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CLIMATE CHANGE STUDIES OF IMPORTANT TRACE GASES

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ABSTRACT

Airborne gas chromatographs (GCs) make precise, well calibrated, and automated measurements of many trace gases that influence climate forcing, stratospheric ozone depletion, and air quality. The detection limits for some gases (e.g. SF_6) are as low as 0.1 parts-per-trillion (ppt, 1 x 10^{-12}). The sampling frequency varies from 1 to 6 minutes depending on the number and types of trace gases measured on each channel. The addition of a mass selective detector-gas chromatograph (MSD-GC) channel has enabled measurements of new molecules important to atmospheric chemistry and transport studies including organic nitrates, hydrocarbons (HC), hydrofluorocarbons (HFCs), and hydrochlorofluorocarbons (HCFCs) on aircraft platforms. The incorporation of an airborne gas chromatograph in the existing upper deck payload on SOFIA will improve the calibration and validation of instruments on NASA's Aura satellite and provide valuable tracer information for atmospheric models.

INTRODUCTION

The Stratospheric Observatory for Infrared Astronomy (SOFIA) is a modified Boeing 747 research plane that has an astronomical observatory for infrared and submillimeter astronomy. It is an airborne observatory projected to fly as much as 960 hours/year for 20 years. This translates into two eight flights of SOFIA each week. At the beginning, these flights will mostly be out of Moffett Field, California. SOFIA will primarily sample the tropopause region of the Earth atmosphere at cruise altitude, and initially include many vertical profiles over Northern California. NOAA/CMDL has a new baseline observatory in that region at Trinidad Head, California. The upper deck payload of SOFIA may have opportunities to operate atmospheric instruments that support some of the Earth Science goals of NASA and the Strategic Plan of NOAA. This platform would be ideal for long-term trace gas monitoring and improving our understanding of the chemistry and transport in the upper troposphere and lower stratosphere (UT/LS). We are proposing to operate one of our automate, NASA-supported, airborne GCs to measure important trace gases involved in future climate change issues (Figure 1).

Whole air samplers (WAS) have been long used to fill many canisters on flights and have a big advantage that many trace gases can be analyzed on different laboratory instruments [Heidt et al., 1989; Blake 2004]. In situ GCs can sample more frequently than a WAS, and the GC typically weighs less and is more compact. Flask samples are generally integrated over periods of minutes (distances ≥10 km) whereas the in situ GC integrates samples in injection loops for only a few seconds. Air samples collected in flasks may also be compromised by decay, adsorption, or growth of some trace gases (e.g. selected halocarbons and HCs) during storage. One other major advantage of the in situ GCs is that the data are available faster than those taken with flasks, and can be viewed in near-real time.

Trace gases are involved in three very important environmental issues facing mankind in the future, including climate forcing by greenhouse gases (carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), chlorofluorocarbons (CFCs), sulfur hexafluoride (SF_6), HFCs, etc.), stratospheric ozone depletion (CFCs, halons, chlorinated solvents, HCFCs, and methyl halides including methyl bromide or CH_3Br, methyl chloride or CH_3Cl, methyl iodide or CH_3I), and air quality (Peroxy Acetyl Nitrate or PAN, CO, HCs).

Fig.1. PANTHER instrument in front of Fred Moore (left) and Geoff Dutton (right) of NOAA/CMDL/CIRES on a NASA DC-8 test flight on December 19, 2002 for the SAGE III Ozone Validation Experiment 2 (SOLVE-2) airborne campaign.

UNIQUE SCIENTIFIC OPPORTUNITIES FOR ATMOSPHERIC SCIENCES

Monitoring the trace gas mixing ratios in the UT/LS could help resolve some of the following atmospheric science questions:

1. Trace gas abundance relationships (Figure 2) at the tropopause can be used to estimate the stratospheric lifetimes and in some cases the atmospheric lifetimes of source gases [Volk et al., 1997].
2. Observations of Asian air pollution as it makes its way eastward at higher altitudes across the Pacific Ocean and the United States are possible with the SOFIA aircraft. PAN, CO_2, and CO would provide useful information on the transport and chemistry of gases involved in air quality.
3. Correlative comparison studies with trace gas measurements on NASA's new Aura (Latin for "breeze") satellite. The instruments on Aura will make measurements of the long-lived source gases including N_2O, CH_4, CFC-11, CFC-12, and CO, which are all measured by our airborne GCs.
4. Develop climatologies of important trace gases like SF_6. We have a good understanding of the manmade emission history of the gas from it use in electrical power transformers and switchgear. Measurements of SF_6 above the tropopause permit estimations of the elapsed time since air masses entered the stratosphere (i.e. mean ages) by relating the stratospheric SF_6 mixing ratio to those at the surface, where this is in strong, nearly linear growth (0.24 ppt yr^{-1} or 5% yr^{-1}). Comparisons of the measured atmospheric distributions of trace gases like SF_6 in the atmosphere to those simulated by General Circulation Models (GCMs) are important tests for accessing model transport. The goal is to develop better models for predicting climate change driven by the more-biologically active greenhouse gases like CO_2, N_2O, and CH_4.
5. Do the short-lived halocarbons like bromoform ($CHBr_3$); chloroform ($CHCl_3$), etc. enter the tropical tropospause and contribute to ozone depletion? While the stratospheric halogen burden contributed by regulated source gases (CFCs, methyl bromide, chlorinated solvents and halons) are either decreasing or leveling off, contributions by short-lived bromine gases (lifetime<<1 year) could be increasing due to climate change and/or manmade contributions. Short-lived brominated source gases are especially of great interest because bromine is 45 times more effective than chlorine at destroying

TABLE 1
MOLECULES MEASURED BY NOAA/CMDL USING GC-MSD

Trace Gas Molecule	Formula	Monitored Ion (m/e)
GC/MSD system EI mode*:		
Acetone	$CH_3C(O)CH_3$	58
Benzene	C_6H_6	78
Bromoform	$CHBr_3$	173
Bromodichloromethane	$CHBrCl_2$	129
Carbon Tetrachloride	CCl_4	117&119
Carbonyl Sulfide	COS	60
CFC-11	CCl_3F	101&103
CFC-12	CCl_2F_2	85
CFC-113	CCl_3CF_3	103
CFC-114 & 114a	$C_2Cl_2F_4$	135
Chlorobromomethane	CH_2BrCl	130
Chloroform	$CHCl_3$	83
Chloroiodomethane	CH_2ICl	176
Chlorodibromomethane	$CHBr_2Cl$	129
Dibromomethane	CH_2Br_2	174
Diiodomethane	CH_2I_2	268
Ethyl Chloride	C_2H_5Cl	64
Halon-1211	$CBrClF_2$	85
HCFC-22	$CHClF_2$	51
HCFC-141b	$C_2H_3Cl_2F$	81
HCFC-142b	$C_2H_3ClF_2$	65
HFC-134a	CH_2FCF_3	83
Isoprene	$H_2C=C(CH_3)CH=CH_2$	67
Methyl Bromide	CH_3Br	96, 94; 96
Methyl Chloride	CH_3Cl	50&52
Methyl Iodide	CH_3I	142
Methyl Nitrate	CH_3ONO_2	46
Methyl Chloroform	CH_3CCl_3	97&61; 97 & 99
Methylene Chloride	CH_2Cl_2	49
Perchloroethylene	C_2Cl_4	166
Trichloroethylene	C_2HCl_3	130
GC/MSD system NICI mode*:		
Peroxyacetyl Nitrate (PAN)	$CH_3COO_2NO_2$	62
Peroxypropionyl Nitrate (PPN)	$CH_3CH_2C(O)OONO_2$	62

*m/e is mass: charge. EI is the more common electron ionization mode. NICI is the negative ion chemical ionization.

stratospheric ozone. There is also evidence that more inorganic bromine (BrO, etc.) is in the stratosphere than we can explain from the long-lived bromine source gases (CH_3Br and halons [Wamsley et al, 1998].

Scientific results derived from our airborne GCs have appeared in major assessments of climate forcing [IPCC 2001] and stratospheric ozone depletion [WMO 1998]. We have developed a time history (1991-2004) for many of trace gases and budget species in different altitude ranges. We continue to annually monitor the distributions of seven trace gases in the lower and middle stratosphere during September/October balloon flights up to 32 km from Ft. Sumner, New Mexico [Moore et al., 2003]. One advantage of our measurement program is that our airborne, oceanic, and ground station measurements are on the same calibration scales, and we have the ability to make new standards when required.

POTENTIAL CANDIDATE INSTRUMENTS FOR SOFIA

There exist two NOAA airborne gas chromatographs that could be perfect additions to the existing SOFIA astronomical payload. Both have flown extensively on NASA and other platforms.

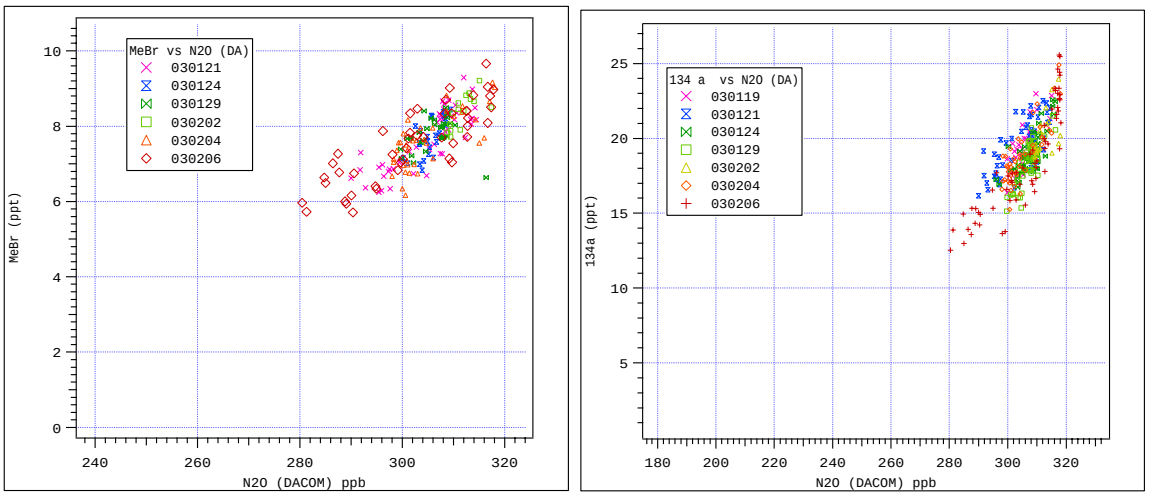

Fig. 2 CH_3Br (MeBr) (left) and HFC-134a (right) in parts-per-trillion (ppt) versus N_2O from DACOM (NASA Langley tunable diode spectrometer, preliminary data) in parts-per-billion (ppb) during SOLVE-2 airborne campaign in January-February 2003. Individual flights for each symbol use YYMMDD for date.

Calibration checks are done routinely during flights, as well zero air injections to test for pump and instrument contamination.

The **Airborne Chromatograph for Atmospheric Trace Species (ACATS-IV)** has flown on the NASA ER-2 high altitude aircraft and University of North Dakota Citation small jet aircraft. It also has completed two trips from Moscow to Khabarovsk on the Trans-Siberian Railway in July 2001 and March 2004 to monitor the expected decline in Russian emissions of halocarbons mandated by the Montreal Protocol [Hurst et al., 2004]. ACATS-IV has four electron capture detectors-gas chromatographic (ECD-GC) channels in a compact packing weighing ~50 kg, and occupying 49x84x33 cm [Elkins et al., 1996; Romashkin et al., 2001]. It draws 1kW at startup and 500 W during standards operations, mostly as 110VAC at 400 Hz and 28 VDC. Twelve trace gases are now measured: N_2O, SF_6, CFC-12 (CCl_2F_2), and halon-1211 ($CBrClF_2$) every 70 seconds, and CFC-11 (CCl_3F), CFC-113 ($CClF_2$-CCl_2F), chloroform ($CHCl_3$), methyl chloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), hydrogen (H_2), CH_4, and CO every 140 seconds. N_2O and the chlorine and bromine containing compounds destroy ozone with a range of efficiencies. All of the measured gases are greenhouse gases, except for CO and H_2, which are involved in OH chemistry. A similar instrument of this type is the Lightweight Airborne Chromatograph Experiment (LACE), which was designed to operate at high altitudes (32 km), and has three ECD-GC channels [Moore et al., 2003]. The advantage of these ECD-GC instruments is their maturity, ease of operation, and proven reliability.

PAN and other Trace Hydrohalocarbon ExpeRiment (PANTHER) is a five-channel gas chromatograph (Figure 1) with one MSD and four ECDs [Elkins et al., 2001; 2002]. The MSD uses two cryogenically cooled adsorption traps to condense gases of interest out of an air sample of ~80 cm^3. PANTHER weighs 90 kg, and is 72x61x37 cm. It uses 2 kW for startup and 750 W for operation, about 80% for 28 VDC and 20% for 110 VAC (60 or 400 Hz). The chromatography on the MSD channel takes a total of six minutes, but with two traps (one for freezing the 1st sample and one for running the 2nd sample into the MSD-GC) it is possible to measure 10 or more trace gases every three minutes. One advantage of the MSD is that its detector is very linear and has a single ion mode that permits recording single mass to charge ratios once every few milliseconds. This aids us in resolving coeluding peaks. The MSD-GC can measure more types of non-electophilic molecules that the ECD-GC cannot. Table 1 shows a listing of the molecules that have been observed in the atmosphere from NOAA/CMDL MSD-GC systems. PANTHER flew successfully on the NASA DC-8 aircraft during SOLVE-2 operating out of Kiruna, Sweden in December 2002 through February 2003 and on the NASA WB-57F aircraft during the

pre-Aura Validation Experiment (pre-AVE) out of Costa Rica and Houston during January 2004. PANTHER would be available on a limited basis for focused studies.

RECENT SCIENTIFIC RESULTS FROM PANTHER

Tracer-tracer abundance relationships reveal important information on the atmosphere, for example, at the tropopause they can be used to quantity ratios of the stratospheric lifetimes. During SOLVE-2, we measured a number of methyl halides and replacement CFC compounds for the first time using the new MSD-GC channel. The altitude range of the DC-8 is similar to that of SOFIA. Figure 2 shows the tracer-tracer correlation of CH_3Br and HFC-134a versus N_2O. CH_3Br accounts for more than 50% of the total organic bromine in the atmosphere and is produced naturally and by mankind (10-30%). We observed considerable structure of all of the tracers near the troposphere that was caused by transport. The higher value of the slope for HFC-134a is the result of its large atmospheric growth of about 18% per year, which makes it an excellent tracer to study transport in the UT/LS.

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