Collaborative Research:

CONvective TRansport of Active Species in the Tropics (CONTRAST)

Scientific Program Overview (SPO) Document

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PROJECT SUMMARY

Intellectual merit: We propose here the CONvective TRansport of Active Species in the Tropics (CONTRAST) experiment to be conducted from the island of Guam (13.5N, 145E) during January-February, 2014. The main scientific objective of the project is to measure the chemistry and transport of reactive chemical species into the tropical Tropopause Transition Layer (TTL) over the Western Pacific warm pool region. During the boreal winter season, tropospheric air masses are preferentially transported into the lower stratosphere in this region. Thus, the sources, chemistry, and transport of trace gases and their degradation products in the region can substantially impact the chemistry of the lower stratosphere. Considerable attention is being given to the role of tropical convection on the delivery of reactive gases to the TTL. For example, uncertainties in the abundance of reactive halogen species and the fate of short lived organic halogen compounds, particularly bromocarbons, in the tropical upper troposphere leads to significant uncertainties in the photochemistry of stratospheric ozone, especially in the lowermost stratosphere. Despite the recognized importance of this region to shaping the chemical composition of the tropical upper troposphere and lower stratosphere, relatively few chemical measurements have been made to date, partially because of the lack of suitable airborne platforms and instruments to reach the required altitudes. This limitation is no longer a factor with the deployment of the NSF GV aircraft and the development of suitable instrumentation for that platform.

Detailed in-situ measurements of a suite of gases and particles as well as meteorological parameters from the GV during CONTRAST will elucidate the roles of active convection and long-range transport on the chemical composition of the tropical atmosphere, and the altitude variation of these processes. The western Pacific region is also found, from ozonesonde measurements or remote sensing platforms, to have extremely low ozone concentrations. CONTRAST will provide detailed in-situ measurements of a suite of chemicals to characterize the region's chemical environment. The unique low-ozone environments in the upper troposphere are expected to result in very low levels of OH radicals, which can be expected to increase the lifetime of reactive gases whose main loss is through OH radical oxidation. The simultaneous occurrence of deep convection and prolonged lifetime of organic compounds in the TTL can have substantial impact on the stratospheric halogen budget. Because the chemical and radiative properties of this region are a key factor in the mechanisms that link climate forcing and atmospheric composition, the CONTRAST experiment will provide measurements necessary for diagnosing, constraining, and improving chemistry-climate models.

The proposed payload and operational range of the GV during CONTRAST will allow important progress to be made in characterizing the chemistry of the tropical upper troposphere, including the altitude region of main convective outflow (12-14 km). Moreover, the timing of the CONTRAST experiment has been designed to take advantage of collaborations with two other airborne studies planned for the same time and geographic location. These are the NASA EV1 project ATTREX (Airborne Tropical Tropopause Experiment) and the European CAST (Coordinated Airborne Studies in the Tropics). With complementary instrument payloads, coordinated flights of the GV, the NASA Global Hawk and the UK Bae146 will provide an unprecedented examination of the full atmospheric column, from surface to >19 km, in the Tropical Western Pacific.

Broader scientific impact: The CONTRAST mission will improve the fundamental understanding of convective transport processes in the tropics, and the role of convection in chemistry-climate interaction. Better understanding of the processes in this region will improve process-oriented chemistry/climate models and their validation by providing a unique suite of benchmark measurements, especially in the characterization of active halogen chemistry. The project will train students in atmospheric chemistry who are directly involved in the deployment and subsequent data analysis and modeling activities. Broader education and outreach activities will be developed using web-based tools and media.

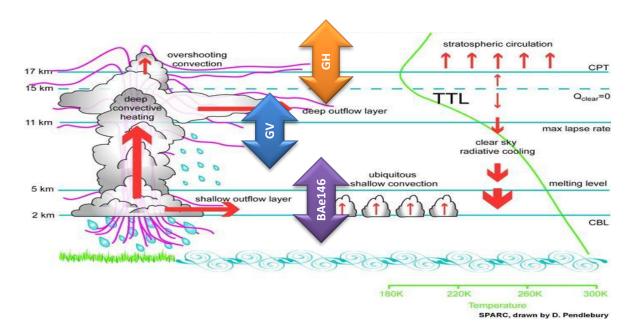
1. Introduction and Scientific Rationale

The upper troposphere and lower stratosphere (UTLS) is important for chemistry-climate coupling largely because of the significant radiative forcing caused by ozone, water vapor, clouds and aerosols in this region of the atmosphere [*Shepherd*, 2008] The tropical tropopause layer (TTL) is particularly important because it is the primary gateway to the stratosphere [*Fueglistaler et al.*, 2009]. The vast majority of tropospheric air that enters the stratosphere originates from deep convection in the tropical western Pacific that detrains in the lower altitude portion of the TTL [*Bergman et al.*, 2012]. The overall transport of emissions from the boundary-layer to the stratosphere involves rapid transport by deep convection from the surface to the bottom of the TTL (time scales of minutes to hours), followed by slow ascent through the TTL (time scales of months). Despite its importance, the composition of air in the UTLS over the tropical western Pacific is not well characterized.

The convective transport process that rapidly redistributes chemical compounds between surface emission sources and the UT is especially important for the budget of short-lived chemicals, many of which play a significant role in the ozone production and loss processes in the troposphere and stratosphere. The contribution of convective transport to the chemistry of the upper troposphere is a high priority research area because of potential impacts of on chemistry/climate coupling [e.g., *Shepherd*, 2008].

We propose a field project, CONvective TRansport of Active Species in the Tropics (CONTRAST), using the NSF/NCAR research aircraft GV to investigate the role of convective transport in TTL chemistry and the vertical distribution of the short-lived species in the western Pacific region. The proposed flights will be based from Guam (13.48°N, 144.8°E) and will occur during January-February 2014. The timing is designed for coordination of the GV flights with flights of the Global Hawk (GH) at higher altitudes as part of the NASA Airborne Tropical TRopopause Experiment (ATTREX) program and of the BAe-146 at lower altitudes as part of the NERC Coordinated Airborne Studies in the Tropics (CAST) program. Combined measurements from the three aircraft would span the surface to the lowermost stratosphere, providing an unprecedented opportunity to assess the role of convection on atmospheric composition in the tropical western Pacific (Figure 1). CONTRAST has unique science goals and will also conduct extensive sampling of the TTL during January-February 2014, providing an important connection between the highest altitudes sampled by CAST (top of free troposphere) and the lowest altitudes probed extensively by ATTREX (top portion of the TTL and lower stratosphere).

Figure 1. Diagram showing the convective processes in relation to the TTL, and typical altitude regions sampled by the CONTRAST GV, the ATTREX Global Hawk (GH), and CAST BAe-146 aircraft.



The western Pacific during Boreal winter season is characterized by intense deep convection. This region makes the dominant contribution for the transport across the TTL into the stratosphere [e.g., *Fueglistaler et al.*, 2004; *Levine et al.*, 2007]. A recent study using trajectory analyses combined with convective influence calculations indicates that during Boreal winter most of the air reaching the tropical stratosphere originally detrained from deep convection in the western Pacific region [*Bergman et al.*, 2012] (Figure 2). Nonetheless, key questions persist:

- What is the impact of deep convection on the photochemical budget of O₃ in the UT and on the supply of halogens to the LS?
- What is the relative importance of typical deep convection detraining at 12 to 13 km versus extreme convection detraining above 15 km for the composition of air entering the stratosphere?
- How important is mixing from the extra-tropical stratosphere for TTL composition over the western Pacific?

As described below, these questions will be addressed by data collected during CONTRAST.

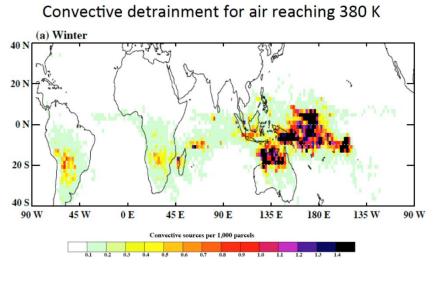


Figure 2. The geographical distribution of convective sources for air entering the tropical stratosphere within the CONTRAST area of operation during Jan-Feb 2007. Shown are convective sources in the Pacific region: Equator-20°N;135°-180°E. Shading represents the fraction (parts per 1000) of air parcels at 380 K in the sub-region that have convective sources in 2° longitude by 2° latitude bins. Convective sources are determined from 60d back trajectory calculations initiated at 380 K and terminated when the encounters parcel convective cloud. (Adapted from Bergman et al., 2012)

Persistent deep convection creates a unique chemical environment of extremely low ozone (O_3) in the middle and upper troposphere of the western Pacific, though the rates of ozone loss and production in these layers has not been quantified. The absence of O_3 creates a distinct photochemical condition that potentially extends the lifetime of many very short-lived (VSL) halogen species [*Kley et al.*, 1996]. In addition, the low O_3 environment alters the partitioning of inorganic halogen species that have formed following the decomposition of these source species. Characterizing the composition of the western Pacific TTL region is critical for understanding the transport of halogens into the stratosphere. CONTRAST will focus on characterizing the photochemical environment of the convective outflow region and determining the abundance of organic and inorganic bromine and iodine species in the TTL, which is subject to considerable uncertainty (e.g., Section 1.3 of WMO, 2011).

The extreme low O_3 environment of the western Pacific TTL has been identified from a number of previous field studies. As an example, Figure 3 shows the LIDAR measurements onboard the NASA DC-8 aircraft in this region during the PEM-west experiment [*Crawford et al.*, 1997]. The figure shows that the layer of the atmosphere between 10-15 km is marked by O_3 below 20 ppbv, a signature of convectively lifted oceanic boundary layer air. Similar features have been observed routinely in long term ozonesonde data [e.g., *Thompson et al.*, 2011]. This layer is expected to have elevated concentration of halogen species such as dibromomethane (CH₂Br₂), bromoform (CHBr₃) and methyl iodide (CH₃I), which

are significant contributors to the input of bromine and iodine into the upper troposphere. Recently, the NCAR global chemistry-climate model (CCM) CAM-Chem [Lamarque et al., 2011] was extended to incorporate VSL halogens, including several species with oceanic sources [Ordóñez et al., 2011]. Figure 4, which shows the calculated distribution of CH_2Br_2 and $CHBr_3$ at 200 hPa from CAM-Chem along with the range of the GV from Guam, highlights the importance of upward transport of halogens in the tropical western Pacific.

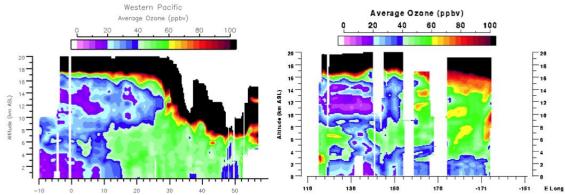


Figure 3. Composite latitudinal and longitudinal cross-sections of ozone of the Western Pacific and across the tropical Pacific during PEM-WEST [*Crawford et al.*, 1997; *Browell et al.*, <u>http://asd-www.larc.nasa.gov/lidar/pwb/pwb_msn.html</u>]. Measurements show the penetration of low ozone air masses to the tropical upper troposphere, and demonstrate that the lowest ozone features are located above the Western Pacific Warm Pool.

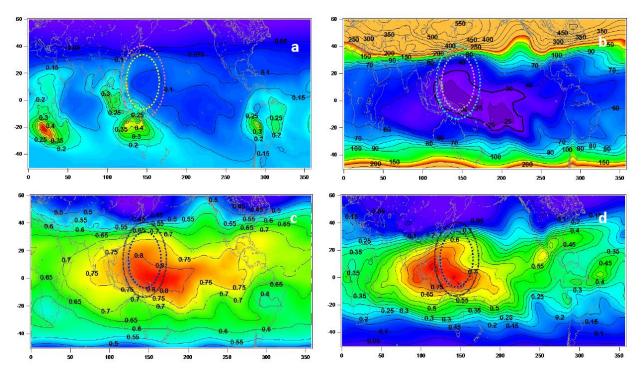


Figure 4. Calculated distributions by the CAM_CHEM model for average January conditions on 200 hPa surface.a) OH (pptv); b) Ozone (ppbv); c) CH₂Br₂ (pptv); d) CHBr₃ (pptv). Concentric ovals indicate the approximate range of the NSF GV aircraft. Calculated distributions reflect the transport of low ozone air, enriched in organic bromine, to the tropical UT, with consequent impact on the OH radical distribution.

Bromine chemistry is important for the photochemistry of O_3 in both the stratosphere and the tropical troposphere. Bromine monoxide (BrO) formed following decomposition of VSL bromocarbons contributes to loss of O_3 in the upper troposphere [*von Glasow et al.*, 2004] and in the lower stratosphere, particularly after large volcanic eruptions [*Salawitch et al.*, 2005]. *Saiz-Lopez et al.* [2011] used the CAM-Chem CCM to estimate the contribution of halogens, and other chemical families, to the loss of O_3 in the tropical UT/LS (Figure 5). This simulation suggests that over tropical regions, halogen chemistry is an important photochemical loss term for O_3 from the boundary layer, to the upper troposphere, and into the stratosphere. Overall, halogen-catalyzed chemistry is calculated to contribute about 25% of the O_3 loss for a broad region of the atmosphere. Particularly relevant to CONTRAST, models suggest that vertical transport and subsequent photochemical breakdown of VSL halocarbons contributes at least 80% of this halogen-driven O_3 loss in the upper troposphere. By affecting the distribution of O_3 in the upper troposphere, these processes could contribute significantly to the local radiative balance [*Saiz-Lopez et al.*, 2011].

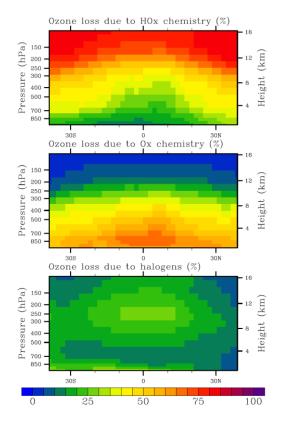


Figure 5. Altitude/Latitude cross sections calculated by the CAM-CHEM model of various photochemical loss terms for O_3 . Note the significant role of halogen induced loss in the upper troposphere. Quantification of this loss process is a major objective of the CONTRAST mission.

The effect of bromine on the photochemistry of O_3 is quite uncertain. Figures 4 and 5 illustrate only one scenario. It has been well established that space-based measurements of total column BrO are much larger than amounts that can be supplied by the decomposition of long-lived bromocarbons. Considerable debate persists, however, regarding whether the short-fall between observed BrO and calculated BrO (from decomposition of long-lived sources) is caused by "excess BrO" in the troposphere, in the stratosphere, or some combination of both atmospheric regions [e.g., Section 2.5.2.1 of *WMO*, *2007*]. Measurements of total column IO, on the other

hand, suggest abundances too low to drive the photochemistry of O_3 in the UTLS [*Wennberg et al.*, 1997; *Butz et al.*, 2006; Section 2.5.2.3 of *WMO*, 2007]. It is not clear why bromine from VSL sources appears to enter the stratosphere whereas iodine from VSL sources appears to be removed in the troposphere.

The chemistry involving VSL halocarbons and the details of convective transport have been identified as a major area of investigation for the process-oriented CCM evaluation project, a joint project of the International Global Atmospheric Chemistry (IGAC) Project and the WCRP's (World Climate Research Programme) SPARC (Stratospheric Processes and their Role in Climate). As convective parameterization has been a significant challenge in climate modeling, accurately representing the impact of deep convection on chemistry is a serious challenge for global chemistry-climate models.

CONTRAST Objectives

CONTRAST is designed to provide a comprehensive suite of measurements needed to characterize the effect of deep convection on the chemical environment of the tropical western Pacific TTL, which is a

pre-requisite for testing and ultimately improving chemical models of the tropics. In addition to measurements of ozone, ozone precursors, and a variety of trace gases, CONTRAST will quantify the amount of bromine injected into the TTL by deep convection, the fate of VSL bromocarbons as air is lofted through the TTL, and the reason(s) for different behavior of bromine versus iodine bearing halogens. Importantly, CONTRAST will provide, for the first time, measurement of a complete set of bromine and iodine gases (inorganic and organic) needed to address the most prominent uncertainty described above.

The main objectives of CONTRAST are to:

- Characterize the chemical composition at the level of convective outflow over the Western Pacific during the deep convective season
- Evaluate the budget of organic and inorganic bromine and iodine in the TTL
- Investigate transport pathways from the oceanic surface to the tropopause using the GV coordinated flights with BAe-146 and Global Hawk

As noted, this proposal is further motivated by an excellent opportunity for collaboration with the ATTREX and CAST missions in January-February 2014. The three aircraft with complementary suites of measurements will cover altitudes from the oceanic boundary to the lower stratosphere (Figure 1). In addition to the complementary instrumentation, the scientific objectives of the missions are complementary, and joint operations enhance each program.

From its inception, the CAST mission included the collaboration with ATTREX in order to relate the CAST measurements in the lower to mid-troposphere to the higher altitude conditions that could be accessible to the GH. Thus, the major objectives of the CAST project were to provide an improved and more quantitative understanding of : 1) transport processes in the Tropical Tropopause Layer (TTL); and 2) VSL compounds in the tropical atmosphere, including their fluxes from the ocean, their atmospheric chemistry, and their transport up into the TTL.

The CAST measurements will allow a more complete characterization of chemical properties in the marine boundary layer and lower free troposphere than would be possible with just GV measurements, and the GV will extend the chemical characterization into the upper troposphere to the lower TTL and at levels of the main convective outflow. Thus we are able to obtain a more complete picture of the inflow and outflow of Western Pacific convection.

ATTREX focuses on the upper troposphere and lower stratosphere, but will benefit from measurements in the lower TTL and in the main convective outflow region which is below the normal operating range of the Global Hawk. The combined measurements from the Global Hawk and the GV will provide excellent definition of chemical gradients and transport through the altitude range of the TTL. The broad goals of the ATTREX mission are to improve understanding of how deep convection, slow large-scale ascent, waves, and cloud microphysics control the humidity and chemical composition of air entering the stratosphere, and to improve global-model predictions of feedbacks associated with future changes in TTL cirrus, stratospheric humidity, and stratospheric ozone in a changing climate.

To meet these broad goals, a range of specific questions were identified in the ATTREX plan. These include questions that relate to the control of stratospheric humidity and temperature structure in the TTL. Of more direct relationship to the CONTRAST objectives are questions regarding TTL radiation and transport and TTL chemistry. For example some of the specific questions addressed by ATTREX in these areas that are closely aligned with CONTRAST are:

- What is the relative importance of typical convection detraining at ~13 km versus extreme convection detraining above 15 km for the humidity and composition of air entering the stratosphere?
- What are the mechanisms for transport from the midlatitudes, and how important are they?
- What is the vertical distribution of BrO and short lived halogen compounds in the TTL and how does it vary seasonally and geographically?
- Are TTL O₃ and halogen observations consistent with photochemical models?

As will be described later, both CAST and ATTREX payloads features both in-situ and remote sensing instrumentation that are complementary to those identified for CONTRAST.

2. Scientific Goals and Hypotheses of CONTRAST

2.1 Characterize the influence of deep convection on the photochemical budget of O_3 at the level of convective outflow over the western Pacific

Deep convection associated with warm surface waters of the tropical western Pacific provides the major source of reactive chemicals and H₂O to the tropical upper troposphere. The chemical composition of air transported out of the TTL defines the chemical boundary for the lower stratosphere. The tropical TTL appears to be characterized by extremely low abundances of O₃, which should lead to a deficiency in the abundance of hydroxyl radical (OH), since OH is supplied by the reaction of H₂O with O¹(D), a photolytic product of O₃. It has been hypothesized that the photochemical budget of O₃ in the tropical TTL is influenced by VSL halogens supplied by deep convection as well as NO_x supplied by lightning. CONTRAST will provide the first extensive measurements of O₃, radicals, and radical precursors in western Pacific TTL.

Data obtained during CONTRAST will provide distributions of O_3 , H_2O , CH_4 , H_2CO , halocarbons, NO and NO₂, BrO, IO, and a suite of short-lived hydrocarbons *inside* and *outside* regions of deep convective influence. Our first goal will be to compare and contrast profiles marked by either the presence or absence of recent, deep convective influence. Deep convective influence will be marked by meteorological analysis as well as the abundance of CH_3I , which is so short-lived (lifetime of 5 to 6 days) that the presence, or lack thereof, of CH_3I will serve as an excellent indicator of whether an air parcel was in recent convective contact with the marine boundary layer.

Hypothesis 2.1.1. The photochemical budget of O_3 in the tropical TTL is determined by the strength of inputs of chemical precursors from convection and lightning. The simultaneous measurement of O_3 , H_2O , CO, CH_4 , and radiation will allow for model estimates of atomic O as well as OH and HO₂ (HO_x). Of course, volatile organic compounds (VOC) could supply HO_x to this region (Wennberg et al., 1998). Acetone (C₃H₆O), perhaps the most important VOC source of HO_x, will be measured both inside and outside regions of deep convective influence. Comparison of measured and modeled H₂CO will further help to evaluate the consistency of our photochemical calculations. We will calculate OH and HO₂ profiles, based on constraints for CONTRAST measurements, for air parcels *inside* and *outside* regions of deep convective influence. Measurements of NO, NO₂, BrO, and IO provide direct constraints on the abundance of radicals that participate in a series of O₃ loss steps. Although we will not have direct measurements of CIO, the abundance of total inorganic chlorine (Cl_y) will be inferred from measurement of the nighttime reservoir of Br_y species (see below). Finally, the western TTL is a region of strong lightning influence. Comparison of NO_x vs CO will provide an empirical measure of the impact of lightning on NO_x. The CONTRAST measurements will be used to construct estimates of the photochemical loss terms of O₃ by O+O₃, HO_x, NO_x, and halogens as a function of altitude, for air parcels

both *inside* and *outside* regions of deep convective influence, in order to test model representations of the photochemical loss of O₃, such as that shown in Figure 5 [from *Saiz-Lopez et al.*, 2011] and discussed in *von Glasow et al.* [2004].

Hypothesis 2.1.2. The low O_3 environment of air undergoing recent, deep convection will increase the atmospheric lifetime of halocarbons lost by reaction with OH. As noted above, the simultaneous measurement of O_3 , H₂O and radiation will allow for model estimates of OH. Of course, VOC's could supply OH to this region (Wennberg et al., 1998). A likely result of the low O_3 environment associated with recent, deep convection is decreased values of calculated OH. CONTRAST measurements of a range of organic trace gases, including halocarbons such as CHBr₃, CH₂Br₂, and bromochloromethane (CH₂BrCl), will allow the effect of OH on the lifetime of these gases to be assessed. Table 1 contains estimates of the lifetime for removal of these gases by reaction with OH and photolysis, taken from Table 2-4 of WMO (2003).

Chemical	$ au_{OH}$ (days)	τ_{J} (days)	τ_{TOTAL} (days)
CHBr ₃	100	36	26
CH ₂ Br ₂	120	5000	120
CH ₂ BrCl	150	15000	150

Table 1. Lifetime at 5 km, 275 K

The lifetimes for loss by reaction with OH shown in Table 1 are for globally averaged, background levels of [OH]. The important aspect to note is that for some species, such as CH_2Br_2 and CH_2BrCl , atmospheric loss is expected to be dominated by reaction with OH. For other gases, such as $CHBr_3$, loss is dominated by photolysis. We expect log-log scatter plots of the abundance of these gases, based on whether the air parcels were sampled *inside* or *outside* regions of deep convective influence, will reveal the signatures of loss by reaction with OH. For a given value of CH_2Br_2 , for instance, the mixing ratio of $CHBr_3$ should be higher inside a convective region than outside (because loss by reaction with OH should be suppressed due to low O_3). CONTRAST will provide the first test of this hypothesis. Although our focus is atmospheric halogens, the hypothesized low [OH] environment of the tropical TTL will result in slow decomposition of any gas whose primary sink is reaction with OH, including CH_4 and CO.

2.2 Evaluate the budget of organic and inorganic bromine and iodine in the TTL

A suite of organic halocarbons are emitted from the tropical ocean by biological processes in near surface waters. Convection transports these gases to the upper troposphere, where they decompose. Past measurements in other parts of the tropics have provided a limited survey of the abundance of organic halocarbons, particularly bromine bearing compounds, at the top of the TTL (e.g., Figure 3, Auxiliary Material, *Salawitch et al.*, 2010). These data clearly establish that the major bromine bearing organic molecules to cross the tropopause in the tropics are CH_2Br_2 and CH_2BrCl , due to their long tropospheric lifetimes (Table 1). All other bromocarbons are mostly lost in the TTL. Whether this distribution is also characteristic of the Western Pacific region, with significant surface emissions and potential for deeper convective penetration into the TTL, will be examined during CONTRAST. As noted above, there is tremendous uncertainty regarding the fate of the inorganic products produced upon decomposition of CBr_y and CI_y species.

Hypothesis 2.2.1. CH_2Br_2 , $CHBr_3$, and other VSL bromocarbons will be elevated in air parcels that have undergone recent deep convection. Figure 4 suggests that air influenced by recent deep convection will have higher abundances of CH_2Br_2 and $CHBr_3$ than air in nearby air parcels. Contrasting profiles will provide an important test for models such as CAM-Chem that was used to generate Figure 4.

The total abundance of organic bromine (CBr_y) and iodine (CI_y) contained in VSL species, for air recently influenced by deep convection, will provide an empirical upper limit for the injection of these halogens into the stratosphere. Measurements of these organic bromocarbons during CONTRAST will provide empirical determination of the total bromine budget of the assemblage of these species for the lower boundary of air sampled during ATTREX.

Hypothesis 2.2.2. When CBr_y and Cl_y species decompose, the resulting inorganic species remain as labile, gas phase species. The test of this hypothesis will be similar to many past studies that have examined atmospheric halogen budgets, such as the study of *Zander et al.* [1996] that provided definitive proof that stratospheric inorganic chlorine species are provided by the decomposition of chlorofluorocarbons. Also, based on the studies cited above, we expect a priori that this hypothesis might be true for bromine and is not likely to be true for iodine! In other words, we expect based on a host of prior studies, summarized in Chapter 2 of *WMO* [2007] and Chapter 1 of *WMO* [2011], that aerosol uptake and washout are more important for iodine than for bromine.

A key aspect enabling this hypothesis to be tested, <u>for the first time during CONTRAST</u>, is the capability for aircraft measurement of concentrations of atomic Br and atomic I, in addition to BrO and IO and other major inorganic halogen species. The low O_3 environment of the tropical UT drives the partitioning of Br_y species towards atomic Br, as shown in Figure 6. During daytime, this photochemical model calculation indicates the vast majority of inorganic bromine should be present as Br. This species converts to either HOBr or BrCl at night, depending on ambient levels of inorganic chlorine, with a brief spike of BrNO₃ occurring just after sunset (Figure 7).

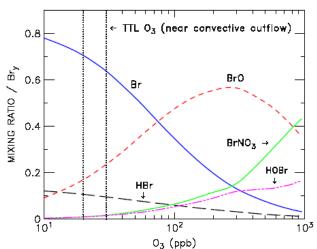


Figure 6. Calculated abundance of inorganic Br_y species, local noon, as a function of O₃. Results are normalized to the total abundance of Br_y (which was set to 4 ppt for this simulation) The photochemical box model of Salawitch et al. [2005] was run for the following inputs: Lat=10°N, T=200 K, p=130 hPa, H₂O=12.5 ppm, CH₄=1.8 ppm, CO=60 ppb, NO_y=400 ppt for O₃ < 100 ppb & NO_y=0.00175×O₃ for O₃ > 230 ppb, and Cl_y=0 The low O₃ environment of the tropical western Pacific TTL is expected to strongly drive the partitioning of inorganic bromine species towards atomic Br. The capability to measure atomic Br and I during CONTRAST is crucial for being able to properly constrain the bromine and iodine budgets.

The CONTRAST flights will include *both daytime and nighttime flights* that, coupled with measurement capability for HOBr and BrCl, will provide definitive quantification of the partitioning of inorganic bromine species. We will define Br_y by summing measured Br and BrO, and I_y by summing measured I and IO. CBr_y and CI_y will be based on the total organic bromine and iodine content of the suite of measured halocarbons. Our preliminary calculations suggest CONTRAST will provide, for the first time, empirical measurement of the vast majority of the total molecular mass of the bromine and iodine families.

If the inorganic products of organic halogen oxidation remain in the gas phase, then Br_y+CBr_y and I_y+CI_y (total Br and total I, respectively) should be relatively constant, with respect to altitude, for air parcels within and without regions of convection. If one family of inorganic halogens is removed by aerosol uptake, there should be a sharp departure from linearity. The CAST flights that will occur at the time of CONTRAST will provide data defining the range of expected values for total Br and total I because, near

the surface, the vast majority of the molecular mass should be present as organic molecules. The ATTREX flights will provide a connection to stratospheric input: as the GH approaches the lower stratosphere, O_3 levels rise, and the titration switches back to BrO, which instruments on the GH will measure.

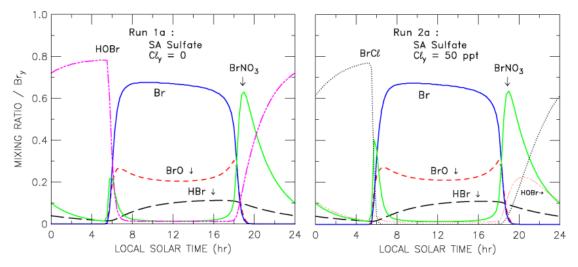


Figure 7. Calculated abundance of inorganic bromine species as a function of local solar time, for conditions of Figure 6, except for $Cl_y = 0$ (left panel) and $Cl_y = 50$ ppt (right panel). The level of Cl_y in the TTL is uncertain: decomposition of VSL chlorocarbons could provide 50 to 100 ppt of Cl_y [Chapter 1, *WMO*, 2011]. Measurement of the HOBr and BrCl during nighttime flights of CONTRAST will provide empirical constraint on levels of Cl_y in the TTL due to decomposition of VSL chlorocarbons and will also provide an important empirical constraint on the diurnal behavior of inorganic bromine species.

2.3 Investigate transport pathways from the oceanic surface to the tropopause using coordinated flights with CAST BAe-146 and ATTREX GH

Limited understanding of both the efficiency of deep convective transport and the rates of transport through the TTL contribute to uncertainties in our ability to predict the composition of air entering the stratosphere. Within the TTL, photochemical reactions and competing physical processes are important for chemical species whose lifetime is comparable to the ~ 2 months that it takes for slow ascent to traverse the TTL. Short-lived precursors of reactive halogen radicals are more likely to reach the stratosphere via rapid and extreme deep convective events that reach the upper TTL. Alternatively, transport through low-O₃ portions of the TTL where the lifetimes of VSL halocarbons lost by reaction with OH are expected to be longer, can provide an effective pathway to the stratosphere (see Section 2.2). In-mixing of air from midlatitudes will increase the age of the air in the TTL and could reduce the input of halogens to the stratosphere (VSL halocarbons are thought to be produced most efficiently in the tropical ocean [Chapter 1, *WMO*, *2011*]. Such in-mixing can also reduce TTL relative humidity and cloud formation [*Fujiwara et al.*, 2009].

Transport of boundary layer air into the TTL is poorly understood, both in terms of the height distribution of convective detrainment in the TTL and in terms of dilution of convective cores by entrainment throughout the free troposphere. Mid-oceanic convergent zones have convective tops that rarely exceed 13.5 km, while a significant percentage of western Pacific boreal winter convection ($\sim 3\%$) reaches the tropopause. These rare convective events can nonetheless be important for transport of VSL halocarbons to the stratosphere, since there is limited tropospheric decomposition and, should decomposition in the troposphere occur, there could be inefficient aerosol uptake and washout due to the arid nature of this region. Entrainment of free tropospheric air into deep convection updrafts is important, particularly for the relatively small convective cores that occur in the tropical maritime regions. Thus, the composition of

air deposited in the TTL at the tops of convection will be a combination of boundary-layer composition and free tropospheric composition.

TTL transport mechanisms are also poorly understood, both in terms of mean rates and variations with longitude and season, reflecting limited observations. In the TTL, latent heat is a small term in the energy budget, and adiabatic cooling (heating) driven by adiabatic ascent (descent) is approximately balanced by radiative heating (cooling). Therefore, calculations or measurements of radiative heating can be used to diagnose large-scale TTL vertical transport. The rate of vertical transport through the TTL and lower stratosphere has been estimated from observations of the water vapor "tape recorder" [*Mote et al.*, 1996; *Niwano et al.*, 2003; *Schoeberl et al.*, 2008], from observations of the CO₂ gradient in the TTL [*Park et al.*, 2010; *Schoeberl et al.*, 2008], and from radiative transfer calculations [*Rosenlof et al.*, 1997]. Since clouds contribute significantly to the TTL radiative heating, there are necessarily strong regional gradients in the radiative heating [*Corti et al.*, 2006; *Yang et al.*, 2010]. As a result, the time scale for vertical transport through the TTL depends sensitively on the pathways taken by air parcels. In boreal winter, the strongest ascent is over the western Pacific [*Fueglistaler et al.*, 2005], with descent occurring below 14 km over much of the tropics. Thus, air parcels that linger in the western Pacific after detrainment from convection can ascend through the TTL in a relatively short time.

Science Goal 2.3. Quantify the relative importance of the following three pathways for trace gas transport from the surface to the stratosphere, based on observations in the tropical TTL:

1) deep convective injection directly into the stratosphere [Danielsen, 1982; Dessler and Sherwood, 2003];

2) convection detrainment into the TTL followed by a slow ascent into the stratosphere [*Holton and Gettelman*, 2001]; and

3) the effect of intrusion from midlatitude lower stratosphere into the tropical TTL, also known as "in-mixing" [*Waugh and Polvani*, 2000; *Konopka et al.*, 2010].

These pathways are expected to have distinct chemical signatures that can be diagnosed with tracer/tracer correlation analysis [e.g., *Marcy et al.*, 2004; *Pan et al.*, 2004, 2007; *Ridley et al.*, 2004; *Avery et al.*, 2011] that will take advantage of measurements from all three aircraft. A combination of tracers with different sources and lifetimes are expected to provide the necessary diagnostics to evaluate different transport pathways. Chemical end members for the potential mixing processes will be well characterized by the combination of CONTRAST/ATTREX/CAST measurements. Thus, marine boundary layer air will be characterized by the measurement of a variety of halocarbons and other marine emissions; air mixing in from the extratropics will be depleted in most organic trace gases, including longer lived halocarbons, and should maintain a high ozone signature; mixing with background air masses from either the N or S hemisphere can be identified from hydrocarbon, HFC, and HCFC signatures.

Mixing timescales can also be attached to the different transport processes. We have already noted the use of short-lived iodine species as a significant indicator of rapid convective transport to the UT. Mixing time scales of convective transport can be inferred from the measured distribution of methyl iodide. Other species with marine origins, such as methyl nitrate and the various bromocarbons, provide additional constraints on the transport timescales. Profiles of these species through the TTL should allow us to evaluate the relative importance of detrainment at different altitudes of convection. Similarly, measurements of CO_2 have been shown to provide a useful "clock" for diagnosing transport rates in the TTL [*Park et al.*, 2007; 2010]. These rates have also been estimated from gradients in hydrochlorofluorocarbon and hydrofluorocarbon mixing ratios. Calculated transport rates are then extremely valuable to assess loss rates and mechanisms for VSLS in the TTL region.

Because this analysis involves measurements from multiple platforms and instruments, a comprehensive effort to compare measurements between platforms will be part of the experimental design. In some

cases, the same investigator has instruments on two platforms, which facilitates comparisons. For other cases, discussions are already underway to compare calibrations and techniques, for example for VSL species measured on the different platforms.

3. Brief description of the experimental design

The experiment will take place during the winter of 2014 based in Guam. The location was chosen to be out of the main convective region, so local conditions are favorable for flight operations. Importantly, the location is well within the range of the tropical warm pool convection to the south and the subtropical jet to the north (See Fig 8). We anticipate approximately 12-15 flights based out of Guam over 6 weeks in the field, plus science ferry flights that will provide measurements in the central and eastern Pacific atmosphere. These flights will investigate regions near and away from active convection over warm pool region, and also transits northward to sample gradients in the lower stratosphere (See EDO). Flights will be coordinated with the collaborating missions (ATTREX and CAST) to achieve individual and common scientific objectives. The flight duration and altitude ranges of the aircraft involved in the mission are highly complementary for studies of tropical convection. The NCAR GV has access to the main altitude of convective outflow altitude centered around 350 K potential temperature (12 - 14 km altitude) and can define conditions in the lower altitudes of the TTL. Furthermore, the GV has the altitude range to reach the lower stratosphere at higher latitudes. The upper altitude limit of the GV (about 14.5 km) leaves off where the lower altitude level of the Global Hawk picks up (about 14 km) going to an eventual altitude ceiling near 19 km. With these two aircraft, we would be able to measure a detailed profile of chemical constituents throughout the TTL and into the lower stratosphere. The UK BAe-146 aircraft has a more limited duration and lower altitude ceiling (about 9 km). This aircraft has a payload designed to characterize chemical emissions and inputs within the marine boundary layer and the lower to mid free troposphere.

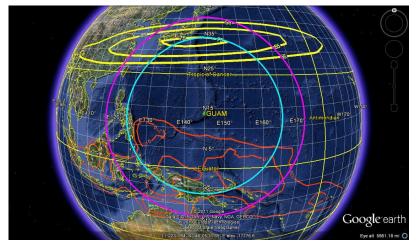


Figure 8. Range of NCAR GV in the CONTRAST study area (cyan (3hr) and purple (4 hr)) from base in Guam; Also shown is contour of outgoing longwave radiation (Red) to demonstrate good access to region of major tropical convection and windspeed (yellow) to indicate access to region of the subtropical jet and mixing gradients between tropics and extratropical air.

Planned measurements from the GV include a range of gases and reactive species necessary to address CONTRAST science goals

(Table 2). Measurement of trace gases with different source emissions, lifetimes (including VSL's), and temporal trends will be used to evaluate transport time scales and mixing processes. These measurements will be done with a combination of whole air sampling, in-situ GC/MS, and high resolution instrumentation for CO, CO₂, and CH₄. Measurements of radiation and relevant reactive gases will define the photochemical environment of the tropical UT to examine the impact of convective inputs of low ozone and elevated marine emissions to the UT. These measurements include actinic flux, ozone, formaldehyde, NO and NO₂, and halogen radical species. The NO_x measurements also provide information on the input of lightning-produced nitric oxide in this area of deep convection. The budget and partitioning of bromine and iodine in the TTL will be evaluated with measurements of the organic halogen precursors and inorganic halogen species.

a whole air sampler and fast GC/MS. The inorganic halogen species will be measured by in-situ instruments (chemical ionization mass spectrometry (CIMS) and resonance fluorescence (ROFLEX) as well as remote sensing (MAXDOAS). The MAXDOAS will provide a link to comparable measurements on the GH and BAe-146 aircraft. Contrast of daytime and nighttime partitioning of inorganic bromine species will test the proposed mechanisms of halogen partitioning that are relevant to the low ozone environment in this region. Finally, aerosol measurements will identify cloud aerosols and aerosol size distributions that may be influential in heterogeneous chemical processing.

Observation	Requirement	Instrument Source & Status	GH	BaE
03	1 ppbv; 10 s	Facility (Fast O3)	Yes	Yes
H ₂ O Vapor	1 – 1000 ppmv; 1 s	Facility (VCSEL)	Yes	Yes
C 0	5%; 10 s	ACD (VUV)	Yes	Yes
CH ₄	5 ppbv; 10 s	ACD (Picarro)	Yes	Yes
C 0 ₂	0.3 ppmv; 10 s	ACD (Picarro)	Yes	Yes
H ₂ CO	25 pptv; 30 s	CU (Laser DFG)	No	No
NO, NO ₂	5 pptv; 10 s	ACD (Chemiluminescence)	No	Yes
BrO, HOBr, Br ₂ , and BrCl (in situ)	2 pptv; 10 s	Facility (CIMS)	No	Yes
BrO, IO, H ₂ CO (remote)	2/1/100 pptv; 10 s	CU-AMAX (DOAS)	Yes	No
Br, I	2 pptv; <10 min	CIAC (Spain) (ROFLEX)	No	No
NMHC, including short lived tracers, HCFCs, halocarbons	Various	Facility (AWAS)	Yes	Yes
Oxygenated VOC, VOC	Various	Facility (TOGA)	No	No
Aerosol (number, size, distribution)	Various	Facility (USHAS)	No	No
Cloud detection		Facility (CDP, 2D-C)	Remote	No
Microwave Temperature Profiler	2 K 6 km above / below aircraft	Facility (MTP)	Yes	No
Radiation (UV/VIS)		Facility (HARP)	Yes	Yes

Table 2. Proposed measurements for the GV and complementary measurements from NASA Global Hawk (GH) and UK BAe-146.

4. Relationship to prior experiments

The study of convection and its impacts on tropospheric chemistry, stratospheric chemistry, meteorology, and climate has been carried out in a variety of programs over many years. The focus on convective processes remains a high priority research area today, as new observational platforms and instrumental techniques open up novel approaches for improved understanding. The CONTRAST mission will advance understanding of chemistry and climate relevance of convective processes from a region long known to be a major avenue for air mass entry to the stratosphere and for contributing to important radiative impacts across the tropics. Several previous experiments have sampled this region, but none have measured a comprehensive suite of chemical tracers for understanding the outflow of convection and the boundary conditions for air in the TTL, and particularly in the Western Pacific. Similarly, recent studies of convection that have contained comprehensive chemical instrument payloads have been designed to study other regions with different convective regimes and chemical emissions. The CONTRAST project, particularly with its multiple aircraft capabilities, will add vital new information for evaluating tropical deep convective processes which can be incorporated into future climate model scenarios.

In the 1970's and 1980's the STEP project in Panama and Darwin sampled the TTL to try to understand the entry of air into the stratosphere. STEP sampled near convection, and measured radon gas near the tropopause, indicating rapid transport from the surface to the tropopause region. STEP also examined the seasonal differences in the water vapor profile in the lower stratosphere, but was mostly focused around the cold point tropopause (18km). Several flights from the TOTE/VOTE and ASHOE/MAESA programs also probed the TTL south of Hawaii. The STRAT campaign was staged from Hawaii during the mid-1990s using the ER-2. STRAT sampled the lower stratosphere in the tropics, but had limited sampling below the cold point near the equator. In 1996, ozone and water vapor measurements were obtained on the ER-2 in the Central Pacific as part of the CEPEX campaign, but without measurements of short-lived species.

Major campaigns have taken place in the tropical Southern Atlantic (TRACE-A); in the Pacific, flying out of Hawaii, Fiji, and Tahiti (PEM-Tropics A and B); and in East Asia (TRACE-P). Analyses of data from these campaigns have shown the importance of ozone precursor emissions from biomass burning in the dry season, and have also invoked an important role for lightning as a source of NO_x upwind of the region of the measurements [*Thompson et al.*, 1996; *Jenkins et al.* 1997; *Schultz et al.*, 1999; *Staudt et al.*, 2002a,b]. These experiments did not, however, probe the TTL above 12km because of the limited altitude of the NASA DC-8.

The European APE-THESEO experiment probed the TTL in the Indian Ocean with the Russian Geophysica high-altitude aircraft. APE-THESEO focused on microphysics and long lived trace species near the cold point, discovering very thin tropical cirrus clouds at the cold point, but with little focus on chemistry or short-lived compounds [e.g., *Stefanutti et al.*, 2004]. Other European campaigns that utilized the Geophysica, plus various balloon and ozonesonde profiles, included SCOUT-ACTIVE (Aerosol and Chemical Transport in Tropical Convection) and SCOUT-AMMA (African Monsoon Multidisciplinary Analysis). The ACTIVE campaign was operated from Darwin in November/December 2005, and examined the "Hector" convective system off Australia. The AMMA mission occurred during the summer monsoon season (Aug., 2006) over Africa.

The CRYSTAL-FACE experiment out of Florida (July 2002) sampled a relatively comprehensive set of chemical tracers, and some short-lived tracers and aerosols from various aircraft platforms. CRYSTAL-FACE has provided several important results, including observations of isotopes of water in the TTL and extensive sampling of convective and cirrus clouds and trace species within them [*Webster and Heymsfield*, 2003]. However, CRYSTAL-FACE sampled mostly subtropical conditions, and while the

cloud processes are analogous to the TTL, the overall conditions in the Western Pacific are far different, with outflow from deep maritime convection in the ITCZ.

The TC4 campaign (Summer, 2007) was the culmination of several earlier Aura Validation Experiments (AVE) which were conducted from Costa Rica [*Toon et al.*, 2010]. The AVE experiments (PreAVE, Winter 2004; and CR-AVE, Winter 2006) utilized the WB-57 platform, and the payload included a number of in-situ aerosol and chemical measurements, and was able to provide several detailed profiles of chemicals, including short-lived halogen species, in the TTL region and to infer transport rates across the TTL [e.g. *Park et al.*, 2007; 2010]. The TC-4 campaign demonstrated the effective use of multiple aircrafts to study tropical convection, with the ability to look simultaneously at inflow and outflow regions as well as transport higher in the TTL [e.g. *Avery et al.*, 2010; *Ashfold et al.*, 2012]. However, the global significance of convection in the TC4 study region is considerably less than that associated with the Tropical Warm Pool, which is the focus of the CONTRAST mission. It is worth noting that the original plans for TC4 were to study the Western Pacific Warm Pool region with multiple aircraft, but deployment costs exceeded available budget limits for the project.

As of this writing, there are currently several missions that will occur during 2012 that are relevant to our proposed research for CONTRAST. The TORERO project will be conducted in January/February in the Eastern Tropical Pacific. Its focus is on the chemistry of oxygenated VOC (OVOC) compounds and halogen chemistry, which has some similarities to the CONTRAST objectives. The stated goal of TORERO is to determine the distributions and controlling factors of OVOC and reactive halogen species concentrations that have recently been observed in the MBL and the FT over the Eastern Pacific Ocean. The primary focus is on understanding the relationship of ocean emissions of VOC and halogen that lead to as yet unexplained abundances of glyoxal (an OVOC) and IO radical in the MBL and the FT. Thus the TORERO project results should be very useful as a contrast to the very different physical environment that CONTRAST will explore over the Western Pacific.

Two other projects that are being planned are the combined DC3/SEAC4RS missions which will occur in early summer to fall, 2012. These missions, too, take advantage of the capabilities of multiple aircraft to target convective processes. The DC3 mission is a 2-aircraft project (NCAR GV and NASA DC8) to study convection and chemistry over the continental US. The focus of the chemical investigation is largely on the inputs of continental boundary layer emissions and subsequent rapid transport and short term (24 -48 hour) chemical processing.

The SEAC4RS project will examine convection associated with the Asian Monsoon circulation, which is a dominant pathway of air entry to the stratosphere in the summertime. The project, to be based in Thailand in late summer 2012, has the goals to examine the sources and transport, particularly of pollutant and biomass burning emissions, from surface sources into the lower stratosphere.

The mission design is similar to the coordinated activity planned for CONTRAST, in that there are 3 aircraft involved: high altitude ER-2; convective outflow altitude NCAR GV; and long-range free-troposphere DC-8, with complementary payloads that include the chemical tracers proposed for CONTRAST. In fact, the SEAC4RS mission will be an excellent complement to the studies of CONTRAST. Both examine major convective systems, but in different seasons and with considerably different source emission characteristics. The SEAC4RS environment is likely to be characterized by large pollutant loads, while the CONTRAST environment will largely deal with clean marine inputs. Certainly, the results and experience from SEAC4RS will help inform the next stages of planning for CONTRAST. In addition, a number of investigators from CONTRAST/ATTREX are also involved in the SEAC4RS project so there will be experience and comparability of data collected in the two campaigns.

The proposed CONTRAST experiment will build upon these previous and upcoming campaigns, examining a set of short-lived chemical tracers that form the boundary condition for the stratosphere, and the aging and transport of the outflow of deep maritime convection in the Western Pacific. None of these previous or planned experiments will have examined the issue of the upper tropospheric bromine budget as is planned for CONTRAST. CONTRAST will carry out studies in a location and season where the chemistry of the stratosphere is uniquely sensitive to the underlying troposphere. This is possible because of: (1) the unique altitude, range and payload capabilities of the GV (2) better measurement capacity for various short-lived species, and (3) synergies with other in-situ and remote sensing platforms that can provide context for observations over the vast regions of the Pacific.

5. Results from past NSF support:

Atlas, E.: Collaborative Research: Stratosphere-Troposphere Analysis or Regional Transport (START) Experiment (2008), NSF# 0723967, 9/1/2007-8/31/2010, \$375,778.

Dr. Atlas was one of the Co-Principal Investigators (with L. Pan, NCAR; K. Bowman, Texas A&M University) of the Stratosphere-Troposphere Analyses of Regional Transport (2008) project. This study was designed to examine the chemical structure of the extratropical UTLS in relation to dynamical processes of a range of scales. One major goal of the START08 project was to use tracer and microphysical measurements to better understand how the observed chemical distributions and relationships map onto the underlying meteorological and dynamical forcing. The experiment was conducted during April-June 2008. Extensive coverage of central North America (25-65°N, 80-120°W) and altitudes from surface to ~ 14.3 km was achieved, and flights were able to sample different meteorological conditions. The Whole Air Sampler on the aircraft (which was built by the PI as a community instrument) typically collected between 48 – 60 samples per flight, with a total of over 1000 samples collected during the mission. From each of these samples, over fifty trace gases were measured. The grant covered the mission planning, deployment, data archiving, and some preliminary analysis. Additional analyses are part of a current NSF grant.

Publications supported by this grant:

- Pan, L. L., et al., (2010): The Stratosphere-Troposphere Analyses of Regional Transport 2008 (START08) Experiment, Bull. Amer. Meteor. Soc. 91, 327-342.
- Pan, L. L., E. L. Atlas, K. P. Bowman, The Stratosphere-Troposphere Analyses of Regional Transport 2008 (START08) Experiment, SPARC Newsletter 34 January 2010.
- Tilmes, S., et al. (2010), An aircraft based upper troposphere lower stratosphere O₃, CO and H₂O climatology for the Northern hemisphere, J. Geophys. Res., 115, D14303, doi:10.1029/2009JD012731.
- Salawitch, R. J., et al. (2010), A New Interpretation of Total Column BrO during Arctic Spring, *Geophys. Res. Lett.*, *37*, L21805, doi:10.1029/2010GL043798.
- Vogel, B., et al. (2011), Transport pathways and signatures of mixing in the extratropical tropopause region derived from Lagrangian model simulations, J. Geophys. Res., 116, D05306, doi:10.1029/2010JD014876
- Homeyer, C.R., et al., (2011), Dynamical and chemical characteristics of tropospheric intrusions observed during START08, J. Geophys. Res., 116, D06111, doi:10.1029/2010JD015098.

REFERENCES

Ashfold, M.J., N. R. P. Harris, E. L. Atlas, A. J. Manning, and J. A. Pyle, Transport of short-lived species into the Tropical Tropopause Layer, *Atmos. Chem. Phys. Discuss.*, *12*, 441-478, 2012.

Avery, M. et al., Convective Distribution of ozone and tracers in the Central American ITCZ region – Evidence from observations during TC4. *J. Geophys. Res.*, 115, D00J21, doi:10.1029/2009JD013450, 2010.

Bergman, J., E. Jensen, L. Pfister, and Q. Yang, Seasonal differences of vertical-transport efficiency in the tropical tropopause layer: On the interplay between tropical deep convection, large-scale vertical ascent, and horizontal circulations, in press, *J. Geophys. Res.*, Jan. 2012.

Butz, A., H. Bösch, C. Camy-Peyret, M. P. Chipperfield, M. Dorf, S. Kreycy, L. Kritten, C. Prados-Roman, J. Schwärzle, and K. Pfeilsticker, Constraints on inorganic iodine in the tropical upper troposphere and stratosphere inferred from balloon-borne solar occultation observations, *Atmos. Chem. Phys.*, *9*, 7229-7242, doi:10.5194/acp-9-7229-2009, 2009.

Corti, T., B. P. Luo, Q. Fu, H. Vömel, and T. Peter, The impact of cirrus clouds on tropical troposphere-to-stratosphere transport, *Atmos. Chem. Phys.*, *6*, 2539–2547, doi:10.5194/acp-6-2539-2006, 2006.

Crawford, J. H., et al., An assessment of ozone photochemistry in the extratropical western, North Pacific: Impact of continental outflow during the late winter/earlier spring, *J. Geophys. Res.*, *102*, 28,469 – 28,487, 1997.

Danielsen, E. F., A dehydration mechanism for the stratosphere , *Geophys. Res. Lett.*, Vol. 9, No. 6, pp. 605-608, doi:10.1029/GL009i006p00605, 1982.

Dessler, A. E. and Sherwood, S. C.: A model of HDO in the tropical tropopause layer, Atmos. Chem. Phys., 3, 2173-2181, doi:10.5194/acp-3-2173-2003, 2003.

Fueglistaler, S., A. E. Dessler, T. J. Dunkerton, I. Folkins, Q. Fu, and P. W.Mote, Tropical tropopause layer, *Rev. Geophys.*, 47, RG1004,doi:10.1029/2008RG000267, 2009.

Fueglistaler, S., Bonazzola, M., Haynes, P. H., and Peter, T.: Stratospheric water vapor predicted from the Lagrangian temperature history of air entering the stratosphere in the tropics, *J. Geophys. Res.*, *110*, D08107, doi:10.1029/2004JD005516, 2005

Fueglistaler, S., H. Wernli, T. Peter, Tropical Troposphere-to-Stratosphere Transport Inferred from Trajectory Calculations, *J. Geophys. Res., 109*, D03108, doi:10.1029/2004JD005516, 2004.

Fujiwara, M., et al., Cirrus observations in the tropical tropopause layer over the western Pacific, *J. Geophys. Res., 114*, D09304, doi:10.1029/2008JD011040, 2009.

Holton, J. R., and A. Gettelman, Horizontal transport and the dehydration of the stratosphere, Geophys. Res. Lett., 28, 2799–2802, doi:10.1029/2001GL013148, 2001.

Jenkins G. S., K. Mohr, V. R. Morris, and O. Arino, The role of convective processes over the Zaire-Congo basin to the southern hemispheric ozone maximum, *J. Geophys. Res., 102*, 8963-18980, 1997.

Kley, D., P. J. Crutzen, H. G. J. Smit, H. Vömel, S. J. Oltmans, H. Grassl, V. Ramanathan, Observations of near-zero ozone concentrations over the convective Pacific: effects on air chemistry, *Science*, *274*, 230-233, doi:10.1126/science.274.5285.230, 1996.

Konopka, P., J.-U. Grooss, G. Günther, F. Ploeger, R. Pommrich, R. Müller, N. Livesey, Annual cycle of ozone at and above the tropical tropopause: observations versus simulations with the Chemical Lagrangian Model of the Stratosphere (CLaMS), *Atmos. Chem. Phys.*, Vol. 10, 121-132, doi:10.5194/acp-10-121-2010, 2010.

Lamarque, J.-F, L. K. Emmons, P. G. Hess, D. E. Kinnison, S. Tilmes, F. Vitt, C. L. Heald, E. A. Holland, P. H. Lauritzen, J. Neu, J. J. Orlando, P. Rasch, G. Tyndall. CAM-chem: description and evaluation of interactive atmospheric chemistry in CESM. *Geosci. Mod. Dev. Discuss.*, *4*, 2199-2278, 2011.

Levine, J. G., Braesicke, P., Harris, N. R. P., Savage, N. H., and Pyle, J. A.: Pathways and timescales for troposphere-to-stratosphere transport via the tropical tropopause layer 15 and their relevance for very short lived substances, *J. Geophys. Res., 112*, D04308, doi:10.1029/2005JD006940, 2007

Marcy, T.P., Fahey, D.W., Gao, R.S., Popp, P.J., Richard, E.C., Thompson, T.L., Rosenlof, K.H., Ray, E.A., Salawitch, R.J., Atherton, C.S., Bergmann, D.J., Ridley, B.A., Weinheimer, A.J., Loewenstein, M., Weinstock, E.M., and Mahoney, M.J., Quantifying Stratospheric Ozone in the Upper Troposphere with in Situ Measurments of HCl, Science, 304, 261-265, 2004.

Mote, P. W., K. H. Rosenlof, M. E. McIntyre, E. S. Carr, J. C.Gille, J. R. Holton, J. S. Kinnersley, and H. C. Pumphrey, An atmospheric tape recorder: The imprint of tropical tropopause temperatures on stratospheric water vapor, *J. Geophys. Res.*, *101*,3989–4006, 1996.

Niwano, M., K. Yamazaki, and M. Shiotani, Seasonal and QBO variations of ascent rate in the tropical lower stratosphere as inferred from UARS HALOE trace gas data, *J. Geophys. Res., 108(D24)*, 4794, doi:10.1029/2003JD003871, 2003.

Ordóñez, C., J.-F. Lamarque, S. Tilmes, D. E. Kinnison, E. L. Atlas, D. R. Blake, G. Sousa Santos, G. Brasseur, and A. Saiz-Lopez. Bromine and iodine chemistry in a global chemistry-climate model: Description and evaluation of very short-lived oceanic sources. *Atmos. Chem. Phys. Discuss.*, *11*, 27421-27474, 2011.

Pan, L. L., J. C. Wei, D. E. Kinnison, R. Garcia, D. J. Wuebbles, and G. P. Brasseur, A set of diagnostics for evaluating chemistry-climate models in the extratropical tropopause region, *J. Geophys. Res.*, 112, D09316, doi:10.1029/2006JD007792, 2007.

Pan, L. L., W. J. Randel, B. L. Gary, M. J. Mahoney, and E. J. Hintsa, Definitions and sharpness of the extratropical tropopause: A trace gas perspective, *J. Geophys. Res.*, *109*, D23103, doi:10.1029/2004JD004982, 2004.

Park, S., Atlas, E. L., Jiménez, R., Daube, B. C., Gottlieb, E. W., Nan, J., Jones, D. B. A., Pfister, L., Conway, T. J., Bui, T. P., Gao, R.-S., and Wofsy, S. C.: Vertical transport rates and concentrations of OH and Cl radicals in the Tropical Tropopause Layer from observations of CO2 and halocarbons: implications for distributions of long- and short-lived chemical species, Atmos. Chem. Phys., 10, 6669-6684, doi:10.5194/acp-10-6669-2010, 2010.

Park, S., R. Jiménez, B. C. Daube, L. Pfister, T. J. Conway, E. W. Gottlieb, V. Y. Chow, D. J. Curran, D. M. Matross, A. Bright, E. L. Atlas, T. P. Bui, R.-S. Gao, C. H. Twohy, and S. C. WofsyThe CO2 tracer clock for the Tropical Tropopause Layer and Lower Stratosphere, ATMOSPHERIC CHEMISTRY AND PHYSICS 7 (14): 3989-4000 2007.

Ridley, B.A., et al., Convective Transport of Reactive Constituents to the Tropical and Mid-Latitude Tropopause Region: I. Observations, *Atmospheric Environment, 38 (9)*, 1259 – 1274, 2004.

Rosenlof, K. H., A. F. Tuck, K. K. Kelly, J. M. Russell, and M. P. McCormick (1997), Hemispheric asymmetries in water vapor and inferences about transport in the lower stratosphere, *J. Geophys. Res.*, *102*, 13,213 – 13,234

Saiz-Lopez, A., J.-F. Lamarque, D. E. Kinnison, S. Tilmes, C. Ordóñez, J. J. Orlando, A. J. Conley, J. M. C. Plane, A. S. Mahajan, G. Sousa Santos, E. L. Atlas, D. R. Blake, S. P. Sander, S. Schauffler, A. M. Thompson, and G. Brasseur, Estimating the climate significance of halogen-driven ozone loss in the tropical marine troposphere, Atmos. Chem. Phys. Discuss., 11, 32003-32029, 2011.

Salawitch, R.J., D.K. Weisenstein, L.J. Kovalenko, C.E. Sioris, P.O. Wennberg, K. Chance, M.K.W., Ko, and C.A. McLinden, Sensitivity of ozone to bromine in the lower stratosphere, *Geophys. Res. Letters*, *32*, L05811, doi:10.1029/2004GL021504, 2005.

Salawitch, R.J *et al.*, A new interpretation of total column BrO during Arctic spring, *Geophys. Res. Lett.*, *37*, L21805, doi:10.1029/2010GL043798, 2010.

Schoeberl, M. R., Douglass, A. R., Stolarski, R. S., Pawson, S., Strahan, S. E., and Read, W.: Comparison of lower stratospheric tropical mean vertical velocities, *J. Geophys. Res, 113*, D24109, doi:10.1029/2008JD010221, 2008.

Schultz, M., et al., On the origin of tropospheric ozone and NOx over the tropical Pacific, *J. Geophys. Res. 104*, 5829-5843, 1999.

Shepherd, T. G., Dynamics, Stratospheric Ozone, and Climate Change, *Atmos. Ocean*, *46*, 117–138 doi:10.3137/ ao.4601062008, 2008.

Staudt, A.C., D. J. Jacob, J. A. Logan, D. Bachiochi, T. N. Krishnamurti, and N. Poisson, Global chemical model analysis of biomass burning and lightning influences over the South Pacific in austral spring, *J. Geophys. Res.*, 107(D14), 4200 - 4216, doi:10.1029/2000JD000296, 2002.

Staudt, A.C., D. J. Jacob, F. Ravetta, J. A. Logan, D. Bachiochi, T. N. Krishnamurti, S. Sandholm, B. Ridley, H. B. Singh, and B. Talbot, Sources and chemistry of nitrogen oxides over the tropical Pacific, *J. Geophys. Res.*, 108(D2), 8239, doi:10.1029/2002JD002139, 2003.

Stefanutti L., et al. The APE-THESEO tropical campaign: An overview, J. Atmos. Chem., 48, 1-33, 2004.

Thompson, A. M., et al., Where did tropospheric ozone over southern Africa and the tropical Atlantic come from in October, 1992? Insights from TOMS, GTE/TRACE-A and SAFARI-92, *J. Geophys. Res.*, 101, 24,251-24,278, 1996.

Thompson, A.M., et al., Strategic ozone sounding networks: Review of design and accomplishments, *Atmos. Environ.*, *45*, 2145 – 2163, 2011.

Toon, O. B., Starr, D. O., Jensen, E. J., Newman, P. A., Platnick, S., Schoeberl, M. R., Wennberg, P. O., Wofsy, S. C., Kurylo, M. J., Maring, H., Jucks, K. W., Craig, M. S., Vasques, M. F., Pfister, L., Rosenlof, K. H., Selkirk, H. B., Colarco, P. R., Kawa, S. R., Mace, G. G., Minnis, P., and Pickering, K. E.: Planning, implementation, and first results of the Tropical Composition, Cloud and Climate Coupling Experiment (TC4), *J. Geophys. Res.*, *115*, D00J04, doi:10.1029/2009JD013073, 2010.

von Glasow, R., R. von Kuhlmann, M. G. Lawrence, U. Platt, and P. J. Crutzen, Impact of reactive bromine chemistry in the troposphere, *Atmos. Chem. Phys. Discuss.*, *4*, 4877–4913, 2004.

Waugh, D. and L.M. Polvani, Climatology of Intrusions into the Tropical Upper Troposphere, *Geophys. Res. Lett*, 27, 3857-3860, 2000.

Webster C. R. and A. J. Heymsfield, Water isotope ratios D/H, ¹⁸O/¹⁶O, ¹⁷O/¹⁶O in and out of clouds map dehydration pathways, *Science*, 302, 1742-1745, 2003.

Wennberg, P. O., J. W. Brault, T. F. Hanisco, R. J. Salawitch, and G. H. Mount, The atmospheric column abundance of IO: implications for stratospheric ozone, *J. Geophys. Res., 102*, 8887-8898, 1997.

Wennberg, P.O., T.F. Hanisco, L. Jaeglé, D.J. Jacob, E.J. Hintsa, E.J. Lanzendorf, J.G. Anderson, R.S. Gao, E.R. Keim, S.G. Donnelly, L.A. DelNegro, D.W. Fahey, S.A. McKeen, R.J. Salawitch, C.R. Webster, R.D. May, R L. Herman, M.H. Proffitt, J.J. Margitan, E.L. Atlas, S.M. Schauffler, F. Flocke, C.T. McElroy, and T.P. Bui, Hydrogen radicals, nitrogen radicals, and the production of O₃ in the upper troposphere, *Science*, *279*, 49-53, 1998.

WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project - Report # 47, Geneva, 2003.

WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project - Report # 50, Geneva, 2007.

WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project - Report # 52, Geneva, 2011.

Yang, Q., Q. Fu, and Y. Hu. Radiative impacts of clouds in the tropical tropopause layer. *J. Geophys. Res.*, 115:D00H12, doi:10.1029/2009JD012393, 2010.

Zander, R., E. Mahieu, M. R. Gunson, M. C. Abrams, A. Y. Chang, M. M. Abbas, C. Aellig, A. Engel, A. Goldman, F. W. Irion, N. Kampfer, H. A. Michelsen, M. J. Newchurch, C. P. Rinsland, R. J. Salawitch, G. P. Stiller, and G. C. Toon, The 1994 northern midlatitude budget of stratospheric chlorine derived from ATMOS/ATLAS-3 observations, *Geophys. Res. Lett.*, 23, 2357–2360, 1996.

I. Table of Participants, Activities, and Estimated Costs

	Institution	Function	Cost Estimate
GV Facility and	NCAR	Deployment pool costs for aircraft	\$ 1,950 K
Aircraft Support		and associated activities	. ,
EOL/CDS/FPS	NCAR	Data management, field catalog,	\$ 450 K
		field planning logistics,	
		education/outreach activities	
Elliot Atlas^	University of Miami	Co-Principal Investigator + Whole	Uncertain (\$500K)
		Air Sampler (HAIS AWAS)	
Ross Salawitch	University of Maryland	Co-Principal Investigator +	Uncertain (\$500K)
		Modeling/Theory Investigations	
Laura Pan	N C A R/A C D	Co-Principal Investigator + Flight	ACD
		Planning/Modeling+ Data	
Alex Evied		Management	
Alan Fried	University of Colorado	Formaldehyde measurement	Uncertain (\$640K)
Alfonso Saiz-	Lab. for Atmos. and	Br/I measurement: ROFLEX	Supported by PI funds
Lopez	Climate Science; Toledo, Spain		Tullus
Dan Riemer^	University of Miami	VOC measurement: HAIS TOGA	Uncertain (\$ 380K)
Greg Huey	Georgia Institute of	In-situ: BrO, BrCl, HOBr/Br2:	Uncertain (\$500K)
areg haey	Technology	HAIS CIMS	
Mark Zondlo^	Princeton University	Water Vapor: HAIS VCSEL	Uncertain (\$ 400K)
Rainer	University of Colorado	BrO + MAXDOAS:GV	Uncertain (\$500K)
Volkhamer		measurement	· · · · · · · · · · · · · · · · · · ·
Eric Apel	NCAR/ACD	VOC measurement: HAIS TOGA	Included
Frank Flocke	NCAR/ACD	CH4/CO2 measurement: PICARRO	ACD
		CRD	
Teresa Campos	NCAR/ACD	CO measurement: VUV	Included
Sam Hall	N C A R/A C D	HARP: GV Radiation	Included
		measurements	
Andy	N C A R/A C D	NO/NO2/O3: GV measurement	ACD
Weinheimer			
Facility support	NCAR/RAF	Aerosols and Cloud instrumentation	included
Julie Haggerty	NCAR/RAF	Microwave Temperature Profiler	Included
John Bergman	NCAR/ACD	Modeling/Meteorology	ACD
Bill Randel	NCAR/ACD	Modeling/Satellite	ACD
Doug Kinnison	NCAR/ACD	Modeling/WACCM	ACD
Jean-Francois	NCAR/ACD	Modeling: Chemistry Climate	ACD
Lamarque	- Destat		A 401/
	Project	Additional Shipping PI support	\$40K
Lonnio Dfister	Project	Contingency	\$200 K
Lennie Pfister	NASA	ATTREX Principal Investigator + meteorology	No cost
Eric Jensen	NASA	ATTREX Principal Investigator	No cost
Neil Harris	University of Cambridge	CAST Principal Investigator	No cost
	oniversity of Californuge	TOTAL ESTIMATE	110 6081
		Deployment + Special Costs	\$2,400 K
		Investigator Costs*	\$2,400 K \$3,420 K
		Additional	\$ 240 K
		Auuitional	¢ 240 N

*If not estimated by individual, assumes \$500K total for 3 year project. ^Affiliated with requested HAIS instruments (AWAS, TOGA, VCSEL); PI's to be involved in mission planning, deployment, and post mission science. Partial TOGA support included in RAF estimate. No support for WAS or VCSEL included in RAF cost estimate.

NAME: William Randel

INSTITUTION: NCAR

POTENTIAL SPONSOR: NCAR

Scientific Interests:

• Large-scale circulation and transport in the UTLS. Dynamics of the tropical tropopause layer, and links between convection and transport to the stratosphere.

Role during the field campaign/Instrument description/etc.:

• Theoretical guidance for flight planning and measurement strategies. Initial interpretation of meteorological and chemical measurements.

<u>Planned activity post campaign</u>

• Analysis of aircraft measurements in the context of large-scale circulation and transport behavior derived from satellite data and meteorological analyses. Use of chemical constituents to derive transport behavior.

NAME: Jean-François Lamarque

INSTITUTION: NCAR

POTENTIAL SPONSOR: (NSF, NCAR, or other?): NCAR

Scientific Interests:

- Upper-tropospheric chemical composition and role of convection
- Role of VSLS halogens in ozone budget in the tropical UT
- •
- •

Role during the field campaign/Instrument description/etc.:

- Chemistry forecast (using CAM-chem)
- •
- •

Planned activity post campaign

• Global tropospheric chemistry modeling (using CAM-chem)

Estimated Budget:

• N/A

NAME: Doug Kinnison

INSTITUTION: National Center for Atmospheric Research (NCAR)

POTENTIAL SPONSOR: Currently funded 50% by NSF (core funding) and 50% NASA ACMAP (Title: The Impact of Short Lived Halogen Species on the Troposphere and Stratosphere)

Scientific Interests:

- What is the role of convection in transporting organic and inorganic species into the tropical tropopause layer (TTL). Specifically, can observations of very short-lived (VSL) halogens help constrain transport pathways into the tropical upper troposphere and lower stratosphere in a 3D chemistry-climate model (CCMs)?
- What is the role that VSL organic bromine and iodine species have on the ozone budget in the tropical troposphere and lower stratosphere?
- How can analysis of aircraft missions improve physical, dynamical, and chemical processes in CCMs for future use in international assessments (e.g., WMO, IPCC)?

Role during the field campaign/Instrument description/etc.:

• Will apply the specified dynamics version of the NCAR Whole Atmosphere Community Climate model (SD-WACCM) in forecast mode to assist in mission operation and planning. SD-WACCM will be nudged with meteorological fields from the NASA Global Modeling and Assimilation Office (GMAO) Goddard Earth Observing System Model, Version 5 (GEOS–5) forcast and reanalysis products. Here, temperature, zonal and meridional winds, and surface pressure are used to drive the physical parameterization that control boundary layer exchanges, advective and convective transport, and the hydrological cycle.

<u>Planned activity post campaign</u>

- We quantify the role of boundary layer ventilation, advection [isentropic transport], and convection, by use of special tracers of transport and use of budget terms for the different chemical species. Based on these analyses, we will adjust model convective transport and cloud processes to attempt to match observations of VSL species in the tropical upper troposphere and lower stratosphere.
- SD-WACCM results will be made available to the CONTRAST science team.

Estimated Budget:

• NA

NAME: John W. Bergman

INSTITUTION: BAERI/NCAR-ACD

POTENTIAL SPONSOR: NASA

Scientific Interests:

- Understand chemical composition of air entering the tropical stratosphere
- Understand transport of air from the tropical boundary layer to the stratosphere
- Identify strengths and weaknesses of LaGrangian transport (air parcel trajectory) models for simulating transport from the tropical boundary layer to the stratosphere.

Role during the field campaign/Instrument description/etc.:

- Work as part of the forecast/nowcast team for flight planning before and during the flights
- Analyze meteorological fields to identify regions of interest for the flights and identify hazardous flying conditions

Planned activity post campaign

- Perform modeling and interpretation of observations that will help us identify the convective sources of and understand the transport mechanisms for air traversing the tropical tropopause layer
- Use aircraft measurements to identify strengths and weaknesses of LaGrangian transport models for simulating transport from the tropical boundary layer to the stratosphere.

Estimated Budget:

• No cost to NSF

NAME: Julie Haggerty

INSTITUTION: NCAR

POTENTIAL SPONSOR: NCAR

Scientific Interests:

Exploring the use of high spatial and temporal resolution temperature profiles from the Microwave Temperature Profiler (MTP) for understanding variability of the vertical temperature structure in the troposphere and lower stratosphere.

Role during the field campaign/Instrument description/etc.:

- Operate the MTP and monitor data quality
- Provide real-time and preliminary post-processed temperature profile data to other PIs

Planned activity post campaign

Since I'm not very familiar with the objectives of CONTRAST at this point, I can't be too specific about post-campaign activities. In general, I would hope to collaborate with PIs who can utilize MTP profiles for dynamic studies, retrievals of other quantities that depend on temperature, locating the tropopause, etc.

Estimated Budget:

n/a

Georgia Tech Chemical Ionization Mass Spectrometer (GT-CIMS)

Principal Investigator: L. Gregory Huey (greg.huey@eas.gatech.edu)

Co-Investigators: David Tanner (tanner@eas.gatech.edu), John Nowak (john.nowak@noaa.gov), and Andy Neuman (andy.neuman@noaa.gov)

Potential Sponsor: NSF

<u>Instrument</u>

A CIMS instrument will be deployed on the NCAR G-V during the CONTRAST mission to measure inorganic halogen compounds. The CIMS consists of a low pressure ion molecule reactor (IMR) coupled to a quadrupole mass filter by an actively pumped collisional dissociation chamber (CDC) and an octopole ion guide. The CIMS utilizes a small vacuum chamber (100 mm OD), 9.5 mm quadrupole rods, and is evacuated with two small turbo pumps (70 1 s⁻¹). The IMR is evacuated with a small scroll pump (100 1 min⁻¹). The CDC is a short 80 mm diameter chamber that houses an octopole ion guide and is evacuated with a hybrid molecular drag pump.

Detected Species and Data

The CIMS will be configured to detect bromine oxide (BrO), hypobromous acid (HOBr), molecular bromine (Br₂), and bromine chloride (BrCl). These species will be detected by association reactions with iodide analogous to the reaction for BrO given below.

$$I^- + BrO \rightarrow IBrO^-$$

Detection limits for all species are expected to be of the order of a few pptv for a one second integration period. BrO will be measured each second with a duty cycle of 50%, the other species will be monitored with the remaining duty cycle. The accuracy of the measurements is expected to be of the order of 30%.

Configuration for CONTRAST

The CIMS instruments will be mounted in a standard HIAPER rack. The rack will house the CIMS, pumps, calibration sources, control and acquisition electronics, and an automated zeroing valve. One large gas cylinders will be mounted external to the rack. The instrument will be calibrated semi-continuously with a standard of Br₂. The background signals will be measured periodically by scrubbing the sampled air with glass wool.

<u>References:</u>

Liao, J., H. Sihler, L.G. Huey, J.A. Neuman, D. J. Tanner, U. Friess, U. Platt, F. M. Flocke, J.J. Orlando, H.J. Beine, A. Weinheimer, *S.J. Sjostedt*, J.B. Nowak, D.J. Knapp, R.M. Staebler, W. Zheng, R. Sander, S. R. Hall, and K. Ullman (2011), A comparison of Arctic BrO measurements by chemical ionization mass spectrometery and long-path-differential optical absorption spectroscopy, *J. Geophys. Res.*, doi:10.1029/2010JD01478.

NCAR NO-NO₂ & O₃ Instruments

Investigators: Andrew J. Weinheimer (wein@ucar.edu) Teresa L. Campos (campos@ucar.edu) Frank M. Flocke (<u>ffl@ucar.edu</u>)

Source of Funding: NCAR [ACD/EOL]

Instrument Description and Background:

The 2-channel NO-NO₂ instrument is integrated with the 1-channel O₃ instrument. Both are based on chemiluminescence detection employing the reaction of NO with O₃ to form excited NO₂, which is detected via photon counting. For NO-NO₂, one sample channel is used to measure nitric oxide via addition of reagent O₃, and the second measures nitrogen dioxide by first flowing sample air through a glass cell illuminated by light-emitting diodes at 395 nm, for the conversion of NO₂ to NO via photolysis. The instrument is similar to instruments previously built at NCAR [Ridley and Grahek, 1990]. The O₃ instrument operates similarly, except with addition of reagent NO to the sample stream.

Configuration on GV for CONTRAST:

The instruments can fly as stand-alone instruments, but for CONTRAST there will be a significant sharing of components. This will result in considerable weight, space, and power savings for the overall payload. The items to be shared include these: data acquisition and control system, power distribution and power supplies, vacuum pump, pressure-control valve, zero air bottle, and inlet. The entire installation will occupy approximately three-fourths of a pair of racks plus some floor space. One rack is devoted to NO-NO₂, and the companion rack is devoted to O₃ along with the VUV instrument for CO and the Picarro instrument for CO₂ and CH₄. Thus the O₃ instrument is fully integrated with NO-NO₂, O₃, CO, and CO₂-CH₄ instruments.

<u>Data:</u>

Data will be recorded at 10 Hz, though the true frequency response is not that fast, and data will be archived at 1 Hz. The precision of 1-s values of NO and NO₂ are estimated to be in the range of 5-10 pptv, dependent on performance characteristics to be determined in flight. Overall uncertainty of 1-sec values is estimated to be 10% or better for large mixing ratios (> 50 pptv). For O₃, overall uncertainty is 5% and the detection limit is better than 0.1 ppbv.

<u>Reference:</u>

Ridley, B.A.; Grahek, F.E. (1990), A small, low flow, high-sensitivity reaction vessel for NO chemiluminescence detectors, J. Atmos. Oceanic Technol, 7, 307-311.

Instrument: Aero-Laser 5002 G-V Carbon Monoxide Instrument (RAF_CO)

Pl contact: Teresa Campos (<u>campos@ucar.edu</u>) or Frank Flocke (ffl@ucar.edu), Community Airborne Research Instrumentation Group, National Center for Atmospheric Research, 3090 Center Green Drive, Boulder, CO 80301, USA. 303-497-1048 or 1457 (v), 303-497-1092 (f)

Instrument Precision: 2 ppbv for a 10-second averaging time Resolution: 1-second Overall Uncertainty: \pm (2 ppbv + 5 %)

Principle of Operation: The NCAR/NSF G-V vacuum UV resonance fluorescence instrument is a commercial version of the instrument published by Gerbig, et al.(Journal of Geophysical Research, Vol. 104, No. D1, 1699-1704, 1999). The source is a flowing RF discharge gas lamp emitting in the VUV. An optical filter provides a narrow band of source radiation centered at 151 nm with a 10 nm bandpass. CO fluorescence is detected using photon counting. The internal data system can accommodate sampling rates from 1-18 samples/second. The instrument was integrated into the HAIS ozone instrument rack and shared a pressure-controlled inlet.

Calibrations: In-flight calibrations are conducted using a working standard and a catalytically scrubbed zero trap for background subtraction. A series of NOAA ESRL/GMD primary standard compressed gases are used in lab measurements to quantify the concentration of the working standard cylinder. Two to three replicates of these standardizations are conducted prior to and after the intensive field phase of the experiment. Additional characterizations are performed as needed upon replacement or re-filling of the working standard cylinder.

Data Set Details: The CO mixing ratio in ppbv is displayed on the analyzer in real-time. Real-time in flight data are transmitted to the Aircraft Data System (ADS) and can be displayed at any station in the aircraft or on the ground using Aeros. Users can connect remotely with the analyzer's internal Windows-based PC and control it through a standard Remote Desktop connection or with similar remote login software. Postprocessing of data is necessary but field data typically is delivered real-time to the RAF data system and is typically accurate to better than 20%. These data (containing signal background measurements and calibrations) are typically available within hours of the end of a flight as part of the RAF data release.

Installation: For CONTRAST, the VUV CO analyzer can be integrated into one standard GV rack together with the Picarro CO2/CH4 instrument and the fast-ozone instrument, with the NO/NO2 analyzer integrated into a second rack. These racks need to be mounted immediately adjacent to one another because there are shared components (data system, pumps, gases). This configuration is currently flown on the GV for the DC3 mission. One calibration gas clinder (shared with Picarro CO2/CH4) is required on the aircraft. The instrument also requires N2 for purging and CO2 in Ar as lamp gas. These two small cylinders typically are part of the rack installation.

Radiation instrumentation on the NCAR/NSF G-V during CONTRAST

NAME: Samuel R. Hall

INSTITUTION: NCAR

POTENTIAL SPONSOR: NCAR/EOL

<u>Scientific Interests:</u> *In situ* solar radiation measurements are critical to atmospheric composition research. Actinic flux radiation drives the chemistry of the atmosphere, including the evolution of ozone, greenhouse gases, halogens and other anthropogenic and natural trace constituents. The evolution of boundary layer and tropospheric constituents convected to the upper troposphere and lower stratosphere requires knowledge of the complex radiative fields expected during the CONTRAST campaign. In addition, spectrally resolved stabilized irradiance allows determination of numerous cloud and aerosol radiative properties. From the stabilized irradiance, the University of Colorado Atmospheric Radiation Group (ARG) determine layer properties, such as reflectance, transmittance and absorbance, surface albedo and other properties using radiative transfer modeling.

<u>Instrument description:</u> The HIAPER Airborne Radiation Package (HARP) instrumentation is a comprehensive atmospheric radiation suite to measure spectrally resolved actinic flux and horizontally stabilized irradiance. HARP was developed in a collaborative effort between NCAR, the University of Colorado, the Leibniz-Institute for Tropospheric Research, Metcon, Inc and Enviscope GmbH. The package is part of the HIAPER Aircraft Instrumentation Solicitation (HAIS), funded by NSF.

Actinic Flux: CCD actinic flux spectroradiometers provide *in situ* down- and up-welling actinic flux density spectra from approximately 280 to 680 nm at a data frequency of up to 1 Hz. From the measured flux, the NCAR Atmospheric Radiation and Measurements (ARIM) group calculates photolysis frequencies for important atmospheric trace gases including O₃, NO₂, CH₂O, HONO, HNO₃, N₂O₅, HO₂NO₂, PAN, H₂O₂, CH₃OOH, CH₃ONO₂, CH₃CH₂ONO₂, CH₃COCH₃, CH₃CHO, CH₃CHO, CH₃CHO, CH₃CHO, CH₃CHO, CH₃CHO, CH₃CHO, CH₃COCHO, CH₃CHO, CH₃COCH₂CH₃, Br₂, BrO, Br₂O, BrNO₃, BrCl, HOBr, BrONO₂, Cl₂, ClO, and ClONO₂ using a modified version of the NCAR Tropospheric Ultraviolet and Visible (TUV) radiative transfer model.

Irradiance: Silicon and InGaAs irradiance detectors provide down- and up-welling flat plate irradiance from 300 to 2400 nm with a data frequency of 1 Hz. The irradiance optical collectors are mounted on actively stabilized platforms to maintain horizontal stability up to 5 degrees in aircraft pitch and roll.

Planned activity post campaign

HARP data will be combined with trace gas measurements to model the chemical steady state and evolution and to determine the radiative environment and energy transfer along the flight path in the CONTRAST region.

NAME: Dr. Alan Fried (PI)

INSTITUTION: Institute for Arctic and Alpine Research (INSTAAR) at the University of Colorado

POTENTIAL SPONSOR: NSF

Scientific Interests:

- Characterization of the efficiency in transporting formaldehyde into the TTL
- Improve our understanding of soluble gas-ice interactions during such vertical transport
- Further development/refinements of theories to describe soluble gas cloud removal efficiencies and/or production from cloud outflow and heterogeneous processing
- Improve our understanding of enhanced formaldehyde production in the presence of elevated NO from lightning and the correlations with enhanced HO₂ production

Role during the field campaign/Instrument description/etc.:

- Instrument preparations prior to field campaign (calibration of standards and flow calibrations; operation of instrument in lab and cross check against another lab instrument; clean/replace cell mirrors as necessary; peak up performance; implement any necessary software and hardware upgrades/modifications; procure necessary backups)
- Operation of CAMS instrument (Compact Atmospheric Multispecies Spectrometer) for fast (1sec) airborne measurements of formaldehyde (CH₂O) during the campaign.
- Formaldehyde is measured using infrared absorption spectroscopy. Specifically, the absorption of an IR laser source (difference frequency generation, DFG, laser) is measured as the laser is scanned through isolated and relatively strong CH₂O absorption features at 3.53-microns. The laser is directed through a low volume multipass absorption cell (1.7-liters, 90-meters pathlength, 164 reflections) where a continuously flowing air stream at a reduced pressure around 50-Torr is sampled. A more comprehensive instrument description is given in the write up that follows.

Planned activity post campaign

- Submittal of field data during the mission and ultimately quality-controlled final data within 6 months of the field campaign.
- Work with modelers to address the various scientific issues above as well as additional ideas that arise once all the data has been submitted

Estimated Budget:

Estimated budget exclusive of field travel and shipping costs:

2013	2014	2015	Total
160 k	280 k	200 k	640 k

These estimates are to cover the partial salaries of 4 soft-money positions at INSTAAR, potential graduate students, and purchase of expendables.

NAME: Daniel Riemer - University of Miami, Eric Apel - NCAR

INSTITUTION:

POTENTIAL SPONSOR: Riemer – NSF, Apel - NCAR

Scientific Interests:

• Assessing the prevalence, transport and atmospheric influence of VOCs in the tropical western Pacific atmosphere, with particular emphasis on marine- sourced, short-lived compounds.

Role during the field campaign/Instrument description/etc.:

• Measurement of an extensive range of VOCs, including NMHCs, OVOCs, and halocarbons, acetonitrile and DMS. Measurements will be made with the HIAPER-TOGA (Trace Organic Gas Analyzer), a high speed chromatography based airborne GC/MS capable of measuring in excess of 60 organic compounds every two minutes at all altitudes accessible by the NSF-GV aircraft.

Planned activity post campaign

• Post campaign efforts include data quality checks, data compilation, and data analysis using simple atmospheric photochemical models, and in collaboration with others, more complex simulations. Because different source emissions and atmospheric lifetimes exist for many of our measured compounds, our data will be useful for evaluating transport times, mixing processes, and loss patterns. The data will also support improved knowledge of linkages between surface ocean emissions and the chemistry in the atmosphere. Finally, better understanding of the upper troposphere photochemical environment, including the photochemical O₃ budget will be possible.

Estimated Budget:

• Estimated budget includes salary, benefits, student costs, supplies, travel, and indirect costs for D. Riemer – Univ. Miami. Estimated costs - \$380,000. The NCAR portion is not included.

NAME:	Prof. Rainer Volkamer
INSTITUTION:	University of Colorado, Boulder
POTENTIAL SPONSOR:	NSF

Scientific Interests:

Combine CU Airborne MAX-DOAS and in-situ observations aboard multiple aircrafts, and satellites in support of CONTRAST goals:

- Characterize the pre- and post-convective chemical composition over the full tropospheric column.
- Measure the chemical gradients in the UTLS associated with the dynamical background of deep convection over the Western Pacific Ocean, and contrast the Western Pacific Ocean with the Eastern Pacific Ocean (investigated during TORERO)
- Study effects of emissions from anthropogenic and natural sources (e.g., marine, terrestrial biogenic, volcanic) on oxidative capacity, and the formation and lifetime of climate active gases (i.e., O3, DMS, methane) and aerosols.
- Establish novel linkages between datasets collected aboard the NASA GH, and UK FAAM aircrafts, satellites and atmospheric models.

Role during the field campaign/Instrument description/etc.:

- Participate in the Science planning of CONTRAST activities
- Deploy the CU AMAX-DOAS aboard the NSF/NCAR GV to provide remote sensing measurements of reactive trace gases directly in the open atmosphere, incl. bromine oxide (BrO, 1ppt), iodine oxide (IO, 0.1 ppt), formaldehyde (HCHO, 120 ppt), glyoxal (CHOCHO, 3ppt), nitrogen dioxide (NO2, 10 ppt), chlorine dioxide (OClO, 0.7 ppt), nitrous acid (HONO, 15 ppt), water vapor (H2O, 2ppm), and oxygen dimers (O4) at three wavelengths (multispectral aerosol extinction, 0.01-0.03 km⁻¹). Values in brackets correspond to detection limits in the free troposphere.

Planned activity post campaign

- Data reduction to derive trace gas vertical column amounts, and vertical profiles for all the above species, and aerosol extinction vertical profiles, and aerosol optical depth at 360nm, 477nm, and 577nm.
- Perform an integrated analysis in context of other remote sensing data aboard the GV, and other platforms that constrain radiation fields (cloud optical thickness, effective radius; aerosol optical properties) as an additional quality assurance measure.
- Exploit existing data synergies for correlative analysis between aerosol/cloud optical properties and chemical indicator gases measured by CU AMAX-DOAS over similar spatial scales.
- Combine CU AMAX-DOAS and in-situ observations aboard the GV, between multiple aircrafts, and satellites. Assess and bridge to spatial scales sampled by satellite (OMI), and predicted by atmospheric models.

Estimated Budget: ca. 500k \$ over three years

CONTRAST-investigator 1-pager

NAME: Mark A. Zondlo INSTITUTION: Princeton University POTENTIAL SPONSOR: NSF

Scientific Interests:

The trends of water vapor in the lower stratosphere significantly modify the surface temperature trends arising from anthropogenic greenhouse gases. Because the tropical western Pacific warm pool is the entrance location for significant amounts of stratospheric air, it is necessary to understand the input levels of water vapor at the base of the tropical tropopause layer and what governs its distribution at fine scales (0.2-100 km). Because the G-V will probe the main detrainment altitudes of tropical convection, CONTRAST provides an ideal case study to examine the transport of water vapor to the base of the TTL as well the mechanisms that form ice supersaturated regions, the precursor conditions necessary for cirrus cloud formation. We will use the photochemical and microphysical tracers during CONTRAST to help understand the distribution of water vapor, and relative humidity, at the base of the TTL. The data will help to improve parameterizations for heterogeneous chemistry of halogen species, HO_x production, and cirrus cloud formation in the TTL.

Role during the field campaign/Instrument description/etc.:

- 1 Hz water vapor measurements at <3% precision from 1-35,000 ppmv; accuracy 5% from the vertical cavity surface emitting laser hygrometer (VCSEL) 25 Hz measurements will also be available upon request
- field support including quick look data submission, routine ground-based maintenance and quality control checks, repairs in the field when possible

<u>Planned activity post campaign</u>

- Calibrations over relevant pressures, temperatures, and mixing ratios
- Analyses of the spatial distribution and variability of relative humidity at sub-grid scales (0.25-100 km) including ice supersaturated regions
- Dynamical conditions that drive the variability of water vapor in the TTL
- Provide a calibrated, quality-controlled water vapor dataset to the archive

Estimated Budget:

 \$400,000/3 years (postdoctoral and grad. student support for ~ two years, materials and supplies, and travel)

J. Principal Scientific Personnel and Collaborators for CONTRAST

Table J.1 Principal Scientific Personnel for CONTRAST

INVESTIGATOR	INSTITUTION	ACTIVITY
Elliot Atlas	University of Miami	Co-Principal Investigator +
		Whole Air Sampler
Ross Salawitch	University of Maryland	Co-Principal Investigator +
		Modeling/Theory
		Investigations
Laura Pan	NCAR/ACD	Co-Principal Investigator +
		Flight Planning/Modeling
Alan Fried	University of Colorado	Formaldehyde measurement
Alfonso Saiz-Lopez	Laboratory for Atmospheric	Br/I measurement: ROFLEX
	and Climate Science; Toledo,	
	Spain	
Dan Riemer	University of Miami	VOC measurement: TOGA
Greg Huey	Georgia Institute of	In-situ: BrO, BrCl, HOBr/Br2:
	Technology	HAIS CIMS
Mark Zondlo	Princeton University	Water Vapor: HAIS VCSEL
Rainer Volkhamer	University of Colorado	BrO + MAXDOAS: GV
		measurement
Eric Apel	NCAR/ACD	VOC measurement: HAIS
		TOGA
Frank Flocke	NCAR/ACD	CH4/CO2 measurement:
		PICARRO CRD
Teresa Campos	NCAR/ACD	CO measurement: VUV
Sam Hall	NCAR/ACD	HARP: GV Radiation
		measurements
Andy Weinheimer	NCAR/ACD	NO/NO2/O3: GV
T 1' T T		measurement
Julie Haggerty	NCAR/RAF	Microwave Temperature
		Profiler
John Bergman	NCAR/ACD	Modeling/Meteorology
Bill Randel	NCAR/ACD	Modeling/Satellite
Doug Kinnison	NCAR/ACD	Modeling/WACCM
Jean-Francois Lamarque	NCAR/ACD	Modeling: Chemistry Climate
COLLABORATORS		ATTDEV Dringing1
Lennie Pfister	NASA	ATTREX Principal Investigator + meteorology
Eric Jensen	NASA	8
	INADA	1
Neil Harris	University of Cambridge	Investigator CAST Principal Investigator



19 Jan 2012

Prof. Elliot Atlas RSMAS Miami, FL 33149

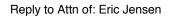
I acknowledge that I am identified by name as a international collaborator in the proposal entitled "CONvective Transport of Active Species in the Tropics (CONTRAST)" that is being submitted by Prof. Elliot Atlas, Prof. Ross Salawitch and Dr. Laura Pan to the National Science Foundation. I understand that this project is designed to provide a comprehensive suite of airborne measurements needed to characterize the effect of deep convection on the chemical environment of the tropical western Pacific TTL. My primary role in this project will be to provide measurements of Br and I atoms via deployment of our Resonance and Off resonance Fluorescence by Lamp Excitation (ROFLEX) instrument.

I understand that the extent and justification of my participation as stated in this proposal will be evaluated during peer review in determining the merits of this proposal. I have read the entire proposal, including the management plan and budget, and I agree that the proposal correctly describes my commitment to the proposed investigation.

Sincerely,

Alfonso Saiz-Lopez Director Laboratory for Atmospheric and Climate Science (CIAC) CSIC - JCCM c/ Rio Cabriel S/N 45007 Toledo, Spain Office: +34 925245364 Fax: +34 925245377 E-mail: a.saiz-lopez@ciac.jccm-csic.es National Aeronautics and Space Administration

Ames Research Center Moffett Field, California 94035-1000



24 January, 2012

Professor Elliot Atlas Marine and Atmospheric Chemistry Rosenstiel School of Marine & Atmospheric Science 4600 Rickenbacker Causeway Miami, FL 33149 USA

Dear Elliot

I am very interested in collaborating with you on the CONTRAST proposal that you are proposing to NSF with Laura Pan and Ross Salawitch. The combination of the CONTRAST measurements and the measurements from the NASA ATTREX project, which I am leading, would greatly enhance the science potential of each program.

ATTREX (Airborne Tropical TRopopause Experiment) is a 5-year mission focused on Tropical Tropopause Layer (TTL). It involves multiple campaigns with the NASA long-range Global Hawk Unmanned Air System, including a January-February 2014 deployment to Guam, which would be coordinated with CONTRAST if it is supported. The ATTREX Global Hawk payload includes measurements of numerous tracers, brominated hydrocarbons, water vapor, clouds, and radiative fluxes. These measurements provide considerable overlap with the planned CONTRAST GV payload, and the two aircraft complement each other in terms of vertical sampling. The Global Hawk will predominantly be sampling the upper TTL (above the ceiling of the GV – approximately 14.5 km), while the GV can sample the primary convective detrainment altitude range (11-14 km).

The combination of the CONTRAST and ATTREX measurements would allow us to fully address the science issues of TTL composition and transport. I am therefore fully supportive of the CONTRAST proposal. If it is successful, we would be happy to collaborate with the CONTRAST investigators, including coordinated flight planning, joint science team meetings, and full data sharing

Sincerely,

Dr. Eric Jensen



European Ozone Research Coordinating Unit

Department of Chemistry, University of Cambridge

European Ozone Research Coordinating Unit Department of Chemistry, University of Cambridge Lensfield Road Cambridge CB2 1EW, England Telephone: +44 (0)1223 311772 Fax: +44 (0)1223 763818 Email: Neil.Harris@ozone-sec.ch.cam.ac.uk Web: http://www.ozone-sec.ch.cam.ac.uk

5 January, 2012

Professor Elliot Atlas Marine and Atmospheric Chemistry Rosenstiel School of Marine & Atmospheric Science 4600 Rickenbacker Cswy Miami, FL 33149 USA

Dear Elliot

Many thanks for sending me the information about the CONTRAST proposal you are preparing with Laura Pan and Ross Salawitch. As we discussed at AGU, there is great potential collaboration between CONTRAST and the UK CAST project which I am coordinating.

CAST (Co-ordinated Airborne Studies in the Tropics) is NERC-funded project which will investigate processes in the Tropical West Pacific in cooperation with the NASA ATTREX project. It will involve the UK NERC BAe-146 with a payload measuring a range of atmospheric tracers in order to study how compounds are transported into the upper troposphere and lower stratosphere. There is a particular emphasis on halogen-containing gases as one of the scientific aims is investigate their role in the chemistry of the Tropical troposphere and stratosphere. The main deployment will be in Guam in January/February 2014, and the BAe-146 will concentrate on surveying the composition of the lower troposphere with the Global Hawk measuring in the upper troposphere and lower stratosphere.

Clearly these plans would be significantly enhanced if the GV could participate within CONTRAST. This would enable measurements to made in the lower part of the main convective outflow which will not be well sampled by the BAe-146 (too high) or the Global Hawk (too low). The range of the GV would mean that much larger areas of the lower atmosphere could be sampled than is possible with the BAe-146.

I am thus very supportive of the CONTRAST proposal. If it is successful, the CAST consortium will willingly collaborate with you as we are with ATTREX. This collaboration includes joint project and science meetings, joint flight planning and data sharing.

Best Wishes

ONPElanie

Dr Neil Harris NERC Advanced Research Fellow

National Aeronautics and Space Administration

Ames Research Center Moffett Field, California 94035-1000

Reply to Attn of: L. Pfister



15 January, 2012

Professor Elliot Atlas Marine and Atmospheric Chemistry Rosenstiel School of Marine & Atmospheric Science 4600 Rickenbacker Causeway Miami, FL 33149 USA

Dear Elliot

I am very interested in collaborating with you on the CONTRAST proposal that you are proposing to NSF with Laura Pan and Ross Salawitch. The combination of the CONTRAST measurements and the measurements from the NASA ATTREX project, for which I am the deputy principal investigator and lead meteorologist, would greatly enhance the science potential of each program.

ATTREX (Airborne Tropical TRopopause Experiment) is a 5-year mission focused on Tropical Tropopause Layer (TTL). It includes a January-February 2014 deployment to Guam, which would be coordinated with CONTRAST if it is supported. The ATTREX Global Hawk payload includes measurements of numerous tracers, brominated hydrocarbons, water vapor, clouds, and radiative fluxes. These measurements provide considerable overlap with the planned CONTRAST GV payload, and the two aircraft complement each other in terms of vertical sampling. The Global Hawk will predominantly be sampling the upper TTL (above the ceiling of the GV – approximately 14.5 km), while the GV can sample the primary convective detrainment altitude range (11-14 km).

As lead meteorologist and flight planner, I expect to collaborate with CONTRAST counterparts to allow the science objectives of both missions to be fulfilled. This includes sharing forecast products, software, and, as appropriate, personnel effort.

The combination of the CONTRAST and ATTREX measurements would allow us to fully address the science issues of TTL composition and transport. I am therefore fully supportive of the CONTRAST proposal.

Sincerely,

Dr. Leonhard Pfister

Biographical Sketch: Elliot L. Atlas

a) Professional Preparation

Antioch College, Yellow Springs, Ohio Chemi	stry	B.S., 1970
Oregon State University, Corvallis, Oregon	Chemical Oceanography	M.S., 1973
Oregon State University, Corvallis, Oregon	Chemical Oceanography	Ph.D., 1975

b) Appointments

Professor, Department of Marine and Atmospheric Chemistry, Rosenstiel School of Marine and Atmospheric Science, University of Miami, (Aug) 2003 – present.

Affiliate Scientist, National Center for Atmospheric Research, Oct., 2003 - present

Senior Scientist, National Center for Atmospheric Research, Section Head, 1999 – 2003

Stratospheric/Tropospheric Measurements Section Head, NCAR, Atmospheric Chemistry Division, 1992-2003.

Scientist III, National Center for Atmospheric Research, Atmospheric Chemistry Division, 1991-1999 Visiting Scientist, National Center for Atmospheric Research, Atmospheric Chemistry Division, 1989-1991

Visiting Research Scientist, Department of Marine Science, University of South Florida, 1988 Associate Research Scientist, Department of Oceanography, Texas A&M University, 1985-1991 Visiting Associate Professor of Environmental Chemistry, University of Pittsburgh, Graduate School of Public Health, 1984

Research Scientist, Chemistry Department, Texas A&M University, 1978-1984

Research Associate, Chemistry Department, Texas A&M University, 1976-1978

Assistant Professor, Department of Geological Sciences, California State University, 1975-1976

c) 5 Publications Relevant to Proposed Research (from over 200 total)

- Ashfold, M.J., N. R. P. Harris, E. L. Atlas, A. J. Manning, and J. A. Pyle, Transport of short-lived species into the Tropical Tropopause Layer, Atmos. Chem. Phys. Discuss., 12, 441-478, 2012
- Saiz-Lopez, A., J.-F. Lamarque, D. E. Kinnison, S. Tilmes, C. Ordóñez, J. J. Orlando, A. J. Conley, J. M. C. Plane, A. S. Mahajan, G. Sousa Santos, E. L. Atlas, D. R. Blake, S. P. Sander, S. Schauffler, A. M. Thompson, and G. Brasseur, Estimating the climate significance of halogen-driven ozone loss in the tropical marine troposphere, Atmos. Chem. Phys. Discuss., 11, 32003-32029, 2011
- R. Hossaini, M. P. Chipperfield, W. Feng, T. J. Breider, E. Atlas, S. A. Montzka, B. R. Miller, F. Moore, and J. Elkins, The contribution of natural and anthropogenic very short-lived species to stratospheric bromine, Atmos. Chem. Phys., 12, 371-380, 2012
- Aschmann, J., B.-M. Sinnhuber, E. Atlas, and S. Schauffler. Modeling the transport of very short-lived substances to the tropical upper troposphere and lower stratosphere. Atmos. Chem. Phys., 9, 9237-9247, 2009.
- Pan, L., K. P. Bowman, E. Atlas, S. C. Wofsy, F. Zhang, J. Bresch, B. A. Ridley, J. V. Pittman, C. Homeyer, P. Romashkin, W. Cooper, Stratosphere-Troposphere Analyses of Regional Transport Experiment. Bulletin of the American Meteorological Society, 91: 327-342, 2010.

d) 5 Additional publications

- Wofsy, S. et al., HIAPER Pole-to-Pole Observations (HIPPO): Fine grained, global scale measurements for determining rates for transport, surface emissions, and removal of climatically important atmospheric gases and aerosols., Proceedings of the Royal Society A:, 10.1098/rsta.2010.0313 Phil. Trans. R. Soc. A 28 May 2011 vol. 369 no. 1943 2073-2086.
- Park, S., Atlas, E. L., Jiménez, R., Daube, B. C., Gottlieb, E. W., Nan, J., Jones, D. B. A., Pfister, L., Conway, T. J., Bui, T. P., Gao, R.-S., and Wofsy, S. C.: Vertical transport rates and

concentrations of OH and Cl radicals in the Tropical Tropopause Layer from observations of CO2 and halocarbons: implications for distributions of long- and short-lived chemical species, Atmos. Chem. Phys., 10, 6669-6684, doi:10.5194/acp-10-6669-2010, 2010B.

- Quack, E. Atlas, G. Petrick, D. Wallace, Bromoform and dibromomethane above the Mauritanian upwelling: Atmospheric distributions and oceanic emissions, J. Geophys. Res., 112, D09312, doi:10.1029/2006JD007614, 2007.
- Ridley, B.A., E. Atlas, H. Selkirk, L. Pfister, D. Montzka, J. Walega, S. Donnelly, V. Stroud, E. Richard, K. Kelly, A. Tuck, T. Thompson, J. Reeves, D. Baumgardner, W. T. Rawlins, M. Mahoney, R. Herman, R. Friedl, F. Moore, E. Ray, J. Elkins, Convective Transport of Reactive Constituents to the Tropical and Mid-Latitude Tropopause Region: I. Observations, *Atmos. Environ.*, 38, 9,1259-1274, 2004.
- Schauffler, S. M., E. L. Atlas, D. R. Blake, F. Flocke, X. Tie, R. A. Lueb, J. M. Lee, V. Stroud, W. Travnicek, Distributions of brominated organic compounds in the troposphere and lower stratosphere, J. Geophys. Res. D17, 21,513-21,536, 1999.

e. Synergistic Activities

Dr. Atlas has worked in a wide variety of research on atmospheric and marine chemistry. Most recently his main focus has been to examine sources, distributions, and chemistry of trace gases associated with tropospheric and stratospheric ozone. Development of new sampling and analytical technologies has been an ongoing and complementary activity. In addition to his own research, Dr. Atlas has been co-chief scientist on several large community research projects (MLOPEX, TOPSE, START08) and has contributed as a science team member on numerous other large-scale community research efforts in both stratospheric and tropospheric chemistry (MIRAGE, AVE missions, SOLVE, POLARIS, NASA GTE, ITCT, ICARTT, TEXAQS, CALNEX, HIPPO, etc.). Dr. Atlas also serves the atmospheric sciences community as the editor for the Journal of Atmospheric Chemistry. While at NCAR, Dr. Atlas actively mentored students and interns and hosted visitors to his laboratory to extend national and international collaborative research.

<u>f. Collaborators and Affiliations</u>

I) necent conaborators		
B. Ridley, NCAR	F. Flocke, NCAR	E. Apel, NCAR
S. Schauffler, NCAR	S. Montzka, NOAA	J. Elkins, NOAA
J. Butler, NOAA	N. Blake, UCI	T. Ryerson, NOAA
B. Yokelson, UM	W. Sturges, UEA	A. Chuck, UEA
B. Quack, Kiel Inst.	D. Riemer, U Miami	D. Blake, UCI
D. Parrish, NOAA	R. Weber, GIT	C. Reeves, UEA
J. Williams, MPI	J. DeGouw, NOAA	C. Warnecke, NOAA
B. Sive, UNH	B. Lefer, UHouston	S. Wofsy, Harvard
K. Bowman, TAMU	S. Tilmes, NCAR	A. Engel, Goethe University
R. Salawitch, UMd	S. Brown, NOAA	R. Volkhamer,CU

ii) Previous Co-Editors (Journal of Atmospheric Chemistry) A. Wahner, KFA Juelich Y. Kondo, U. Tokyo C. Granier, IPSL, Paris

iii) Graduate and Post-doctoral Advisors

M.S. Advisor, Lou Gordon (Oregon State University); Ph.D. Advisor, Ricardo Pytkowicz (Oregon State University); Post-doctoral Advisor, C.S. Giam (Texas A&M University)

iv) Graduate Students Hua Xie (MS student), Katrina Smith (Ph.D. student)

BIOGRAPHICAL SKETCH: ROSS J. SALAWITCH

Professional Preparation

B.S., Applied and Engineering Physics, Cornell University (1997–1981)
M.S., Applied Physics, Harvard University (1981–1982)
Ph.D., Applied Physics, Harvard University (1982–1987)
Postdoctoral Research Fellow, Harvard University (1988–1991)

Appointments

Research Associate, Harvard University (1991–1994) Jet Propulsion Laboratory (1994–2007) Research Scientist, Atmospheric Chemistry Research Element (1994–2003) Principal Scientist, Earth and Space Sciences Division (2003–2007) California Institute of Technology (1998–2007) Visiting Research Associate (1998–2007) Visiting Faculty Associate (2005) Lecturer (2007) University of Maryland, College Park (2007–present) Professor (2007–present)

Publications most relevant to this proposal

- Choi, S. *et al.*, Analysis of satellite-derived Arctic tropospheric BrO columns in conjunction with aircraft measurements during ARCTAS and ARCPAC, *Atmos. Chem. Phys. Discuss.*, *11*, 26173–26243, doi:10.5194/acpd-11-26173-2011, 2011
- Liao, L. *et al.*, Characterization of soluble bromide measurements and a case study of BrO observations during ARCTAS, *Atmos. Chem. Phys. Discuss.*, *11*, 26999–27030, doi:10.5194/acpd-11-26999-2011, 2011.
- Salawitch, R.J., P.O. Wennberg, G.C. Toon, B. Sen, and J.-F. Blavier, Near IR photolysis of HO₂NO₂: Implications for HO*x*, *Geophys. Res. Lett.*, *29*, doi:10.1029/2002GL015006, 2002.
- Salawitch, R.J. *et al.*, Sensitivity of ozone to bromine in the lower stratosphere, *Geophys. Res. Lett.*, *32*, L05811, 2004GL021504, 2005.
- Salawitch, R.J *et al.*, A new interpretation of total column BrO during Arctic spring, *Geophys. Res. Lett.*, 37, L21805, doi:10.1029/2010GL043798, 2010.

Other publications

- Canty, T. *et al.*, Nighttime OCIO in the winter Arctic vortex, *J. Geophys. Res.*, *110*, D01301, doi:10.1029/2004JD005035, 2005.
- Salawitch, R. J., Atmospheric chemistry-biogenic bromine, Nature, 349, 275-277, 2006.
- Sioris, C. E. *et al.*, Latitudinal and vertical distribution of bromine monoxide in the lower stratosphere from SCIAMACHY limb scattering measurements, *J. Geophys. Res.*, 111, D14301, doi:10.1029/ 2005JD006479, 2006.
- Wamsley, P.R. *et al.*, Distribution of halon-1211 in the upper troposphere and lower stratosphere and the 1994 total bromine budget, *J. Geophys. Res.*, *103*, 1513-1526, 1998.
- Wennberg, P.O. *et al.*, Hydrogen radicals, nitrogen radicals, and the production of O₃ in the upper troposphere, *Science*, *279*, 49-53, 1998.

Synergistic Activities

Participant in numerous atmospheric chemistry field campaigns, including the recent NASA ARCTAS and TC4 and European RECONCILE campaigns, as well as past campaigns including AASE, AASE-2, ASHOE/MAESA, POLARIS, SPADE, SOLVE, and VINTERSOL.

Collaborators and co-Editors

B. Anderson (LaRC), E. Atlas (Miami), J. Austin (NOAA), J. Barret (SUNY), R. Basilio (JPL), S. Bekki (UPMC), S. Biraud (LBNL), D. Blake (UCI), G. Boedeker (NIWA), H. Bösch (Leicester), P. Braesicke (Cambridge), L. Brown (JPL), W. Brune (PSU), T.P. Bui (NASA Ames), N. Butchart (UKMO), T. Canty (UMd), R. Castano (JPL), K. Chance (Harvard CFA), C. Chen (JPL), G. Chen (LaRC), M. Chipperfield (Leeds), S. Choi (Ga Tech), B. Connor (BC Cons.), J. Crawford (LaRC), N. Cressie (OSU), D. Crisp (JPL), J. Curry (Ga Tech), A. da Silva (GSFC), N. Deutscher (Bremen), S. Dhomse (Leeds), J. Dibb (UNH), G. Diskin (LaRC), A. Douglass (GSFC), A. Eldering (JPL), V. Eyring (DZLR), B. Fisher (JPL), M. L. Fisher (LBNL), F. Flocke (NCAR), C. Frankenberg (JPL), R. Gao (LaRC), D. Griffith (Wollongong), M. Gunson (JPL), F. Hendrick (BIRA-IASB), R. Hoff (UMBC), L. G. Huey (Ga Tech), D. Jacob (Harvard), B. Johnson (NOAA), P. Johnston (NIWA), J. Joiner (GSFC), E. Kyrö (FMI), L. Jourdain (Orléans), G. Keppel-Aleks (Caltech), D. Kinnison (NCAR), K. Kreher (NIWA), S. Kremser (NIWA), T. Kurosu (JPL), A. Kuze (JAEA), J. Lamarque (NCAR), P. Levelt (KNMI), Q. Li (UCLA), Q. Liang (GSFC), J. Liao (Ga Tech), X. Liu (Harvard CFA), J. Logan (Harvard), L. Mandrake (JPL), J. McDuffie (JPL), J. Messerschmidt (Caltech), C. Miller (JPL), I. Morino (NIES), V. Natraj (JPL), J. A. Neuman (CIRES), J. Nielsen (GSFC), J. Notholt (Bremen), J.B. Nowak (CIRES), D. O'Brien (CSU), C. O'Dell (CSU), S. Oltmans (NOAA), L. Oman (GSFC), G. Osterman (JPL), F. Oyafuso (JPL), L. Pan (NCAR), S. Pawson (GSFC), R. B. Pierce (NESDIS), D. Plummer (EC), I. Polonsky (CSU), J. Pyle (Cambridge), A. Richter (Bremen), J. Robinson (NIWA), J. Rodriguez (GSFC), C. Roehl (Caltech), E. Rozanov (ETHZ), T. Ryerson (NOAA), S. Sander (JPL), R. Schofield (AWI), J. Scinocca (EC), T. Shepherd (Toronto), V. Sherlock (NIWA), W. Simpson (UAF), M. Smyth (JPL), R. Stolarski (Hopkins), K. Strong (Toronto), J. Stutz (UCLA), R. Sussmann (IMK-IFU), H. Suto (JAEA), T. Tanaka (NIES), T. Taylor (CSU), S. Tilmes (NCAR), A. Thompson (PSU), D. Thompson (JPL), G. Toon (JPL), O. Uchino Y(NIES), M. Van Roozendael (BIRA-IASB), T. Warneke (Bremen), D. Waugh (Hopkins), A. Weinheimer (NCAR), P. Wennberg (Caltech), S. Wofsy (Harvard), D. Wunch (Caltech), Y. Yung (Caltech), J. Ziemke (GSFC)

Graduate and Postdoctoral Advisors

M. McElroy and S. Wofsy, Harvard Univ., Cambridge, MA.

Thesis Advisor and Postgraduate-Scholar Sponsor

Graduate students (3 total, all in past 5 yrs): L. Hembeck, N. Mascioli, and J. Nicely, Univ of Md. Postdocs (3 total, none in past 5 yrs): T. Canty and G. Osterman, JPL; M. Rex, AWI, Potsdam, Germany.

Biographical Sketch: Laura Pan (L. Laura Ting)

Atmospheric Chemistry Division (ACD) National Center for Atmospheric Research (NCAR) Boulder, CO 80307-3000

Phone: (303) 497-1467 Fax: (303) 497-1400 Email: liwen@ucar.edu

(a) Professional Preparation

Beijing Normal University, Beijing, China, Physics, B.S., 1981. The Johns Hopkins University, Baltimore, Maryland, Physics, M.S., 1982; Ph.D., 1987. National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, Quantum Physics, Postdoc, 1987-1990.

(b) Appointments

Scientist III, Atmospheric Chemistry Division (ACD), National Center for Atmospheric Research (NCAR), 2008 - present

Scientist II, ACD/NCAR, 2005-2008

Project Scientist II, ACD/NCAR, 1998-2005

Scientist I, ACD/NCAR, 1992-1997

Senior Scientist, Hughes STX Corporation, 1991-1992

Assistant Research Scientist, Institute for Physical Science and Technology (IPST), University of Maryland, 1990-1991.

(c) Selected Publications

(i) Five most related to the project

- Pan L.L. and L. A. Munchak, (2011), Relationship of cloud top to the tropopause and jet structure from CALIPSO data, *J. Geophys. Res.*, 116, D12201, doi:10.1029/2010JD015462.
- Pan, L. L., K. P. Bowman, E. L. Atlas, S. C. Wofsy, F. Zhang, J. F. Bresch, B. A. Ridley, J. V. Pittman, C. R. Homeyer, P. Romashkin, W. A. Cooper, 2010: The Stratosphere-Troposphere Analyses of Regional Transport 2008 (START08) Experiment, *Bull. Amer. Meteor. Soc.* 91: 327-342.
- Grubisic, V., J.D. Doyle, J. Kuettner, S. Mobbs, R.B. Smith, C.D. Whiteman, R. Dirks, S. Czyzyk, S.A. Cohn, S. Vosper, M. Weissmann, S. Haimov, S.F.J. De Wekker, L. L. Pan, and F.K. Chow, 2008: The Terrain-Induced Rotor Experiment. *Bull. Amer. Meteor. Soc.*, 89, 1513-1533.
- Pan, L. L., et al., 2007: Chemical behavior of the tropopause observed during the Stratosphere-Troposphere Analyses of Regional Transport experiment, *J. Geophys. Res.*, 112, D18110, doi:10.1029/2007JD008645.
- Pan, L. L., J. C. Wei, D. E. Kinnison, R. R. Garcia, D. J. Wuebbles, and G. P. Brasseur 2007: A set of diagnostics for evaluating chemistry-climate models in the extratropical tropopause region, *J. Geophys. Res.*, 112, D09316, doi:10.1029/2006JD007792.

(ii) Five Other

• Gettelman, A., P. Hoor, L. L. Pan, W. J. Randel, M. I. Hegglin, and T. Birner (2011), The Extratropical upper troposphere and lower stratosphere, *Rev. Geophys.*, 49, RG3003, doi:10.1029/2011RG000355.

- Homeyer, C. R., K. P. Bowman, L. L. Pan, M. A. Zondlo, and J. F. Bresch (2011), Convective injection into stratospheric intrusions, J. Geophys. Res., 116, D23304, doi:10.1029/2011JD016724.
- Kunz, A., P. Konopka, R. Müller, and L. L. Pan (2011), Dynamical tropopause based on isentropic potential vorticity gradients, *J. Geophys. Res.*, 116, D01110, doi:10.1029/2010JD014343.
- Pan, L. L., W. J. Randel, J. C. Gille, W. D. Hall, B. Nardi, S. Massie, V. Yudin, R. Khosravi, P. Konopka, and D. Tarasick (2009), Tropospheric intrusions associated with the secondary tropopause, J. Geophys. Res., 114, D10302, doi:10.1029/2008JD011374.
- Pan, L. L., W. J. Randel, B. L. Gary, M. J. Mahoney, and E. J. Hintsa, 2004: Definitions and sharpness of the extratropical tropopause: A trace gas perspective, *J. Geophys. Res.*, 109, D23103, doi:10.1029/2004JD004982.

(d) Synergistic Activities

- Program Lead, NCAR UTLS program
- Field Campaigns using the NCAR GV:
 - Principal Investigator, GV platform for the Southeast Asia Composition, Cloud, Climate Coupling Regional Study (SEAC4RS) experiment, Member of SEAC4RS Lean Team, 2011-2012
 - Principal Investigator, Stratosphere-Troposphere Analyses of Regional Transport 2008 (START08) experiment, April-June 2008.
 - Co-Investigator, Terrain-Induced Rotor Experiment (T-REX), March-April, 2006.
 - Principal Investigator, Stratosphere-Troposphere Analyses of Regional Transport 2005 (START05) experiment, December 2005.
- Contributing author for the SPARC report on the Evaluation of chemistry-climate models

Thesis Advisor and Postgraduate-Scholar Sponsor

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