NON-CO_2 CLIMATE GASES

I. INTRODUCTION

Human activities affect the abundance of many greenhouse gases (GHGs), other than CO_2, that also contribute directly or indirectly to anthropogenic climate forcing. Other non-radiative gases, such as carbon monoxide (CO), influence the abundance of GHGs. The contributions of non-CO_2 climate gases, including CO, in climate forcing are shown in Figure 1. Several of these gases, such as ozone (O_3), are short-lived and exhibit large spatial and temporal variability in the atmosphere. Understanding the production and loss processes that affect each gas and monitoring their abundances are essential to quantify and predict anthropogenic climate change.

Water vapor (H_2O) stands apart from the gases in Figure 1, even though it is a GHG. Water vapor, whose distribution in the atmosphere is highly variable, is considered to contribute primarily via feedbacks in the climate system because its atmospheric abundance responds to climate changes.

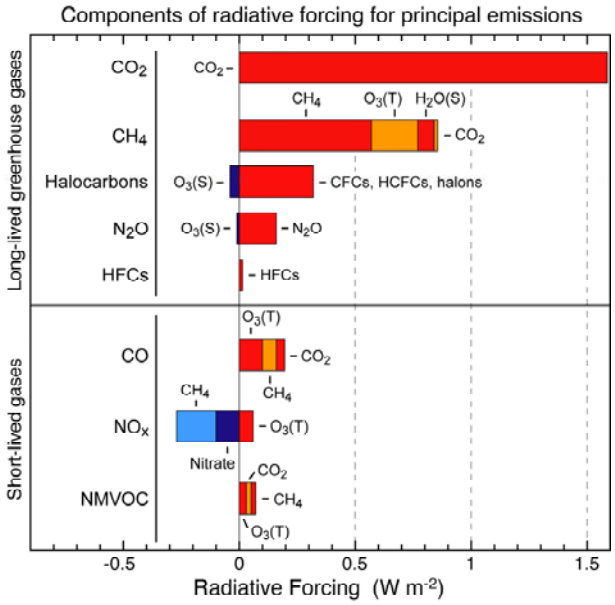

Figure 1. Components of Radiative Forcing (RF) for emissions of principal gases (1750 – 2005). (Adopted from the *IPCC Report* [2007]).

NOAA's Earth System Research Laboratory addresses climate change and climate change processes related to non-CO_2 gases, CO, and H_2O as a part of NOAA's Climate Goal by:

(i) monitoring these gases at and above the surface worldwide and from a variety of platforms,
(ii) comparing reported emissions with industrial inventories and/or modeled natural emissions,
(iii) using numerical models for radiative forcing calculations and gas-phase chemistry studies,
(iv) conducting laboratory studies of atmospheric chemical processes, and airborne and ground based field campaigns.

II. KEY ACHIEVEMENTS

• *Continuation of the time series of non-CO_2 GHG concentrations with measurements from a global station network.* Species include methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), sulfur hexafluoride (SF_6), chlorofluorocarbons (CFCs), halons, hydrochlorofluoro-carbons (HCFCs), and chlorine- and bromine-containing (halogenated) solvents (methyl chloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), bromo-chloromethane (CH_2BrCl),

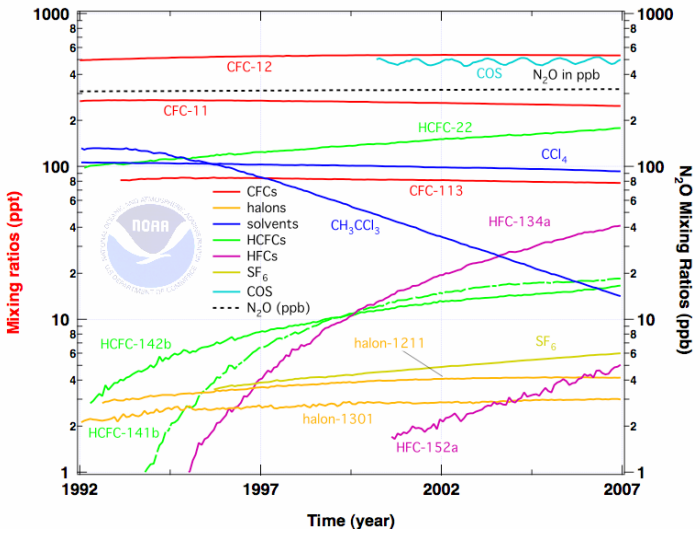

Figure 2 Time series of mixing ratios of non-CO_2 climate gases from NOAA ESRL observations.

etc.) and CO. The extremely high quality of these measurements is established and maintained with internal standards and intercomparisons. Recent time series results are shown in Figure 2. These data provided a part of the basis for accounting for and predicting climate change and stratospheric ozone abundances in the latest Intergovernmental Panel for Climate Change (IPCC) and UNEP/WMO 2006 Scientific Assessment of Stratospheric Ozone assessments, as well as the US Climate Change Science Program (CCSP) Synthesis and Assessment Product 2.4.

• *Continuation of the time series of ozonesonde measurements at three long-term, Northern Hemispheric stations.* Recent records of surface O_3 from U.S. and global background stations over the past 33 years from ESRL show a mixed picture with some locations with increases and others with little change [*Oltmans et al.,* 2006]. A recent NOAA/ESRL analysis of airborne measurements and ozonesonde data has observationally quantified the contributions of transport and local production of upper tropospheric ozone and has shown that upper tropospheric ozone increases due to lightning activity and the stability of the anticyclone over the southeastern US [*Cooper et al,* 2007].

• *Continuation of the time series of Boulder, Colorado, balloon-borne observations of water vapor.* The long-term water vapor record from Boulder balloon-sonde frost-point hygrometers has been reanalyzed, and bias corrections applied [*Scherer et al.,* 2007]. Stratospheric trends from the bias-corrected data set are reduced from those published previously, but are still greater than that attributable to the surface increases in methane.

• *Improved CO measurement calibration.* The calibration scale of CO has now accounted for the small drift in many of its primary calibration tanks. The improved dataset shows a slight decrease of CO mixing ratios in the Northern Hemisphere over the ~18 year period. Short-lived increases in CO growth rate during the El Niño years of 1997-98 and 2003-04 are attributed to drought and increased forest fire activity. In the Southern Hemisphere, CO mixing ratios show high interannual variability but no significant change during the period of observation.

• *Analysis of water vapor trend data.* A dramatic decrease in the input of water vapor into the stratosphere has been noted from satellite measurements at the end of 2000 [*Randel et al.,* 2006; *Rosenlof and Reid,* 2008] and possible dynamical mechanisms for that change proposed. An apparent increase in the zonally averaged Lagrangian upwelling circulation near the tropical tropopause associated with a drop in temperatures near the tropopause has been identified as the cause.

• *Studies related to the microphysics of water vapor in the upper troposphere and lower stratosphere.* A theoretical reanalysis was completed of the vapor pressure, molar heat capacity, and latent heat of vaporization of both ice and liquid water using previously collected data and using recent data on the molar heat capacity of supercooled water. Improved temperature dependent expressions for water vapor pressure at atmospheric conditions were derived [*Murphy and Koop,* 2005]. Another key theoretical/observational study demonstrated a sharp increase in relative humidity with respect to ice inside clouds at 202K and hypothesized a mechanism involving the presence of a new class of nitric acid containing ice particles [*Gao et al.,* 2004]. These studies may provide information essential for prediction of cirrus clouds, which are a key part of the climate system in the upper troposphere.

• *Acquisition of data for key non-CO_2 GHG in the upper troposphere and lower stratosphere (UT/LS) using instruments on board manned and unmanned aircraft.* NOAA/ESRL scientists from all four divisions participated in the 2006 NOAA Unmanned Aircraft Systems (UAS) Demonstration. NASA WB-57F high-altitude aircraft measurements were made on two missions to sample the tropical UT/LS. These data provide key constraints on the budget of non-CO_2 gases and the role of transport in controlling their atmospheric distribution.

• *Progress in studies of water vapor instrumentation for the upper troposphere and lower stratosphere.* A new, easier-to-operate, science-quality, *balloon-borne*, water-vapor sonde based

on the long deployed NOAA CMDL instrument has been developed and is being routinely deployed world wide [*Vömel et al.* 2007]. In addition, a new *airborne* water-vapor instrument has been developed for low (< 10 ppm) mixing ratios. NOAA/ESRL scientists have taken leadership roles in bringing atmospheric scientists together to address discrepancies in UT/LS water vapor measurements by different instruments.

• *Measurements of ground-level and vertical distributions of carbonyl sulfide (COS).* COS is a climate gas and a significant source gas for the stratospheric sulfate aerosol layer. COS has a strong seasonal cycle, just like that of CO_2, because it is assimilated by plants as is CO_2 during photosynthesis [*Montzka et al.,* 2006]. This finding will enable quantification of the terrestrial, gross primary production of CO_2 and the influence of the terrestrial biosphere on atmospheric CO_2.

• *Major intensive field campaigns have enabled characterization and quantification of tropospheric ozone.* Two major field campaigns, the Intercontinental Transport and Chemical Transformation (ITCT2004) and Gulf of Mexico Atmospheric Composition and Climate Study in 2006 produced a wealth of data whose interpretation enables better characterization of tropospheric ozone.

III. PAYOFFS

• Ground-based observations and trends in non-CO_2 GHGs have formed the basis for quantifying major components of anthropogenic climate forcing. Understanding the abundance and controlling processes of these components enables projections of future climate change. An unforeseen benefit of the Montreal Protocol was shown to be the cumulative reduction of ~8 Gt CO_2-equivalent yr^{-1} in climate forcing by 2010 compared to the first commitment goal of 2 Gt CO_2-equivalent yr^{-1} for the Kyoto Protocol [*Velders et al.,* 2007].
• Ozone observations, the derived trends, and process studies that included intensive field campaigns all help constrain how human activities are contributing to regional and global increases in ozone and improve predictive capabilities..
• Water vapor observations and the derived trends have constrained processes that control water vapor abundances in the upper troposphere and lower stratosphere. This enables better calculation of climate change via quantification of water vapor feedbacks and forcing via formation of cirrus clouds.

IV. FUTURE PLANS

NOAA/ESRL will continue the current approach of making long-term measurements of non-CO_2 climate gases, and CO and H_2O; undertaking theoretical studies of observational data to identify controlling processes and predictive capabilities; and striving to improve instrumentation and sampling strategies to address outstanding questions related to non-CO_2 GHGs.

• *Add important non-CO_2 climate gases (e.g., PFCs, NMVOCs) to the ESRL flask and in-situ gas-chromatograph halocarbon network. Develop an improved calibration system.*
• *Participate in a new global sampling strategy for non-CO_2 climate gases using the NCAR HIAPER aircraft: NSF HIaper Pole-to-Pole Observations of Greenhouse Gases (HIPPO).*
• *Provide regional estimates of North American emissions of CFCs, HCFCs, HFCs, and PFCs.*
• *Add regular water vapor profile measurements using balloon-borne cryogenic frostpoint hygrometers at polar and tropical locations.*
• *Make use of the longer-term ozonesonde and surface ozone measurements from the NOAA/ESRL tropospheric ozone-monitoring network to assess possible changes in tropospheric ozone and the implications for climate forcing.*

Publication Highlights

Cooper, O. R., et al., (2007), Evidence for a recurring eastern North America upper tropospheric ozone maximum during summer, *J. Geophys. Res.*, **112**, D23304, doi:10.1029/2007JD008710.

Gao, R. S., et al. (2004), Evidence that nitric acid increases relative humidity in low-temperature cirrus clouds, *Science*, **303(5657)**, 516-520.

IPCC Report, Forster, P., V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D.W. Fahey, J. Haywood, J. Lean, D.C. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz and R. Van Dorland (2007): Changes in Atmospheric Constituents and in Radiative Forcing. *In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA. (Conway, Dlugokencky, Elkins, Montzka, Reid, Rosenlof are contributing authors).

Montzka, S.A., P. Calvert, B. Hall, J.W. Elkins, P. Tans, and C. Sweeney (2007), On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO_2 , *J. Geophys. Res.*, **112**, D09302, doi:10.1029/2006JD07665.

Murphy, D. M., and T. Koop (2005), Review of the vapour pressures of ice and supercooled water for atmospheric applications, *Q. J. Royal Met. Soc.*, **131(608),** 1539-1565.

Oltmans, S.J., et al., (2006), Long-term changes in tropospheric ozone, *Atmos. Environ.*, **40**, doi:10.1016/j.atmosenv.2006.01.029, 3156-3173.

Randel W. J., F. Wu, H. Vömel, G. E. Nedoluha, and P. Forster (2006), Decreases in stratospheric water vapor after 2001: Links to changes in the tropical tropopause and the Brewer-Dobson circulation, J. Geophys. Res., 111, D12312, doi:10.1029/2005JD006744.

Rosenlof K.H. and G. C. Reid (2008) Trends in the temperature and water vapor content of the tropical lower stratosphere: The sea-surface connection, in press, *J. Geophys. Res.* Paper #2007JD009109.

Scherer M. et al. (2007) Trends and variability of midlatitude stratospheric water vapour deduced from the re-evaluated Boulder balloon series and HALOE, Atmos. Chem. Phys. Discuss., 7, 14511-14542, 2007 (accepted in ACP)

Velders, G. J. M., S. O. Andersen, J. S. Daniel, D. W. Fahey, and M. McFarland (2007), The importance of the Montreal Protocol in protecting climate, *PNAS*, **104(12),** doi/10.1073PNS.0610328104. 4814-4819.

Vömel, H., et al. (2007), Accuracy of tropospheric and stratospheric water vapor measurements by the cryogenic frost point hygrometer: Instrumental details and observations, *J. Geophys. Res.*, **112,** D08305, doi:10.1029/2006JD007224

WMO Report, Clerbaux, C., and D. Cunnold (Lead Authors), J. Anderson, P. Bernath, A. Engel, P.J. Fraser, E. Mahieu, A. Manning, J. Miller, S.A. Montzka, R. Prinn, S. Reimann, C.P. Rinsland, P. Simmonds, D. Verdonik, D. Wuebbles, Y. Yokouchi, (2007), Long-lived compounds, Chapter 2 in Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project—Report No. 50/, World Meteorological Organization, Geneva.