

Advanced Global Atmospheric Gases Experiment (AGAGE)

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INTRODUCTION

In this global network program continuous high-frequency gas chromatographic measurements of biogenic and anthropogenic gases are carried out at globally distributed sites in order to quantitatively determine the source and sink strengths and circulation of a large number of chemically and radiatively important long-lived gases. The program that started in 1978 is conveniently divided into three parts associated with three changes in instrumentation: the Atmospheric Lifetime Experiment (ALE), the Global Atmospheric Gases Experiment (GAGE) and the Advanced Global Atmospheric Gases Experiment (AGAGE).

AGAGE began during the 1993-1996 time period. AGAGE, which continues to the present, has two instrumental components. First, a highly improved gas chromatographic system measures five biogenic/anthropogenic gases (CH_4 , N_2O , CHCl_3 , CO , and H_2) and five anthropogenic gases (CCl_3F , CCl_2F_2 , CH_3CCl_3 , $\text{CCl}_2\text{FCClF}_2$, and CCl_4) [Prinn *et al.*, 1995; Fraser *et al.*, 1996; Cunnold *et al.*, 1997; Simmonds *et al.*, 1998a]. Each species is measured 36 times per day using an electron capture detector (ECD), flame ionization detector (FID), or mercuric oxide reduction detector (MRD); the latter detector is for CO and H_2 and is currently present at only two of the stations, Mace Head, Ireland, and Cape Grim, Tasmania.

Second, a new gas chromatographic-mass spectrometric system (GC-MS) began measuring a wide range of hydrochlorofluorocarbons and hydrofluorocarbons (CH_2FCF_3 (HFC-134a), $\text{CH}_3\text{CCl}_2\text{F}$ (HCFC-141b), CH_3CClF_2 (HCFC-142b), etc.) [Simmonds *et al.*, 1998b] that are now serving as interim or permanent alternatives to the chlorofluorocarbons and other long-lived halocarbons regulated by the Montreal Protocol [UNEP, 1996]. Also measured by the GC-MS system are the methyl halides (CH_3Cl , CH_3Br , CH_3I) and the halons (CBrF_3 , CBrClF_2). AGAGE also included development and use of new, much more accurate absolute calibrations for most of the measured gases.

The ALE, GAGE, and AGAGE stations have been located in five globally distributed localities: (a) Ireland: first at Adrigole, 52°N, 10°W (1978-1983), then at Mace Head, 53°N, 10°W (1987-present); (b) USA West Coast: first at Cape Meares, Oregon, 45°N, 124°W (1979-1989), then at Trinidad Head, California, 41°N, 124°W (1995-present); (c) Ragged Point,

Barbados, 13°N, 59°W (1978-present); (d) Cape Matatula, American Samoa, 14°S, 171°W (1978-present); (e) Cape Grim, Tasmania, 41°S, 145°E (1978-present).

The AGAGE operation at Samoa has significant added value because it enables a direct intercomparison with the similar real-time measurements (and also with the flask measurements) by CMDL. This intercomparison has already aided us in determining the net effect of calibration and instrumental differences on the measurements by each group, so that the data from both the AGAGE and CMDL networks can be utilized in combination by theoreticians to investigate chemical and meteorological phenomena.

RECENT PROGRESS

Accomplishments over the entire period from 1978 through the present have recently been published [Prinn *et al.*, 2000]. In the publication, the instrumentation and calibrations used in the ALE, GAGE and AGAGE experiments and a history of the majority of the anthropogenic ozone-depleting and climate-forcing gases in air, based on these experiments, is described in detail. 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 20 years and show both the evolution of latitudinal gradients and the high frequency variability from sources and circulation. These experiments enable estimation of the long-term trends in total chlorine contained in long-lived halocarbons involved in ozone depletion, and these measurements are summarized using inverse methods to determine trace gas lifetimes and emissions. Finally, a combined observational and modeled reconstruction of the evolution of chlorocarbons by latitude in the atmosphere over the past 60 years is provided that can be used as boundary conditions for interpreting trapped air in glaciers and oceanic measurements of chlorocarbon tracers of the deep oceanic circulation.

The ALE/GAGE/AGAGE data are available through the U.S. Department of Energy (DOE) CDIAC World Data Center (e-mail to: cpd@ornl.gov, Dataset No. DB-1001). Some specific conclusions from the data are [Prinn *et al.*, 2000]:

(1) For ozone-depleting gases, ALE/GAGE/AGAGE and other measurements show: (a) Major changes in the rates of accumulation of many ozone-depleting gases occurred in the

1990s. Mole fractions of CH_3CCl_3 , CCl_4 , and CCl_3F have been decreasing for several years; mole fractions of $\text{CCl}_2\text{FCClF}_2$ reached approximately constant levels and are now beginning to decrease very slowly; the rate of accumulation of CCl_2F_2 has slowed significantly. However, mole fractions of N_2O continue to steadily increase. The latitudinal gradients of CCl_3F , CCl_2F_2 , $\text{CCl}_2\text{FCClF}_2$, CH_3CCl_3 and to a lesser extent, CCl_4 , are essentially zero, or are rapidly approaching zero, consistent with rapid decreases in their largely northern hemispheric emissions [see also Fraser *et al.*, 1996; Simmonds *et al.*, 1998a; Prinn *et al.*, 1995]. (b) International compliance with the Montreal Protocol is so far resulting in chlorofluorocarbon and chlorocarbon mole fractions equal to or lower than target levels. (c) Levels of total chlorine contained in 10 dominant halocarbons in the global lower troposphere have apparently reached maximum values of about 3.6 ppb and are beginning to decrease slowly (to about 3.5 ppb in 1997). This decrease is driven largely by declines in CH_3CCl_3 and to a lesser extent, CCl_4 [see also Cunnold *et al.*, 1997; Prinn *et al.*, 1999; Kurylo *et al.*, 1999].

(2) Optimal estimations using global ALE/GAGE/AGAGE measurements and atmospheric chemical models show: (a) The chlorofluorocarbons have atmospheric lifetimes consistent with destruction in the stratosphere being their principal removal mechanism. (b) Estimation of the lifetime of CH_3CCl_3 continues to provide an accurate determination of the weighted-average global OH concentration, but the rapidly decreasing mole fractions of CH_3CCl_3 will ultimately limit its usefulness for this purpose. (c) Multi-annual variations in chlorofluorocarbon and chlorocarbon emissions are consistent approximately with variations estimated independently from industrial production and sales data where available ($\text{CCl}_2\text{FCClF}_2$ and CCl_2F_2 are exceptions).

(3) The mole fractions of the major hydrochlorofluorocarbons and hydrofluorocarbons that are replacing the regulated halocarbons are rising rapidly in the atmosphere (specifically in the 1994 to 1998 time period at rates of about 44% per year for CH_2FCF_3 , 13% per year for CH_3CClF_2 , and 28% per year for $\text{CH}_3\text{CCl}_2\text{F}$ at Mace Head, Ireland). With the exception of CHClF_2 , which was in use well before the latter three species, they are not yet at levels to significantly contribute to atmospheric chlorine loading [see also Miller *et al.*, 1998; Simmonds *et al.*, 1998b]. In the future, these replacement species could provide independent estimates of the global-weighted average OH concentration provided their industrial emissions are more accurately documented.

(4) The current rapidly changing magnitudes and geographical locations of emissions of chlorocarbons and chlorofluorocarbons may mandate a more dense measurement network than provided presently by AGAGE alone in order to obtain accurate solutions to inverse problems involving regional emissions and lifetime estimation; at a minimum, the data from all existing networks (ALE/GAGE/AGAGE, CMDL, etc.) should be carefully intercalibrated, so they can be utilized to better compute global and regional average concentrations.

(5) 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 that are sufficiently accurate to be used for identifying regional noncompliance with the Montreal Protocol [see also Derwent *et al.*, 1998a, b].

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