Renewal Proposal for the Third Year and Performance Report for the Second Year of the 4-year NASA Grant NAG5-12669 entitled ADVANCED GLOBAL ATMOSPHERIC GASES EXPERIMENT (AGAGE):
MIT Contribution

Principal Investigator and Grantee Institution

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Submitted: 28 December 2004

Attention:
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1-202-358-0237
1. Research Objectives

We seek funding from NASA for the third year (2005) of the four-year period January 1, 2003–December 31, 2006 for continued support of the MIT contributions to the multi-national global atmospheric trace species measurement program entitled Advanced Global Atmospheric Gases Experiment (AGAGE). The case for real-time high-frequency measurement networks like AGAGE is very strong and the observations and their interpretation are widely recognized for their importance to ozone depletion and climate change studies and to verification issues arising from the Montreal Protocol (ozone) and Kyoto Protocol (climate). The proposed AGAGE program is distinguished by its capability to measure over the globe at high frequency almost all of the important species in the Montreal Protocol and almost all of the significant non-CO₂ gases in the Kyoto Protocol. The proposed program comprises:

1. Operation of the existing automated AGAGE GC-multidetector instruments to measure 8-10 gases at the five AGAGE sites.
2. Operation of the new automated AGAGE Medusa GC-MS instruments to measure 37 gases at all five AGAGE sites.
3. Development and use of new, more accurate, absolute calibrations for all AGAGE species and the renewal of these calibrations at regular intervals in the future.
4. Analysis of the data using improved 2D and 3D models for solving inverse problems to obtain emissions and lifetimes from the data.
5. Publication of the results, public archiving of the data, and contributions to national and international assessments of ozone depletion and climate change.
6. Cooperation with NIES/Japan to establish an AGAGE-compatible GC-MS measurement program at Hateruma, Japan (funded by NIES), and for cooperation with SOGE/Europe to extend AGAGE-type measurements into Europe.


Major accomplishments in the past 3 years in the AGAGE program have largely been published, are in press, have been submitted for publication, and/or have been presented at major scientific conferences (see section 3 for listing).

(a) Analysis Accomplishments (2002-2004)

Methyl chloroform was used widely as a solvent before its phase-out was introduced under the Montreal Protocol. Subsequently, its atmospheric concentration has declined steadily and recent European methyl chloroform consumption and emissions were estimated to be less than 0.1 gigatons per year. However, data from a short-term tropospheric measurement campaign (EXPORT) indicated that European methyl chloroform emissions could have been over 20 gigatons in 2000, almost doubling previously estimated global emissions. Such enhanced emissions would add significant uncertainty to the global abundances of hydroxyl radicals derived from the methyl chloroform method -- the dominant reactive atmospheric chemical for removing trace gases related to air pollution, ozone depletion and the greenhouse effect. Reimann et al. (2004) use long-term high-frequency AGAGE and SOGE data from Mace Head, Ireland, and Jungfraujoch, Switzerland, to infer European methyl chloroform emissions. They find that European emission estimates declined from about 60 gigatons per year in the mid-1990s to 0.3-1.4 and 1.9-3.4 gigatons per year in 2000-03, based on Mace Head and and Jungfraujoch data, respectively. Their European methyl chloroform emission estimates are therefore higher than calculated from consumption data, but are considerably lower than those derived from the EXPORT campaign in 2000.

The hydroxyl free radical (OH) is the major oxidizing chemical in the atmosphere, destroying about 3.7 petagrams (Pg) of trace gases each year, including many gases involved in ozone depletion, the greenhouse effect and urban air pollution. Measurements of 1,1,1-trichloroethane (methyl chloroform, CH₃CCl₃), which reacts with OH, provide the most accurate method available for determining the global behavior of OH. Prinn et al. (2004) report that
CH$_3$CCl$_3$ levels rose steadily from 1978 to reach a maximum in 1992 and have since decreased rapidly to levels in 2003 less than 40% of the levels when measurements began in 1978. Analysis of these observations shows that global average OH levels have remained fairly steady from 1979 to 2003 with only a small maximum around 1989 and a larger minimum around 1998, and with OH concentrations in 2003 being comparable to those in 1979. This post-1998 recovery of OH contrasts with the situation 3 years ago when reported OH was decreasing. The 1997-1999 OH minimum coincides with, and may be caused by, major global wildfires and an intense El Nino event during this time.

Continuous measurements of methane since 1986 at the Global Atmospheric Gases Experiment/Advanced Global Atmospherics Gases Experiment (GAGE/AGAGE) surface sites have been described by Cunnold et al. (2002). The measurements combined with a 12-box atmospheric model and an assumed atmospheric lifetime of 9.1 years indicates net annual emissions (emissions minus soil sinks) of 545 Tg CH$_4$ 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 by Prinn et al. (2002) 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 the 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. The 2-D model combined with the annual cycle in OH from Spivakovsky et al. (2000) provide 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% per decade from 1985 to 2000, in qualitative agreement with Prinn et al. (2001) for the Southern Hemisphere.

We have carried out a critical evaluation of emissions of potential new gases for OH estimation (Huang and Prinn, 2002a, b). Accurate determination of global and regional tropospheric OH concentrations is very important and can be achieved by measuring gases that react with OH and whose emissions are well known. CH$_4$CCl$_3$ has been used for this purpose. Prior studies have shown that three of the new chlorofluorocarbon (CFC) substitutes, HFC-134a (CH$_2$FCF$_3$), HCFC-141b (CH$_3$CCl$_2$F), and HCFC-142b (CH$_3$CClF$_2$), could be used potentially to derive accurate global-average OH concentrations in the future provided that the industrial emissions of these gases can be reliably estimated. As a test of their currently available emission estimates, we optimally determine the monthly emissions for these three gases using global measurements from the NOAA-CMDL and Advanced Global Atmospheric Gases Experiment (AGAGE) networks. We conclude that current published industrial estimates [Alternative Fluorocarbon Environmental Assessment Study (AFEAS)] of HCFC-142b and HCFC-141b need to be increased by 18% over the 1992-2000 period and 10% over the 1993-2000 period, respectively, while the emissions of HFC-134a (from 1993 to 2000) are only 4% more than those yielding the best agreement with atmospheric observations. Estimates of global-average OH concentrations using measurements and AFEAS emissions differ statistically from the average OH derived from CH$_3$CCl$_3$ for HCFC-141b and HCFC-142b but not for HFC-134a. On the other hand, OH trends deduced from all three HCFC/HFC gases are implausibly large, implying problems with the AFEAS (2002) estimates of the temporal variations in their emissions. As the viability of CH$_3$CCl$_3$ for estimating OH declines in the future, additional evaluations of the emissions and OH kinetics of HCFC-141b, HCFC-142b, and HFC-134a therefore have high priority.

AGAGE Observations of Methyl Bromide and Methyl Chloride at Mace Head, Ireland, and Cape Grim, Tasmania in 1998-2001 have been reported by Simmonds et al. (2004). At Mace Head, both gases have well defined seasonal cycles with similar average annual decreases of 3.0% yr$^{-1}$ (CH$_3$Br) and 2.6% yr$^{-1}$ (CH$_3$Cl), and mean northern hemisphere baseline mole fractions of 10.4 ppt and 535.7 ppt, respectively. We have used a Lagrangian dispersion model and local meteorological data to segregate the Mace Head observations into different source regions, and interpret the results in terms of the known sources and sinks of these two key halocarbons. At Cape Grim, CH$_3$Br and CH$_3$Cl also show annual decreases in their baseline mixing ratios of 2.5% yr$^{-1}$ and 1.4% yr$^{-1}$,
respectively. Mean baseline mole fractions were 8.0 ppt (CH$_3$Br) and 541.1 ppt (CH$_3$Cl). Although CH$_3$Cl has a strong seasonal cycle, there is no well-defined seasonal cycle in the Cape Grim CH$_3$Br record. The fact that both gases are steadily decreasing in the atmosphere at both locations implies that a global scale change has occurred which is affecting a common, major source of both gases (possibly biomass burning) and/or their major sink process (destruction by hydroxyl radical).

An update of in situ AGAGE HFC/HCFC measurements made at Mace Head, Ireland and Cape Grim, Tasmania from 1998-2002 have been reported (O’Doherty et al., 2004). HCFC-142b, HCFC-141b, HCFC-22 and HFC-134a show continued rapid growth in the atmosphere at mean rates of 1.1, 1.6, 6.0 and 3.4 ppt/yr respectively. Emissions inferred from measurements are compared to recent estimates from industry data. Minor updates to the industry estimates of emissions are reported together with a discussion of how to best determine OH concentrations from these trace gas measurements. In addition AGAGE measurements and derived emissions are compared to those deduced from NOAA-CMDL flask measurements (which are mostly made at different locations). European emission estimates obtained from Mace Head pollution events using the NAME dispersion model and the best-fit algorithm (simulated annealing) are presented as 3-year rolling average emissions over Europe for the period 1999-2001. Finally, the measurements of HCFC-141b, HCFC-142b and HCFC-22 discussed in this paper have been combined with the ALE/GAGE/AGAGE measurements of CCl$_3$F, CCl$_2$F$_2$, CCl$_2$FCCIF$_2$, CCl$_4$ and CH$_3$CCl$_3$ to produce the evolution of tropospheric chlorine loading.

The oxidizing capacity of the atmosphere has been critically evaluated (Prinn, 2003a, b). Oxidation processes have played a major role in the evolution of the atmosphere. Observations of trace gases in AGAGE and elsewhere in 1978-2003 have provided important constraints on the atmosphere’s major oxidizing free radical OH. Annually, OH removes about 3.7 Pg of trace gases from the atmosphere. Chemicals in ice cores have recorded some information about the oxidizing capacity of past atmospheres. Models have been developed for fast photochemistry and for coupled chemical and transport processes that can explain some of the observations, but there are important discrepancies between models and observations for OH and O$_3$ that still need to be resolved.

The role of non-CO$_2$ trace gases in climate change have been reviewed and critically discussed (Prinn, 2004 a, b; Sabine et al., 2004). Current global emissions of these trace gases, expressed as equivalent amounts of carbon in CO, using GWPs with a 100-year lifetime, are 3.8, 2.1, and 1.5 PgC equivalent respectively for CH$_4$, N$_2$O and CO. This accentuates the importance of measuring these gases and understanding their global budgets. Estimation of the emissions of these and other gases from AGAGE and other data has been critically reviewed (Prinn, 2002). Estimations of CO$_2$, CH$_4$, N$_2$O and CHCl$_3$ emissions from Europe using AGAGE Mace Head data have been reported by Biraud et al. (2002). European emissions of halogenated greenhouse gases have also been determined from AGAGE Mace Head data (Greally et al., 2002; O’Doherty et al., 2003). Back-attribution techniques for inverting AGAGE Ireland measurements to deduce European emissions have been reported by Manning et al. (2003). Also, Cox et al. (2003) identify regional sources of CH$_3$Cl, CHCl$_3$, and CH$_2$Cl$_2$ using AGAGE Tasmania observations.

Finally, background ozone observations collected at Mace Head on the West coast of Ireland since 1987 show a significant positive trend of 0.49 ± 0.19 ppb year-1 through to 2003 (Simmonds et al. 2004). However, this upward trend has not been consistent over time with a major growth rate anomaly evident in 1998-1999. This major ozone perturbation is correlated with variations of CO$_2$, CO, CH$_4$, H$_2$ and CH$_3$Cl in the same timeframe, and is consistent with large-scale biomass burning events in tropical and boreal regions during 1997-1999 coupled with an intense El Niño event. Background ozone in the Northern Hemisphere marine boundary layer has also increased by about 5 ppb from 1987 to 2003. However, over this same period this rate of change has been greater during the spring months (March-May) with an ozone increase of about 9 ppb.

(b) Experimental Accomplishments (2003-2004)

Field operations at the five AGAGE stations have continued normally and without major incident over the past year. The five AGAGE GC-multidetector instruments continued to produce excellent data, and the transitions between tertiary calibration standards at the stations have generally been seamless. The two ADS GC-MS instruments at the Mace Head and Cape Grim stations have
also continued to operate well, and have produced unique data and valuable overlap measurements with the new AGAGE Medusa GC-MS instruments at these stations for a very broad range of natural and anthropogenic halocarbons. These ADS GC-MS systems will be retired from station operations in early 2005, as the program shifts fully to the Medusa GC-MS instruments. The quality-controlled data from the AGAGE instruments, together with their background monthly means, continue to be archived at the CDIAC World Data Center in a timely fashion.

Progress in the completion and deployment of the AGAGE Medusa GC-MS instrument systems has been good, although there have also been some minor problems to overcome in making the transition to routine operation of these new instruments. This past year was an intensive construction and testing period at the SIO AGAGE laboratory, with assistance provided through long-term visits by Dr. Brian Greally of Bristol University (UK) and Mr. Ove Hermansen of SOGE and NILU (Norway). Four Medusas have now been completed: Medusa-1 is in operation at SIO and has become the primary AGAGE GC-MS calibration instrument; Medusa-2 is in operation at the Mace Head station; Medusa-3 is in operation at the Cape Grim station after having been installed in January 2004; and Medusa-4 is in operation at SIO and is being used for testing and development work prior to deployment at the Trinidad Head station early in 2005. Two remaining Medusas, Medusa-5 and Medusa-6, are in their final stages of assembly and testing at SIO, and will be deployed to the Barbados and Samoa stations, respectively, in 2005.

It was not unexpected that with a completely new instrument there would be some problems in making the transition to routine real-time measurements at remote sites, but somewhat unexpectedly the greatest problems were with the Polycold Cryotiger cryogenic refrigeration systems that lie at the heart of the Medusa design. Although originally marketed with a 100,000 hour MTBF (mean time before failure), these units have performed very erratically. They may work flawlessly for months on end, and then fail to re-start after they are switched off or after there is a power outage. Through a non-disclosure agreement and close cooperation with the factory, we have contributed toward resolving the causes of these problems, and considerable progress has thus been made in improved quality control, procedures to cope with clearing blockages in the cold end in the field, and redesigning the refrigerant transfer plumbing and the cold end itself to make such failures much less frequent and easier to correct. We expect these changes to be tested and implemented in all of the Medusa instruments in early 2005.

Several important Medusa instrument improvements have been made during the past year. The questions of blanks and non-linearities have been approached methodically. In the process, we found that some of the lower volatility species had measurable blanks in some instruments but not in others. This was traced to having packed the HayeSep-D adsorption traps in the Medusa from the same end as the analytes enter the traps (standard procedure in chromatography), which left minute traces of adsorbent on the internal walls of the inlet tubes that are not cooled or heated. This blank problem was solved by replacing the traps with ones that are packed from the other end. Otherwise, our tests have confirmed that the Medusa system is quite linear over wide ranges of concentration for all the gases we measure. We also found that the response of the instrument to CF$_4$ depended slightly on the CO$_2$ content of the sample because CO$_2$ altered the tailing of the CF$_4$ peak. This effect was removed by modifying our postflushing and transferring procedures to further separate these compounds prior to chromatographic analysis. Fine tuning of postflushing procedures to reduce O$_2$, N$_2$, CO$_2$, H$_2$O, Kr and Xe contamination of the injected gases has also improved GC-MS detector stability and filament life.

Working together with Agilent engineers under another non-disclosure agreement, we have also managed to greatly reduce the time used by the 5973 MSD to switch masses in SIM mode. This has improved our instrumental signal to noise ratio and/or allowed us to sample more ions in the chromatogram. The “final” ion list for the Medusa instruments is very actively being worked on by the SIO and Bristol laboratories and will be completed in January 2005. The fumigant SO$_2$F$_2$ and several hydrocarbons are being added to the current list of 37 (mainly halogenated) gases now being measured by the Medusas (including all of the halogenated gases measured by the
AGAGE multidetector systems), with precisions ranging from 0.1% to about 5%, depending on abundance.

Because of the large amounts of calibration gas (24 liters/day) consumed by the Medusa analyses, which are twice as frequent as the ADS analyses, a new hierarchical calibration scheme was implemented. Tertiary standards, calibrated at SIO and previously at Bristol for ADS species, are used for both the AGAGE GC-multidetector and Medusa GC-MS instruments, but the Medusa tertiary standard measurements are infrequent and a quaternary, initially uncalibrated, whole air tank is used to transfer the calibration of the tertiary standard to the individual air measurements. Using the new Essex 35-liter DOT-approved 60-atmosphere standard gas canisters (also developed with AGAGE collaboration), this allows the tertiary standards to last 6 to 9 months, depending on the frequency of tertiary/quaternary comparisons.

With so many new species being added to the AGAGE measurement program, it will take many years for SIO gravimetric calibrations (see below) to catch up to the measurements. For this reason, and also to structure the data processing and the calibration process, we have adopted a relative calibration scheme for AGAGE (beginning with the R1 calibration scale) that we are in the process of implementing. In this scheme, air measurements are reported as values relative to an arbitrarily chosen whole air canister (R1), and these values are propagated over time. As new calibrations are obtained, from either the SIO gravimetric work, the Bristol calibrations that are based on commercial Linde mixtures, or other sources such as NOAA/CMDL or NIES, these can be related to the R1 values and the data can easily be converted.

In the area of gravimetric primary calibration, 17 new ambient-level primary standards have been made to augment our earlier calibration work and together to define the SIO-2004 calibration scale. These include nine new AGAGE compounds (CF$_4$, Halon-1301, CFC-115, HFC-134a, HFC-152a, HCFC-142b, Halon-1211, CFC-114, and HCFC-141b) as well as additional standards for six compounds included in the SIO-1998 scale (HCFC-22, CFC-12, CFC-11, CFC-113, CH$_3$CCl$_3$, and CCl$_4$). The new SIO-2004 scale addresses three important issues: (1) to assess the stability over the last six years of selected compounds in primary standard tanks included in the SIO-1998 scale; (2) to reduce the dependence on instrument non-linearity corrections by preparing standard tanks that track the observed changes in the atmosphere; and (3) to prepare standards for nine new compounds measured by the Medusa GC-MS. This work has involved the preparation of hundreds of sealed and weighed micro-capillary tubes containing the required amounts of the above pure species, exhaustive blank measurements, gravimetric determinations of the diluent N$_2$O, preparation of the ambient-level mixtures, and accurate determination of their N$_2$O concentrations.

3. References

(a) Principal Papers (papers in 2002-2004 appearing, in press, or submitted which report work supported wholly or partly by this grant and its predecessor):


**(b) Other Papers:**


4. **Work Proposed for Third Year**

We seek funding for continuation of the MIT contribution to the AGAGE program for the third year of the four-year period January 1, 2003 to December 31, 2006. The overall program includes the following major tasks, all of which contribute substantially to our understanding of all the important non-CO₂ greenhouse gases and ozone-depleting gases:

1. Development and use of new, more accurate, absolute calibrations for all AGAGE species and the renewal of these calibrations at regular intervals in the future.
2. Operation of the existing AGAGE GC-multidetector instruments at the five AGAGE sites.
3. Operation of the new AGAGE Medusa GC-MS instruments at all five AGAGE sites.
4. Cooperation with NIES/Japan to establish an AGAGE-compatible GC-MS measurement program at Hateruma, Japan funded by NIES.
5. Cooperation with SOGE/Europe to extend AGAGE-type measurements into Europe for assessing European emissions. SOGE is funded by European agencies.
6. Analysis of air by MIT from selected waste dumps in the USA and Europe to test current industry estimates of emissions which underly the analysis of AGAGE observations using inverse methods.
7. Analysis of the data using improved 2D and 3D models for solving inverse problems to obtain emissions and lifetimes from the data.
8. Publication of the results, public archiving of the data, and contributions to national and international assessments of ozone depletion and climate change.

We emphasize that the number of gases measured by the GC-multidetector and GC-MS and the total number of calibrated measurements taken each year is very large (41 gases; 1.8 million/year). This places major burdens on station scientists, data processing, absolute calibration, theoretical analysis, and publication production. To address this with the least increase in costs, we have already worked extensively to automate as much of the data acquisition and data processing as possible. To avoid duplication of effort, as much of the instrument-related data processing as possible is now centralized at SIO. There are 1.75 post-doctoral associates in the MIT effort to help carry out theoretical analyses to address the large numbers of measured gases.

The budgets also include two AGAGE science team meetings each year. These meetings, in which the instrument performance and data over the previous half year are carefully reviewed, technical problems and remedies are discussed among the investigators, and theoretical analyses and draft publications are planned and reviewed by the entire team, have been an essential element in the successful running of ALE, GAGE, and AGAGE. Meetings are usually planned to be close to or at one of the AGAGE stations or SIO, Bristol University, GaTech or MIT. In this way, the relevant station scientists can usually combine the meeting with their scheduled station servicing trips, and the travel burden is spread reasonably among the AGAGE team members. These meetings are also a primary mode through which we in AGAGE interface with our colleagues in CMDL, SOGE, and NIES. Relevant leaders from these complementary organizations attend the meetings, which include presentations from them about their experimental and theoretical results. This helps to ensure that the quantitative relationships between the measurements by all these groups including AGAGE are well understood enabling outside users of AGAGE, CMDL, NIES, and SOGE data to maximize the scientific return from these global measurements.

The objectives of the SIO experimental component of AGAGE during the coming year remain essentially unchanged from those described in the original research proposal. The highest priority continues to be assigned to the smooth operation of the stations and their instruments, the provision of working standards for these measurements, and the timely quality control of the data they produce. As noted above, as the deployment of the new GC-MS instruments at the stations, especially the Medusas, with their more-frequent analyses, is massively increasing the scale of station operations and data processing.

During the third year we expect to complete and deploy the remaining two Medusa systems that are designated to support the 5-station AGAGE network. We will deploy Medusa-4 at Trinidad Head, where the container laboratory is being reconfigured and outfitted with improved air
conditioning, in the first months of 2005. Medusa-5 will be completed and deployed at Barbados by mid-year, a change from the earlier deployment order to correspond with the next AGAGE meeting being held at that site. Finally, we expect to complete Medusa-6 and deploy it at Samoa by the end of 2005. Medusa-1 will remain at SIO for calibration work and for testing and local atmospheric measurements. We will also continue to assist the Bristol and CSIRO groups in building Medusas for their laboratories under separate UK and Australian funding, and continue to work with NIES to assure that their parallel GC-MS program at Hateruma Island in the Western Pacific is compatible with the AGAGE program and standards.

As is discussed above, all AGAGE measurements will be maintained on the R1 relative calibration scale, the SIO-2004 calibration scale will be applied to the 19 compounds for which this calibration work has been completed, and we will continue to apply Bristol University calibrations based on commercial mixtures and calibrations from other sources as the measurement and calibration efforts evolve. To assure continuity in this process and in the R1 calibration scale, we will continue to maintain a suite of whole air “gold tanks” that are routinely calibrated against these provisional standards as well as against the SIO-2003 primary standards.

5. Personnel

Professor R. Prinn (MIT) will act as principal investigator for overall leadership and coordination of AGAGE (which includes chairing the AGAGE international science team), and for data processing and theoretical analysis. He will be aided in the theoretical analysis at MIT by J. Huang and a new postdoctoral associate and in the Waste Dump Project by a graduate student.

Dr. P. Simmonds (INSCON and Bristol University) will be the AGAGE co-investigator in charge of the Ireland and Barbados stations and will share responsibility with R. Weiss for the AGAGE Medusa GC-MS system operation. He will be the principal contact between AGAGE and SOGE. He will be assisted at Bristol University by S. O’Doherty and B. Greally at Mace Head by G. Spain.

Dr. P. Fraser (CSIRO) will be the AGAGE co-investigator supervising the Tasmanian AGAGE project, the Cape Grim archive maintenance and analysis, and intercomparisons with other laboratories. He will be aided at CSIRO by P. Steele, P. Krummel, B. Dunse, N. Derek, and at BoM/Cape Grim by L. Porter, S. Baly, and R. Parr.

Professor D. Cunnold (GaTech) will be the AGAGE co-investigator in charge of meteorology-related data processing and archiving, and will work with Prof. Prinn (MIT) on theoretical analysis. He will be aided at GaTech by R. Wang for data processing and J. Li for theoretical analysis.

Professor R. Weiss (who is to be supported by two separate grants from NASA to SIO) will act as principal investigator for the experimental parts of AGAGE with specific responsibility for the Samoa and California stations, absolute calibration, and the AGAGE Medusa GC-multidetector system operation and instrument-related data processing. He will share responsibility with P. Simmonds for the AGAGE Medusa GC-MS systems and with R. Prinn for the AGAGE cooperation with NIES at Hateruma. He will be aided at SIO by B. Miller, P. Salameh, C. Harth, J. Muehle, S. Morris and D. Deeds.

6. Year 3 of 4 AGAGE Budget: January 1, 2005 to December 31, 2005

Institution summarizes the budget proposed to NASA for the period, January 1, 2005 through December 31, 2005 below. In this proposal, we request funding for the MIT contribution. Funds for the SIO contribution are being requested in a separate proposal from SIO. The estimated overall budgets for this period (MIT plus SIO) are provided here for planning information:

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<th>Year 3</th>
<th>$311,130</th>
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<td>(a) MIT in-house</td>
<td>$311,130</td>
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In addition to these funds requested from NASA, we note that routine operations of the Cape Grim, Tasmania station are funded by Australia (CSIRO, Bureau of Meteorology, about $132,500 total for 4 years), routine operations of the Mace Head, Ireland station are funded by the United Kingdom (Department of Environment, Food and Rural Affairs), and NOAA supports approximately 50% of the routine operations at Ragged Point, Barbados, and also provides infrastructure support at Cape Matatula, Samoa through a cooperative agreement. The Hateruma station will be supported fully by NIES in Japan. The SOGE stations, other than Mace Head, are fully supported by the European Union. Finally, development costs for the models used in theoretical analysis are supported significantly by other NASA and NSF grants. Thus the funds requested for AGAGE from NASA will (as in the past) be leveraged significantly by contributions from other federal agencies and other countries.

### Year 3

<table>
<thead>
<tr>
<th>SALARIES &amp; WAGES:</th>
<th>(in months)</th>
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<tr>
<td>Prof. R. Prinn (summer mo)</td>
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<tr>
<td>Dr. J. Huang, Res. Scientist</td>
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<tr>
<td>Postdoctoral Associates (J. Ortega, Q. Tan)</td>
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<tr>
<td>Project Support Staff</td>
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</tr>
<tr>
<td>Graduate Research Assistants (E. Hodson, X. Xiao)</td>
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<tr>
<td>SALARY &amp; WAGES SUBTOTAL:</td>
<td>$126,718</td>
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<tr>
<td>Employee Benefits (25% FY05; 27% FY06; excludes GRAs)</td>
<td>$22,377</td>
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<tr>
<td>Vacation Accrual (excludes Prinn summer month and GRAs)</td>
<td>$6,939</td>
</tr>
<tr>
<td>TOTAL EB &amp; VA:</td>
<td>$29,316</td>
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Total Salaries & Wages, EB & vacation accrual 156,033

### MATERIALS & TUITION:

| RA Tuition (subsidized 65%) not subject to indirect costs | 10,206 |
| Computer equipment upgrade (No MTDC) | 3,000 |
| Permanent Equipment (exempt from F&A) | 3,000 |
| Software & NCCS access | 1,000 |
| Network Connections & Data Facilities | 1,200 |
| Lab supplies & gases | 3,000 |
| Publication expense | 2,121 |
| SUBTOTAL M&S + TUITION: | $23,527 |

### TRAVEL:

| Domestic: Waste dump project | 2,200 |
| Foreign: Barbados (AGAGE), Italy (AGAGE), Tenerife (NDSC), Waste dump project | 15,350 |
TOTAL TRAVEL: $17,550

TOTAL DIRECT COSTS: $197,110
MTDC BASE: $183,904
INDIRECT COSTS (FY05: 60% F&A on MTDC base; FY06: 62% F&A on MTDC base) $114,020
MIT BUDGET $311,130

SUB CONTRACTS: Year 3

INSCON Mace Head, Ireland (Appendix A) $69,703
INSCON: Barbados Station (Appendix A) $54,881
CSIRO: Cape Grim Station (Appendix B) $38,400
Georgia Tech: Data Analysis Appendix C $154,144
TOTAL SUBCONTRACT EXPENSE: $317,128

Carry Forward Funds:

Total Proposal Expense: $628,258

Budget Notes

Professor Prinn’s academic year salary is fully supported by MIT (TEPCO Professorship and Center Director). Support for one-half summer month each year for Professor Prinn is requested.

Dr. Jin Huang will carry out much of the day-to-day 2-D and 3-D inverse modeling for all of the AGAGE industrial gases. The postdoctoral associates will aid Prof. Prinn and Dr. Huang with a focus on inverse modeling of the pollution events for most AGAGE gases at all AGAGE stations to determine regional emissions, and to check those estimated from industrial data. This latter large task will also be supported (in method development) by an existing theory grant from NASA to MIT.

Partial funding for two project support staff provides 10% salary support for Prof. Prinn’s administrative coordinator and financial administrator. These personnel participate directly in the research effort through handling purchasing, and manuscript and report preparation. Employee benefits rate is applied to all staff salaries. Vacation accrual is also applied, except to Professor’s summer salary. RA’s are exempt from both of these charges.

Graduate Research Assistant Tuition: MIT Graduate Research Assistant tuition for academic year 2004-2005 is $29,160, but is subsidized by MIT 65%; remaining expense to the program is $10,206. Indirect F&A expense is not applied to tuition.

Materials & Services: Computer equipment upgrade expense of $3,000 in year 3, is for the annual purchase of 2 computer processor nodes to either replace outdated equipment or expand the existing 64-processor computer cluster.

Funding of $1,000 in year 3 is requested for annual software licensing fees and access for NASA NCCS computation time for 3-D model use in AGAGE data analysis by inverse methods.

Permanent equipment involves purchase of detectors for GC used in Waste Dump Project.

Computer facility expenses of $1,200 include such items as network connections and telephone usage.
Modest funds ($3,000) are requested for the purchase of laboratory supplies, minor equipment, office supplies, and photocopy charges.

Publication expense is based on publication of 1-2 papers each year in the *Journal of Geophysical Research*.

**Travel: Domestic**
Waste Dump Project (California). Estimated Expenses: airfare $800, ground transport $100, hotel $900, food $400, total $2,200.

**Travel: Foreign**
1: AGAGE meeting in Barbados (Spring 2005, May 17-19 2005), Ragged Point station and trips to waste dumps for emissions measurements. Estimated expenses: airfare $1100, ground transport $100, hotel $600, food $250, registration $100, miscellaneous $50; total per traveler: $2,200 times 2 = $4,400.

2: AGAGE meeting in Bologna, Italy (Fall 2005, October 17-22 2005). Estimated expenses: airfare $1,400, ground transport $100, hotel $1,000, food $250, registration $100, miscellaneous $50; total per traveler: $2,900 times 2 = $5,800.

3: NASA Network for Detection of Stratospheric Change (NDSC) Steering Committee meeting in Tenerife. Estimated expense: airfare $1,400, ground transport $100, hotel $600, food $200, miscellaneous $50; total per traveler: $2,350.

4. Waste Dump Project (Europe). Estimated expenses: airfare $1,200, ground transport $100, hotel $1,000, food $500, total $2,800.

**Appendix A.**

**INSCON Subcontract Budgets: January 1, 2005 to December 31, 2005**
Partial Support of the AGAGE Stations at Mace Head, Ireland and Ragged Point, Barbados.

### (i) Barbados Station

<table>
<thead>
<tr>
<th><strong>Salaries &amp; Wages</strong></th>
<th><strong>In months</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. P. Simmonds</td>
<td>2.5</td>
</tr>
<tr>
<td>Station Caretaker</td>
<td>2.0</td>
</tr>
<tr>
<td>Secretary</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Subtotal Salaries &amp; Wages:</strong></td>
<td>22,729</td>
</tr>
<tr>
<td><strong>Overhead &amp; Admin (32%)</strong>:</td>
<td>7,273</td>
</tr>
<tr>
<td><strong>Subtotal:</strong></td>
<td>30,002</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Station Supplies &amp; Services</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplies, freight &amp; consumables</td>
<td>8,169</td>
</tr>
<tr>
<td>Building maintenance</td>
<td>478</td>
</tr>
<tr>
<td><strong>Subtotal:</strong></td>
<td>8,647</td>
</tr>
</tbody>
</table>

| **Materials & Services** |        |
| GC-MS & GC-MD parts, valves, pumps, regulators & Essex high-pressure canisters | 7,851  |

| **Travel** |        |
| Site visits to Ragged Pt., Barbados (airfare, hotel, etc.) | 7,957  |
| Local U.K. travel | 424    |
| **Subtotal Travel:** | 8,381  |

| **Barbados Budget Total:** | $54,881 |


### (ii) Mace Head Station

**SALARIES & WAGES:**

<table>
<thead>
<tr>
<th>Name</th>
<th>In months</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. S. O’Doherty</td>
<td>4.0</td>
</tr>
<tr>
<td>Dr. B. Greally</td>
<td>1.0</td>
</tr>
<tr>
<td>Dr. P. Simmonds</td>
<td>0.45</td>
</tr>
</tbody>
</table>

**SUBTOTAL SALARIES & WAGES:** 31,271

**Overhead & Admin (32%):** 10,007

**SUBTOTAL:** 41,278

**STATION SUPPLIES & SERVICES:**

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases &amp; consumables</td>
<td>6,153</td>
</tr>
<tr>
<td>Freight &amp; Shipping</td>
<td>424</td>
</tr>
<tr>
<td>Rent &amp; Utilities</td>
<td>5,145</td>
</tr>
<tr>
<td>MS spare parts</td>
<td>4,030</td>
</tr>
</tbody>
</table>

**SUBTOTAL:** 15,753

**MATERIALS & SERVICES**

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-MS &amp; GC-MD parts, valves, pumps, regulators &amp; Essex high-pressure canisters</td>
<td>6,684</td>
</tr>
</tbody>
</table>

**TRAVEL:**

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site visits to Mace Head, Ireland (airfare, hotel, etc.)</td>
<td>2,971</td>
</tr>
<tr>
<td>Local U.K. travel</td>
<td>318</td>
</tr>
<tr>
<td>Supplemental travel budget for Dr. A. McCulloch to attend one AGAGE meetings</td>
<td>1,700</td>
</tr>
</tbody>
</table>

**SUBTOTAL TRAVEL:** 5,989

**MACE HEAD BUDGET TOTAL:** $69,703

**Budget notes**

Dr. S. O’Doherty will work full-time on AGAGE, however, only 4 man-months per year are requested from NASA. The U.K. DEFRA will provide funding for the balance of 6 man-months.

Professor P. Simmonds will devote 5 months to AGAGE. Support is requested from NASA for 2.95 months only.

Travel is requested for Dr. A. McCulloch to attend one AGAGE meeting at Barbados.

**INSCON STATEMENT OF WORK**

1. International Science Consultants (INSCON) will provide all of the manpower, facilities, consumables, and equipment for continuous operation of the AGAGE stations at Ragged Point, Barbados (50% funded by this subcontract) and Mace Head, Ireland (partially funded by this subcontract). This will include a daily technician visit to provide regular logistical support, and routine maintenance of the station.

2. Dr. P. Simmonds will act as the overall project scientist and will be supported by Dr. Simon O’Doherty and Dr. Brian Greally (principal field scientists, based at Bristol University).

3. Dr. Simmonds and/or Dr. O’Doherty, or Brian Greally will attend the regular 6-monthly AGAGE project meetings, and maintain regular and close contacts with other members of the AGAGE team.

4. Site visits will be performed by a field scientist at regular 3–4-month intervals for detailed servicing, repairs, and intercalibrations of the AGAGE instruments.

5. AGAGE-MD data will be determined from repetitive 20-minute measurements with a target precision of better than 1.0% for the following trace gases, CFCl₃, CF₂Cl₂, CF₂ClCFCl₂, CH₃CCl₃, and CCℓ; and with a target precision of better than 0.5% for N₂O and CH₄. Calibration measurements will be obtained every alternate 20 minutes from secondary reference calibration.
standards maintained at the station, and supplied by Scripps Institution of Oceanography. Each secondary calibration standard will be used at the station for approximately 6-12 months before being returned to Scripps for re-calibration against the AGAGE primary standards.

(6) Dr. Simmonds will act as the Project scientist for the collaborative research program at Bristol University, UK (funded by the UK DEFRA) to operate an automated GC-MS instrument for high frequency measurements of the HCFCs and HFCs and other key halocarbons in the atmospheric research station at Mace Head, Ireland. Both the older AGAGE ‘ADS’ GC-MS, and the new ‘MEDUSA’ GC-MS will be operated in parallel for a 6-9 month overlap period.

(7) All raw AGAGE GC-MD and GC-MS data, in the form of peak heights (and/or peak areas) for all measured species, will be submitted to the AGAGE database at Georgia Institute of Technology for detailed statistical processing. The accumulated database will be used for the preparation and submission of research papers to appropriate scientific journals, and for presentations at various scientific meetings.

Secondary field standards of the HCFCs and HFC's will be prepared at Bristol University and periodically intercalibrated with absolute measurements at the Scripps Institution of Oceanography. INSCON will be responsible for archiving the data base at Bristol University and the calibrated data at the Georgia Institute of Technology.

INSCON will also provide technical and calibration support of GC-MS operations and standards for the Cape Grim GC-MS instrument maintained by CSIRO.

Appendix B.

CSIRO, Australia Subcontract Budget: January 1, 2005 to December 31, 2005

This budget provides partial support for the AGAGE operations at CSIRO and at the Cape Grim Baseline Air Pollution Station (CGBAPS) and for international travel for CSIRO personnel under the supervision of Dr Paul Fraser, Chief Research Scientist, CSIRO Atmospheric Research, PMB #1, Aspendale, Victoria 3195, Australia.

<table>
<thead>
<tr>
<th>Year 2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SALARIES &amp; WAGES: IN MONTHS</strong></td>
<td><strong>Year 2</strong></td>
</tr>
<tr>
<td>Dr. P. Fraser</td>
<td>0.6</td>
</tr>
<tr>
<td>Technical Officer</td>
<td>5.0</td>
</tr>
<tr>
<td><strong>SUBTOTAL SALARIES &amp; WAGES:</strong></td>
<td>21,708</td>
</tr>
<tr>
<td>Overhead (33%)</td>
<td>10,692</td>
</tr>
<tr>
<td><strong>TOTAL SALARY &amp; WAGES +OH:</strong></td>
<td>32,400</td>
</tr>
<tr>
<td><strong>TRAVEL:</strong></td>
<td></td>
</tr>
<tr>
<td>International travel</td>
<td>6,000</td>
</tr>
<tr>
<td><strong>TOTAL CSIRO Subcontract:</strong></td>
<td><strong>$38,400</strong></td>
</tr>
</tbody>
</table>

**Budget Details:**

1. Participation in mandatory AGAGE semi-annual meetings by Australian investigators (Drs. P. Fraser, P. Steele & B. Dunse, Mr. P. Krummel, Mr. L. Porter, Mr. S. Baly, Ms. N. Derek, Mr. R. Parr) requires significant international travel, since seven of eight meetings are outside Australia. At least two Australian representatives (from Fraser, Krummel, Porter) will attend each non-Australian AGAGE Meeting and all the above staff involved in the AGAGE program will attend each Australian AGAGE Meeting.

In year 3 of AGAGE, there will be two AGAGE Meetings (in Europe and Barbados). The budget is based on two Australian participants at each international Meeting, with costs based on previous Meetings (AGAGE and others) in the USA, Europe, Barbados and Japan (assuming costs inflate at 3% per year). If there are more than two Australian participants per non-Australian Meeting, the additional costs will be met by CSIRO.
2. This proposal supports a Technical Officer for 5 months at Cape Grim to assist in the operation of the AGAGE GC-MD and two AGAGE GC-MS systems (ADS and Medusa) and salary support (0.6 months) for Dr. P. Fraser (Chief Research Scientist) as the Australian AGAGE Co-Principal Investigator. The AGAGE GC-MD measures ten species - three CFCs, chloroform, methylchloroform, carbon tetrachloride, methane, carbon monoxide, hydrogen and nitrous oxide. The AGAGE GC-MS systems measure about thirty species made up of CFCs, HCFCs, HFCs, PFCs, sulfur hexafluoride, methyl halides, halogenated hydrocarbons, methylchloroform, carbon tetrachloride, trichloroethylene, perchloroethylene, benzene and toluene. Currently, the personnel who are significantly involved in the day-by-day AGAGE program at Cape Grim are L. Porter (Senior Technical Officer), S. Baly (Technical Officer) and R. Parr (Technical Officer).

3. No Cape Grim instrumental or operating costs are contained in this budget. There are no salary costs to cover participation by Steele, Dunse, Krummel, Baly and Derek. CSIRO provides significant ‘in-kind’ support for the MIT-AGAGE program at Cape Grim with all necessary personnel, instrumental and operating costs, local travel and additional international travel costs. Approximate total CSIRO/BoM support of the MIT-AGAGE program during 2003-2006 will be $132,500.

4. CSIRO/BoM provide MIT-AGAGE access to the Cape Grim laboratory, the GASLAB laboratory, the Cape Grim air archive and Antarctic firn air archive at no cost to MIT.

**Appendix C.**

**Georgia Institute of Technology Subcontract Budget: January 1, 2005 – December 31, 2005**

Partial support for data processing and scientific analysis in the AGAGE program to be carried out at Georgia Tech under the supervision of Prof. D. Cunnold.

<table>
<thead>
<tr>
<th>SALARIES &amp; WAGES:</th>
<th>YEAR 3 (in months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prof. D. Cunnold</td>
<td>1.25</td>
</tr>
<tr>
<td>Dr. R. Wang, Research Scientist</td>
<td>5.0</td>
</tr>
<tr>
<td>Dr. Jinlong Li, Post Doc</td>
<td>8.0</td>
</tr>
<tr>
<td>M. Keever, Computer Sys. Spec.</td>
<td>0.5</td>
</tr>
<tr>
<td>K. Plummer, Admin. Asst.</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Salary & Wages Subtotal:** 73,938

**Benefits (at 23.5%)** 17,376

**Subtotal: Salary & Wages + EB:** $91,314

**Materials, Operating Exp, etc.** 2,500

**Publications** 1,500

**Travel** 8,000

**Total Direct Costs:** $103,314
<table>
<thead>
<tr>
<th>Description</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indirect Costs (@49.2%)</td>
<td>50,830</td>
</tr>
<tr>
<td><strong>Grand Total</strong></td>
<td><strong>$154,144</strong></td>
</tr>
</tbody>
</table>

1. Includes additional software update packages (~$1,500); miscellaneous supplies (~$250); service contracts, hardware, and software ($750).

2. Includes 2 trips per year to attend scheduled AGAGE meetings for each of two Georgia Tech scientists. The scheduled meetings in year 3 are in Barbados and Italy.