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

James W. Hannigan, M.T. Coffey and Rebecca Batchelor
National Center for Atmospheric Research
Boulder, Colorado USA
Contact jamesw@ucar.edu

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 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.]

![Seasonal Cycle](image1)

**CO**
Carbon monoxide is the third most abundant carbon-containing gas in the atmosphere (after CO₂ and CH₄). Sources of CO are fossil fuel combustion, agricultural activities, and biomass burning. CO is a precursor of tropospheric O₃ and CO₂. The seasonal cycle 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 -2.13 ± 1.05 %/year.

![Long-term trend](image2)

**C₂H₆**
Ethane is the most abundant non-methane hydrocarbon. It is emitted to the atmosphere through fossil fuel use and production, biomass use and biomass burning. The main removal of ethane is by OH oxidation. As for CO and C₂H₄, the phase of the seasonal cycle reflects the rate of reaction with OH when the rate of reaction with NO is relatively constant. The long-term trend in C₂H₆ at Mauna Loa for the period from 1995 to 2009 is 2.76 ± 1.12 %/year.

**HCN**
Hydrogen cyanide is a precursor of tropospheric O₃. 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 O(1D) oxidation, uptake of HCN in the ocean is a significant loss pathway. It is less reactive than CO, C₂H₆, and C₂H₄ 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 1995 to 2009 is 0.18 ± 0.10 %/year.

**HCOOH**
Formic acid is one of the two most abundant organic acids in the atmosphere. Together with acetic acid they can constitute the predominate source of atmospheric acidity in remote regions, such as the Arctic. Carbonyl sulphides may account for a quarter of atmospheric non-methane hydrocarbons. It is highly volatile in water and one of the most abundant organic acids in rain. Tropospheric sources include fossil fuel burning emissions, biogenic-soil reactions, and hydrocarbon oxidation. Tropospheric acidity 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 ± 2.64 %/year.

**O₃** (tropospheric)
Tropospheric ozone is a significant greenhouse gas, and considered a pollutant in the lower atmosphere. CO, NOₓ 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 O₃ at Mauna Loa for the period from 1995 to 2009 is 2.76 ± 1.12 %/year.