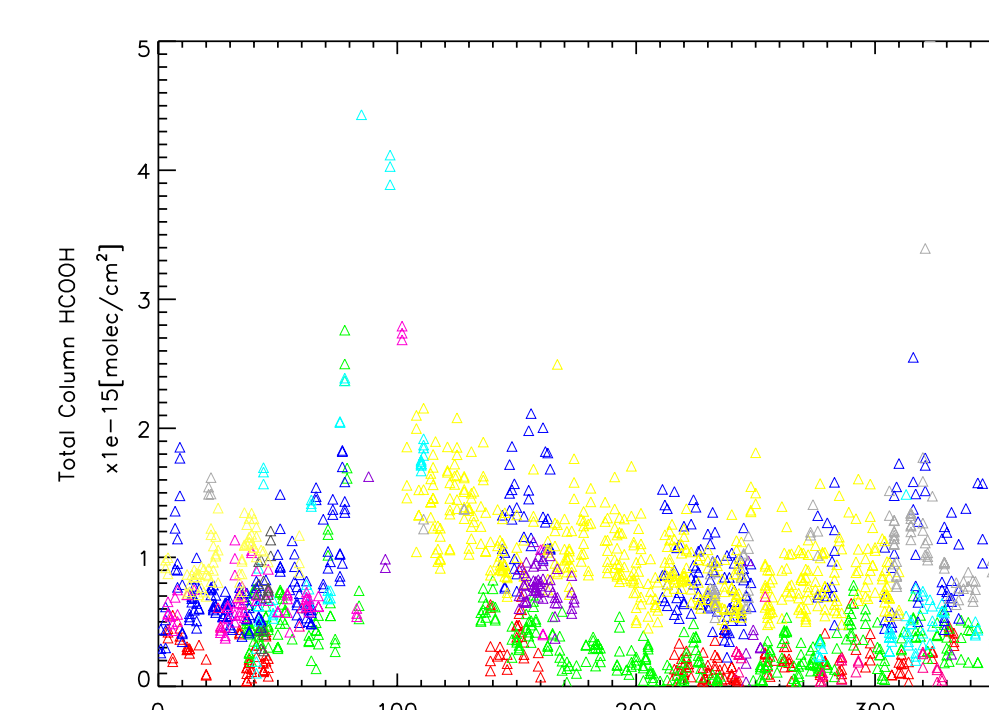
HCN

Hydrogen cyanide also is a precursor of tropospheric O_3 . The main source of HCN is biomass burning which accounts for the seasonal cycle that peaks in summer, even far from burning source regions. In addition to the destruction of HCN by OH and $\text{O}(^1\text{D})$ oxidation uptake of HCN in the ocean is a significant loss pathway. It is less reactive than CO , C_2H_6 and C_2H_2 and has a rather uncertain lifetime of 2-4 months near the surface and possibly a few years in the free atmosphere, thus making transport an important issue. The long-term trend in HCN at MLO for the period from 1999 to 2009 is $0.18 \pm 1.55\%$ /year.



HCOOH

Formic acid is one of the two most abundant organic acids in the atmosphere. Together with acetic acid they can constitute the predominant source of atmospheric acidity in remote regions, such as Thule. Carboxylic acids may account for a quarter of atmospheric non-methane hydrocarbons. It is highly soluble in water and one of the most abundant organic acids in rain. Tropospheric sources include fossil fuel burning emissions, alkene-ozone reactions and hydrocarbon oxidation. Formic acid is removed from the atmosphere primarily by the aqueous-phase oxidation in clouds, washout by rain or by dry deposition. Its lifetime against gas phase oxidation by OH is several weeks. In the boundary layer the lifetime of formic acid may be only a few days. The long-term trend in HCOOH at Mauna Loa for the period from 1995 to 2009 is $5.62 \pm 2.64\%$ /year.



O₃ (tropospheric)

Tropospheric ozone is a significant greenhouse gas, and considered a pollutant in the lower atmosphere. CO , NO_x and VOCs are precursors in the formation of ozone. As a powerful oxidizer it is involved in many chemical reactions in the troposphere. The long-term trend in tropospheric O_3 at Mauna Loa for the period from 1995 to 2009 is $2.76 \pm 1.12\%$ /year.

