Final Report to the
National Aeronautics and Space Administration
Washington, DC 20546

Attention: Dr. Michael Kurylo, Manager
Upper Atmosphere Research Program
Office of Earth Science, Code YS

for
NASA Grant NAG5-3974
(NASA-Goddard Space Flight Center)

entitled
ADVANCED GLOBAL ATMOSPHERIC GASES EXPERIMENT (AGAGE):
MIT CONTRIBUTION

for the four year period
January 1, 1999 to October 31, 2003

Principal Investigator
Ronald G. Prinn, Massachusetts Institute of Technology
ACCOMPLISHMENTS OF NASA GRANT NAG5-3974

The accomplishments of the Advanced Global Atmospheric Gases Experiment (AGAGE) over the last 4 years have been substantial and documented in a large number of peer-reviewed publications and recorded in data publicly archived for the period June 1978-March 2003 at national and international data centers.

In the following sections we provide, for the 1999-2003 time period, a summary of selected recent research highlights, a complete listing of all central AGAGE publications, a review of AGAGE contributions to international and national assessments, and a list of other publications by the AGAGE team relevant to the project.

(1) RECENT (1999-2003) RESEARCH HIGHLIGHTS

In this section we present abstracts of papers representative of the large number of AGAGE-related papers listed later in Sections (2) and (5). Full references for these abstracts are provided in these two Sections.

A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, J. Geophys. Res., 2000


ABSTRACT. We describe in detail the instrumentation and calibrations used in the ALE, GAGE and AGAGE experiments and present a history of the majority of the anthropogenic ozone-depleting and climate-forcing gases in air based on these experiments. Beginning in 1978, these three successive automated high frequency in-situ experiments have documented the long-term behavior of the measured concentrations of these gases over the past twenty years, and show both the evolution of latitudinal gradients and the high frequency variability due to sources and circulation. We provide estimates of the long-term trends in total chlorine contained in long-lived halocarbons involved in ozone depletion. We summarize interpretations of these measurements using inverse methods to determine trace gas lifetimes and emissions. Finally, we provide a combined observational and modeled reconstruction of the evolution of chlorocarbons by latitude in the atmosphere over the past sixty years which can be used as boundary conditions for interpreting trapped air in glaciers and oceanic measurements of chlorocarbon tracers of the deep oceanic circulation. Some specific conclusions are: (a) International compliance with the Montreal Protocol is so far resulting in chlorofluorocarbon and chlorocarbon mole fractions comparable to target levels, (b) Mole fractions of total chlorine contained in long-lived halocarbons (CCl2F2, CCl3F, CH3CCl3, CCl4, CHClF2, CCl3FCClF2, CH2Cl, CH2Cl2, CHCl3, CCl3=CCl2) in the lower troposphere reached maximum values of about 3.6 ppb in 1993 and are beginning to slowly decrease in the global lower atmosphere, (c) The chlorofluorocarbons have atmospheric lifetimes consistent with destruction in the stratosphere being their principal removal mechanism, (d) Multi-annual variations in chlorofluorocarbon and chlorocarbon emissions deduced from ALE/GAGE/AGAGE data are consistent approximately with variations estimated independently from industrial production and sales data where available (CCl2F2 (CFC-12) and CCl3FCClF2 (CFC-113) show the greatest discrepancies), (e) The mole fractions of the hydrochlorofluorocarbons and
hydrofluorocarbons, which are replacing the regulated halocarbons, are rising very rapidly in the atmosphere but, with the exception of the much longer manufactured CHClF₂ (HCFC-22), they are not yet at levels sufficient to contribute significantly to atmospheric chlorine loading. These replacement species could in the future provide independent estimates of the global weighted-average OH concentration provided their industrial emissions are accurately documented. (f) In the future, analysis of pollution events measured using high frequency in-situ measurements of chlorofluorocarbons and their replacements may enable emission estimates at the regional level which, together with industrial end-use data, are of sufficient accuracy to be capable of identifying regional non-compliance with the Montreal Protocol.


**Abstract.** The hydroxyl radical (OH) is the dominant oxidizing chemical in the atmosphere. It destroys most air pollutants and many gases involved in ozone depletion and the greenhouse effect. Global measurements of 1,1,1-trichloroethane (CH₃CCl₃, methyl chloroform) provide an accurate method for determining the global and hemispheric behavior of OH. Measurements show that CH₃CCl₃ levels rose steadily from 1978 to reach a maximum in 1992 and then decreased rapidly to levels in 2000 that were lower than the levels when measurements began in 1978. Analysis of these observations shows that global OH levels were growing between 1978 and 1988, but the growth rate was decreasing at a rate of 0.23 ± 0.18% year⁻¹, so that OH levels began declining after 1988. Overall, the global average OH trend between 1978 and 2000 was −0.64 ± 0.60% year⁻¹. These variations imply important and unexpected gaps in current understanding of the capability of the atmosphere to cleanse itself. [These conclusions depend on the validity of industry estimates of emissions- see Section 9.3 for further discussion.]


**Abstract.** Continuous measurements of methane since 1986 at the GAGE/AGAGE surface sites are described. The precisions range from approximately 10 ppb at Mace Head, Ireland during GAGE to better than 2 ppb at Cape Grim, Tasmania during AGAGE (i.e. since 1993). The measurements exhibit good agreement with coincident measurements of air samples from the same locations analyzed by CMDL except for differences of approximately 5 ppb before 1989 (GAGE lower) and about 4 ppb from 1991 to 1995 (GAGE higher). These results are obtained before applying a factor of 1.0119 to the GAGE/AGAGE values to place them on the Tohoku University scale. The measurements combined with a 12 box atmospheric model and an assumed atmospheric lifetime of 9.1 years indicates net annual emissions (emissions - soil sinks) of 545 Tg CH₄ with a variability of only ±20 Tg from 1985 to 1997 but an increase in the emissions in 1998 of 37 ±10 Tg. The effect of OH changes inferred in Prinn et al. (2001) is to increase the estimated methane emissions by approximately 20 Tg in the mid-1980s and to reduce them by 20 Tg in 1997 and by more thereafter. Using a 2D, 12 box model with transport constrained by the GAGE/AGAGE chlorofluorocarbon measurements, we calculate that the proportion of the emissions coming from the Northern Hemisphere is between 73 and 81%, depending on the OH distribution used. However this result includes an adjustment of 5% derived from a simulation of the 2D estimation procedure using the 3D MOZART model. This adjustment is needed because of the very different spatial emission distributions of the chlorofluorocarbons and methane which makes chlorofluorocarbon derived transport rates
inaccurate for the 2D simulation of methane. The 2D model combined with the annual cycle in OH from Spivakovsky et al. (2000) provides an acceptable fit to the observed 12 month cycles in methane. The trend in the amplitude of the annual cycle of methane at Cape Grim is used to infer a trend in OH in 30-90°S of 0% ± 5%/decade from 1985 to 2000, in qualitative agreement with Prinn et al. (2001) for the Southern Hemisphere.

Continuous high frequency observations of hydrogen at the Mace Head baseline atmospheric monitoring station over the 1994-1998 period, J. Geophys. Res., 2000


Abstract. Continuous high frequency (every 40 minutes) automatic measurements of hydrogen have been made at the Mace Head atmospheric research station on the Atlantic Ocean coast of Ireland throughout 1994-1998. These observations represent one of the most comprehensive in-situ records of a trace gas that has received comparatively little attention. Individual measurements have been sorted by four independent methods to separate clean, maritime air masses from regionally polluted European air masses. Hydrogen concentrations in mid-latitude Northern Hemisphere baseline air show a distinct seasonal cycle with highest concentrations during spring and lowest concentrations during late autumn, with a peak-to-trough amplitude of 38 ± 6 ppb, averaged over the observed seasonal cycles from 1994 to 1998. The mean hydrogen concentration in mid-latitude northern hemisphere baseline air on 1st January 1995 was estimated as 496.5 ppb with an upwards trend of 1.2 ± 0.8 ppb yr⁻¹. Evidence has also been obtained for European pollution sources with source strength of about 0.8 Tg yr⁻¹ and for deposition of hydrogen to soils. The observation of slightly elevated hydrogen concentrations relative to baseline levels in tropical maritime air masses points to a latitudinal gradient in hydrogen with higher concentrations in lower latitudes of the Northern Hemisphere and in the Southern Hemisphere. This is confirmed by comparable hydrogen observations at Cape Grim, Tasmania, which are consistently higher than measurements recorded at Mace Head. Mean hemispheric concentrations of 504 and 520 ppb have been estimated for the northern and southern hemispheres, respectively, for 1st January 1996, corresponding to a total atmospheric hydrogen burden of 182 Tg.


Abstract. Measurements of atmospheric chloroform (CHCl₃) by in situ gas chromatography using electron capture detection are reported from the Advanced Global Atmospheric Gases Experiment (AGAGE) network of atmospheric research stations. They are some of the most comprehensive in situ, high-frequency measurements to be reported for CHCl₃ and provide valuable information not only on clean "baseline" mixing ratios but also on local and regional sources. Emissions from these sources cause substantial periodic increases in CHCl₃ concentrations above their baseline levels, which can be used to identify source strengths. This is particularly the case for measurements made at Mace Head, Ireland. Furthermore, these local sources of CHCl₃ emissions are significant in relation to current estimates of global emissions and illustrate that the understanding of competing sources and sinks of CHCl₃ is still fragmentary. These observations also show that CHCl₃ has a very pronounced seasonal cycle with a summer minimum and winter maximum presumably resulting from enhanced destruction by OH in the summer. The amplitude of the cycle is dependent on sampling location. Over the 57 months of in situ measurements a global average baseline concentration of 8.9±0.1 ppt was determined with no appreciable trend in the baseline detected.
European greenhouse gas emissions estimated from continuous atmospheric measurements and radon 222 at Mace Head, Ireland, *J. Geophys. Res.*, 2000

S. Biraud, P. Ciais, M. Ramonet, P. Simmonds, V. Kazan, P. Monfrais, S. O'Doherty, T. G. Spain, and S. G. Jennings

**Abstract.** Flux estimates of CO$_2$, CH$_4$, N$_2$O, and CFCs over western Europe have been inferred from continuous atmospheric records of these species at the atmospheric research station of Mace Head, Ireland. We use radon (222Rn) which has a fairly uniform source over continents as a reference compound to estimate unknown sources of other species. The correlation between each species and 222Rn is calculated for a suite of synoptic events that have been selected in the Mace Head record over the period 1996/97. In the following, we describe the method and its uncertainties, and we establish data selection criteria that minimize the influence of local sources over Ireland, in the vicinity of the station, in order to select synoptic events originating from western Europe. We estimate western European flux densities of 45-30 $\times\ 10^3$ kg C km$^{-2}$ month$^{-1}$ during wintertime for CO$_2$, of 4.8-3.5 $\times\ 10^3$ kg CH$_4$ km$^{-2}$ yr$^{-1}$, 475-330 kg N$_2$O km$^{-2}$ yr$^{-1}$, 2.5-1.8 kg CFC-11 km$^{-2}$ yr$^{-1}$ for CFC-11, and 4.2-2.9 kg CFC-12 km$^{-2}$ yr$^{-1}$ for CFC-12. Our estimates are independent, although in good agreement with those produced by inventories, except for CFC-11 where our estimate is much lower than the inventory.

Estimating source regions of European emissions of trace gases from observations at Mace Head, *Atmos. Environ.*, 2001

D. B. Ryall, R. G. Derwent, A. J. Manning, P. G. Simmonds and S. O'Doherty

**Abstract.** A technique is described for identifying probable source locations for a range of greenhouse and ozone-depleting trace gases from the long term measurements made at Mace Head, Ireland. The Met. Office's dispersion model NAME is used to predict concentrations at Mace Head from all possible sources in Europe, then source regions identified as those which consistently lead to elevated concentrations at Mace Head. Estimates of European emissions and their distribution are presented for a number of trace gases for the period 1995-1998. Estimated emission patterns are realistic, given the nature and varied applications of the species considered. The results indicate that whilst there are limitations, useful information about source distribution can be extracted from continuous measurements at a remote site. It is probable that much improved estimates could be derived if observations were available from a number of sites. The ability to assess emissions has obvious implications in monitoring compliance with internationally agreed quota and protocols.

(2) **MAJOR PUBLICATIONS**

The central accomplishments of the ALE/GAGE/AGAGE program from 1999 to 2003 are documented in the following journal publications and theses. Other relevant 1999-2003 publications are given in Section (5).


Greally, B.R., Development of an analytical system for the determination of highly fluorinated compounds in air samples, *Ph.D Thesis*, University of Bristol, Bristol, United Kingdom, 363 pp., 1999.


Midgley P.M. and A. McCulloch, *Production, Sales and Emissions of Halocarbons from Industrial Sources*, Ch. 6 of The Handbook of Environmental Chemistry Vol 4. Part E,


(3) INTERNATIONAL ASSESSMENTS (1999-2003)

ALE/GAGE/AGAGE measurements and derived lifetimes, OH concentrations, and emissions are of considerable policy significance and are widely used in international ozone layer and climate assessments. In the 1999-2003 time frame, AGAGE team members have specifically contributed to the following major international assessments:


4) NATIONAL ASSESSMENTS (1999-2003)

AGAGE data and/or AGAGE scientists have also contributed to various national assessments.


The Mace Head, Ireland observations coupled with the UK Meteorological Office particle dispersion "NAME" model have also been used to provide greenhouse gas inventories for the Irish Government.

The following papers use AGAGE Cape Grim data and/or involve AGAGE scientists to assess Australian and New Zealand environmental issues:


Here we list other publications in the 1999-2003 time period supported by, and/or relevant to, AGAGE. These include technique papers, program reports, meeting abstracts, and advanced theoretical analyses of AGAGE data:


