Aviation-Climate Change Research Initiative
(ACCRI)

Subject specific white paper (SSWP) on

UT/LS chemistry and transport

SSWP # I

Darin Toohey, PI
University of Colorado-Boulder

Linnea Avallone, co-I
University of Colorado-Boulder

Martin Ross, co-I
Aerospace Corporation

January 25, 2008

Table of Contents

Executive Summary

Aircraft emissions of particles, particle precursors, NOx, and water vapor, can have significant impacts on chemistry in the upper troposphere and lower stratosphere (UT/LS). Previous groups have assessed the important terms involving UT/LS chemistry and noted the following issues that limit the ability to reduce uncertainties in assessments of aircraft impacts:

- Incomplete knowledge of exhaust emissions of gases (primarily sulfur oxides) and particles (e.g., soot) and their geographic and altitudinal distributions.
- Important discrepancies between modeled and measured distributions of key HOx and NOx radical species involved in ozone formation and destruction.
- Poor understanding of the sources of NOx in the upper troposphere, especially lightning.
- Incomplete knowledge of the evolution of NOx and NOy in aircraft plumes during the first ~24 hours following emission.
- Incomplete understanding of, and potential non-linearities in, the coupling among CH_4, CO, OH and O_3 in the troposphere.
- Potential scavenging and removal of NOx by aerosols and cirrus.
- Limited understanding of atmospheric transport, especially that between the stratosphere and troposphere.

This SSWP summarizes important results in key areas since the last major aircraft impacts assessment [IPCC 1999]. Significant progress has been made in the areas of:

- Measurements of emissions of chemi-ions, NOx, and trace organic species from aircraft engines.
- Observations constraining the lightning and convective fluxes of NOx to the upper troposphere.
- Measurements of HOx, its precursors, and coupled NOx/HOx chemistries in the UT.
- Rates rate and extent of conversion of NOx to NOy in the UT.
- New observations of water vapor and particles that help to constrain important processes that determine stability of cirrus clouds and persistent contrails.
- Model studies of the impact of aircraft emissions of particles on ozone in the UT/LS.
- Model studies of the potential role for destruction of ozone in the UT by heterogeneous reactions involving halogen species.

In addition to studies that can lead to improvements in our understanding of the impacts of aircraft emissions, there are longstanding issues and new observations that raise important new questions about our understanding of UT/LS chemistry that may have significant, including:
- Ongoing discrepancies of upwards of 30% between observations of water vapor in the cold, dry upper troposphere and lower stratosphere that limit our ability to

46   predict formation and persistence of cirrus clouds and, hence, their impact on the
47   budgets of trace species that control ozone abundances in the UT/LS.
48   • Important discrepancies between modeled and observed HOx species (primarily
49   HO_2) at high NO values in the region where subsonic aircraft emissions represent
50   the most significant perturbation to chemistry.
51   • New observations of heterogeneous activation of chlorine in the tropopause
52   region.
53   • Observations that indicate greater abundances of inorganic bromine than
54   previously believed, presumably due to more efficient transport of short-lived
55   bromine sources to the UT.
56   • Observations of significant uptake of nitric acid in ice particles and an increased
57   role for HNO_3 in the stability of ice in the UT/LS.
58

59 Perhaps the most significant new result related to the impacts of some of these new
60 findings is that of Sovde et al. [2007] that shows a reversal in the sign of ozone response
61 to increased aircraft emissions in the UT, primarily as a result of heterogeneous chemistry
62 on particles. If confirmed, this result could have important implications for the sign and
63 magnitude of climate impacts due to aircraft.
64

65 These results, if studied with the best modeling tools available, should help constrain the
66 role of aircraft emissions on chemistry in the UT/LS. It is expected that the new result
67 will imply a diminished enhancement of ozone due to NOx/hydrocarbon chemistry in the
68 UT, and possibly ozone losses in some regions where aircraft emissions enhance the
69 production of particulate surfaces areas or the lifetimes of cirrus clouds. Constraints on
70 OH abundances throughout the troposphere should reduce the uncertainties in modeled
71 impacts of aircraft emissions on the lifetime of methane, which is currently believed to
72 have a negative forcing on climate. Finally, modeling studies of the sensitivity of ozone
73 and HOx to heterogeneous processes, including sedimentation of particles that contain
74 HNO_3 and halogen activation, should help to define the range of possible impacts these
75 processes, which are currently poorly understood, could have.
76

77 Ideally, to make the best use of the new results in a future aircraft impacts assessment, the
78 following issues will need to be better understood. Progress in all areas is likely to take
79 the concerted efforts of a number of research groups involved in atmospheric
80 measurements (both in situ and from satellites) and modeling programs designed to
81 explore the new results in great detail. Among the issues identified in this SSWP are:
82

83
84
85
86
87
88
89
90
91

- Resolving discrepancies in water vapor measurements should be the highest priority for addressing remaining uncertainties in UT/LS chemistry. It would also be desirable to develop a standard for water vapor measurements under cold, dry conditions so that more costly large-scale intercomparisons and validations can be infrequent. This top priority cannot be overlooked – anything less, and it is likely that in a few years' time, a similar group will be making the same recommendation. Validations of temperature should be a nearly equal priority, and should be feasible with a small augmentation to a water vapor program.

92
93
94
95
96
97
98
99
100
101

- Addressing gaps in measurement capabilities for species that are important in assessing the impact of heterogeneous reactions and plume dispersion processes. Programs should be started very soon, even with limited funds, so that investigators have confidence that in a few years' time they will be able to participate in missions of opportunity. Priority should be placed on instrumentation with a heritage, even if from other platforms, so that development of calibrations and standards does not take up a significant fraction of the available resources. Instruments using new techniques would be desirable in a few cases for corroboration of the most critical measurements.

102
103
104
105
106
107
108
109

- Developing a strategy for model simulations to assess the range of possible impacts and that incorporate new results, especially those relating to plume dispersion and non-linear effects. The program should focus on assessing the range of impacts over a wide set of boundary conditions for those processes that are currently unconstrained by observations (e.g., redistribution of nitric acid by sedimentation, chlorine and bromine chemistry, unknown coupled HOx/NOx chemistry, errors in water vapor and supersaturation).

110
111
112
113

- Guided by results from studies of the above issues, new questions should be developed to help guide measurement programs (dedicated or flights of opportunity).

114
115
116
117
118
119
120
121
122
123

- Convene annual meetings of investigators participating in aviation impacts-related activities to foster frequent exchange of ideas. Rather than a comprehensive meeting, discussion of presentations and discussions should focus on results of studies that reduce the critical uncertainties in aircraft impacts or studies that highlight new and important processes that could result in a major shift in understanding of those processes. The community should be conditioned to respond quickly and productively to new developments and shifting priorities, much like the atmospheric chemistry community responded to the ozone hole and methyl bromide issues.

1. Introduction and Background

Exhaust emissions from aircraft contribute to degradation of urban air quality near airports [Carslaw et al., 2006; Farias and Simon, 2006; Peace et al., 2006, and Pison and Menut, 2004] and can influence background atmospheric chemistry in major flight corridors [Klemm et al., 1998]. They may also impact global climate directly by enhancing the greenhouse effect and indirectly by altering the properties of background atmospheric aerosol and cloud particles in the upper troposphere and lower stratosphere (UT/LS), thereby affecting absorption, emission, and transmission of both visible and infrared radiation [IPCC, 1999]. In order to accurately attribute the atmospheric impacts of current aviation operations, and reliably predict future impacts, it is necessary to have a good understanding of the gaseous and particulate emissions of different aircraft types, as well as an understanding of the fundamental chemical and dynamical processes that occur in the relevant regions of the atmosphere.

The goals of this White Paper are to summarize the ways in which aircraft emissions impact atmospheric chemistry in the UT/LS, to examine what has been learned since the last major assessments, and to prioritize future scientific studies that can reduce the most important uncertainties that remain and that address new problems that have arisen.

2. Processes that Impact Climate

2.a. Current State of the Science

Two previous assessments have thoroughly reviewed the important properties of emission products that are thought to be the most relevant to atmospheric chemistry [IPCC, 1999; Brasseur et al., 1998]. Based on these reports, the most important products of combustion of aircraft fuel (e.g., kerosene) are CO_2, H_2O, NOx, soot, and oxides of sulfur. All of these species interact strongly with infrared or visible light, serving to directly warm or cool the planet. Some can alter the nature and radiative properties of particulate matter (e.g., aerosols and clouds) or can promote formation of new particles by changing the extent of supersaturation through influence on temperature and water vapor abundances. Some, such as NOx and soot, can also have important indirect impacts on the atmosphere, including subtle shifts in chemical balance that can alter the natural abundances of radiatively important gases such as O_3 and CH_4, or cause the redistribution of naturally occurring species such as H_2O and HNO_3 via sedimentation of large particles. Finally, through influences on radiation balance, these emissions can impact atmospheric transport, especially between the troposphere and stratosphere.

These different, and in some cases offsetting, effects have been studied before in some detail. IPCC [1999] identified warming due to enhancements of CO_2, contrails and cirrus, and O_3 (which is thought to be increased by NOx chemistry), and cooling by CH_4 (which is thought to decrease as a result of enhancements of OH by NOx chemistry), as the most likely to have significant impacts on climate. It was believed that only one of these processes, warming by CO_2, was well understood, whereas the relative scientific understanding of the others was listed as fair to poor. An update of this assessment by Sausen et al. [2005], recognized that work published since the turn of the century reduced some of the key uncertainties. Nevertheless, the limited understanding of those processes

170 continues to represent a major hurdle to reducing the overall uncertainties in aviation
171 impacts [Wuebbles et al., 2006]. Of particular interest are impacts of NOx on the
172 chemistry of ozone and on the budget of methane, which together could represent more
173 than half of the total impact of aircraft emissions on climate. If aviation transport
174 continues to grow, it is estimated that the number of flights will double from present rates
175 by about 2025 [Cox, 2007]. Unless major changes to combustion systems can be
176 implemented, aircraft emissions can also be expected to nearly double by 2025.
177 Consequently, the impacts of aviation operations on climate and the oxidative capacity of
178 the atmosphere are of great interest.
179
180 Both the IPCC [1999] and the Workshop on the Impacts of Aviation on Climate Change
181 [Wuebbles et al., 2006, hereafter called the "2006 Workshop"] concluded that the
182 following processes that influence NOx chemistry contributed most to uncertainties in
183 assessments of the impact of the chemistry of aircraft exhaust on Earth's climate:
184   (1) Incomplete knowledge of exhaust emissions of gases (primarily sulfur oxides) and
185   particles (e.g., soot) and their geographic and altitudinal distributions.
186   (2) Important discrepancies between modeled and measured distributions of key HOx
187   and NOx radical species involved in ozone formation and destruction.
188   (3) Poor understanding of the sources of NOx in the upper troposphere, especially
189   lightning.
190   (4) Incomplete knowledge of the evolution of NOx and NOy in aircraft plumes
191   during the first ~24 hours following emission.
192   (5) Incomplete understanding of, and potential non-linearities in, the coupling among
193   CH_4, CO, OH and O_3 in the troposphere.
194   (6) Potential scavenging and removal of NOx by aerosols and cirrus.
195   (7) Limited understanding of atmospheric transport, especially that between the
196   stratosphere and troposphere.
197
198 In addition, we note the critical nature of understanding the processes controlling water
199 vapor in the UT/LS [see IPCC 1999]. Water vapor is important not only because it is a
200 greenhouse gas that is directly emitted by aircraft but also because it is a significant
201 source of odd-hydrogen (HOx) in the UT/LS. Species in the HOx family produce and
202 destroy ozone, largely determine the lifetimes of CH_4 and CO, and also influence NOx
203 chemistry under the conditions that prevail in the UT/LS. Finally, H_2O is the major
204 condensable species, playing a key role in the formation of ice particles and polar
205 stratospheric clouds in the UT/LS (see SSWPs III and IV). As discussed in detail in a
206 separate SSWP, the relative humidity variable, RHi, is the critical quantity for
207 understanding formation, growth, and evaporation of ice-containing particles in the
208 UT/LS. Therefore, direct emissions of water vapor to the atmosphere, as well as indirect
209 influences of other trace combustion products on water vapor distributions and
210 temperatures in the UT/LS, can have major impacts on the chemistry of the atmosphere.
211
212 Due to the strong non-linear coupling between NOy, particles, and water/ice
213 precipitation, all of these factors are influenced by processes discussed in other SSWPs,
214 most importantly, that on clouds and aerosols. Thus, the discussion here will overlap
215 strongly with other SSWP topics that address uncertainties in water vapor measurements

216 and parameterizations of aerosol properties and clouds. Of particular interest to UT/LS
217 chemistry are factors that limit the ability to predict the presence of ice and the extent of
218 uptake of nitric acid. The rates of heterogeneous reactions that repartition NOx into NOy
219 and that release active forms of chlorine vary by several orders of magnitude, depending
220 on the abundances of condensed HNO_3, a quantity that itself is non-linear with respect to
221 temperature and relative humidity (essentially a threshold with temperature or RHi) [e.g.,
222 see WMO 2006 and references therein]. In addition, a significant confounding factor is
223 that heterogeneous reactions between halogens and temporary NOx reservoirs can release
224 photolytic sources of HOx, which, in turn, destroy methane and accelerate the gas-phase
225 formation of HNO_3. Enhancements of reactive chlorine also alter methane abundances. It
226 is safe to say that highly accurate measurements of water vapor are critical for any
227 assessment of atmospheric chemistry that is influenced by heterogeneous chemistry.
228
229 These issues are explored in detail in the following two major sections. The remainder of
230 Section 2 will summarize studies that have led to significant improvements in our
231 understanding of aircraft impacts on chemistry in the UT/LS. Section 3 will report on
232 recent observations that raise important new questions about chemical processes in the
233 UT/LS; new modeling efforts will be necessary to determine their proper roles in future
234 aviation impacts assessments.
235

2.b. The Role of UT/LS Chemistry in Aviation Impacts on Climate

236
237 The 2006 Workshop considered the combined impacts of NOx emissions on ozone
238 abundances and, through perturbations to HOx chemistry, on methane abundances, to
239 comprise the bulk of the total uncertainty in climate forcing due to aviation [Wuebbles et
240 al., 2006]. This SSWP examines recent results that address the various aspects of UT/LS
241 chemistry that were identified in the 1999 IPCC and 2006 Workshop reports and listed in
242 the previous section. Figure 1, reproduced from Sausen et al. [2005], updates a similar
243 figure from IPCC [1999]. It shows the Global Radiative Forcing (RF) framework that has
244 largely informed the bulk of recent scientific research into the impacts of aviation on
245 climate. As is clear from Figure 1, terms relating to chemistries of NOx and HOx are
246 among the three largest contributors to the aircraft RF, and, as will be shown in Section 3
247 below, the third term related to contrails is itself influenced by NOx chemistry via the
248 role of HNO_3 in ice stability and contrail evolution. Consequently, uncertainties in the
249 chemistry of aircraft emissions in the UT/LS dominate the overall uncertainty in climate
250 forcing due to aviation.
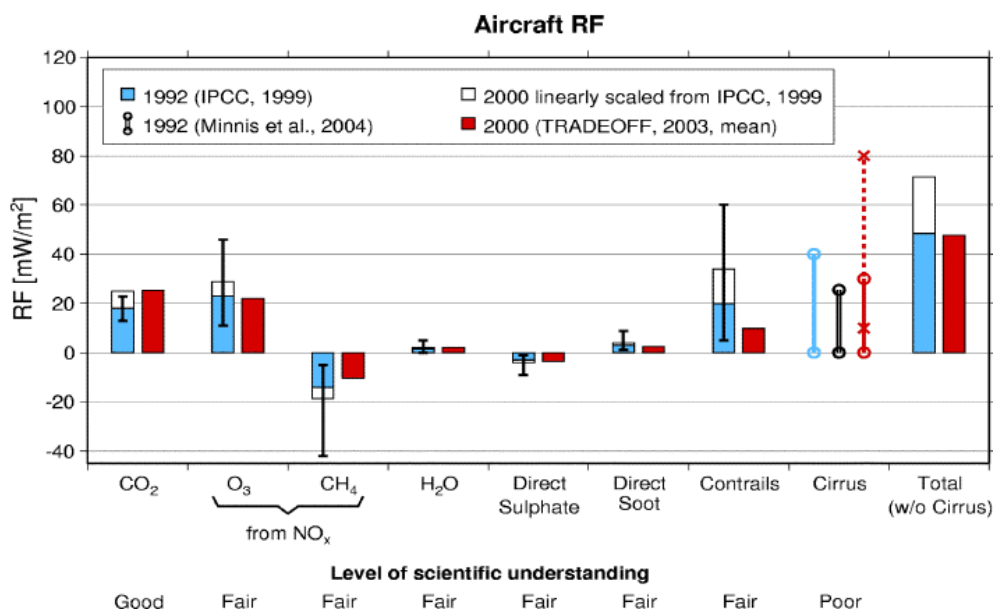
Figure 1. Global radiative forcing (RF) [mW m^{-2}] from aviation for 1992 and 2000, based on IPCC (1999) and TRADEOFF results. The whiskers denote the 2/3 confidence intervals of the IPCC (1999) values. The lines with the circles at the end display different estimates for the possible range of RF from aviation-induced cirrus clouds. In addition the dashed line with the crosses at the end denotes an estimate of the range for RF from Sausen et al., [2005].

A key result of research conducted in the 1990s and summarized in Chapter 2 of IPCC [1999] was that the response of ozone to changes in NOx reverses sign in the lower stratosphere. Formation of ozone by photochemistry initiated by oxidation of volatile organic compounds dominates in the upper troposphere, whereas catalytic destruction of ozone by NOx dominates in the middle stratosphere. The discovery in the early 1990s of a shift in the relative roles of halogens and NOx in the lower stratosphere due to heterogeneous conversion of N_2O_5 to HNO_3, lead to reexamination of the impacts of emissions from supersonic aircraft. Model studies soon found that NOx enhancements near 20 km due to supersonic aircraft (or upward transport of subsonic aircraft emissions) would lead to increases in ozone, thereby reducing reactive halogens [e.g., Weisenstein et al., 1993]. Figure 2, taken from the 1999 IPCC Report, reveals this dual nature, and illustrates why transport and mixing processes are critical in determining the response of ozone to aircraft NOx emissions. Although the simulation shown in Figure 2 was designed simply to illustrate the sensitivity of ozone to a change in NOx, and not to predict the true response of ozone to a specific perturbation due to aviation, it still serves to frame the discussion of impacts and uncertainties that follows. For example, it is easy see that emissions that remain in the upper troposphere will lead to an increase in ozone, whereas those that reach the stratosphere will increase ozone below 24 km, but decrease it above. The net impact of NOx emissions thus depends strongly upon the vertical distribution of the resultant perturbation to background levels. Consequently, the impact

280
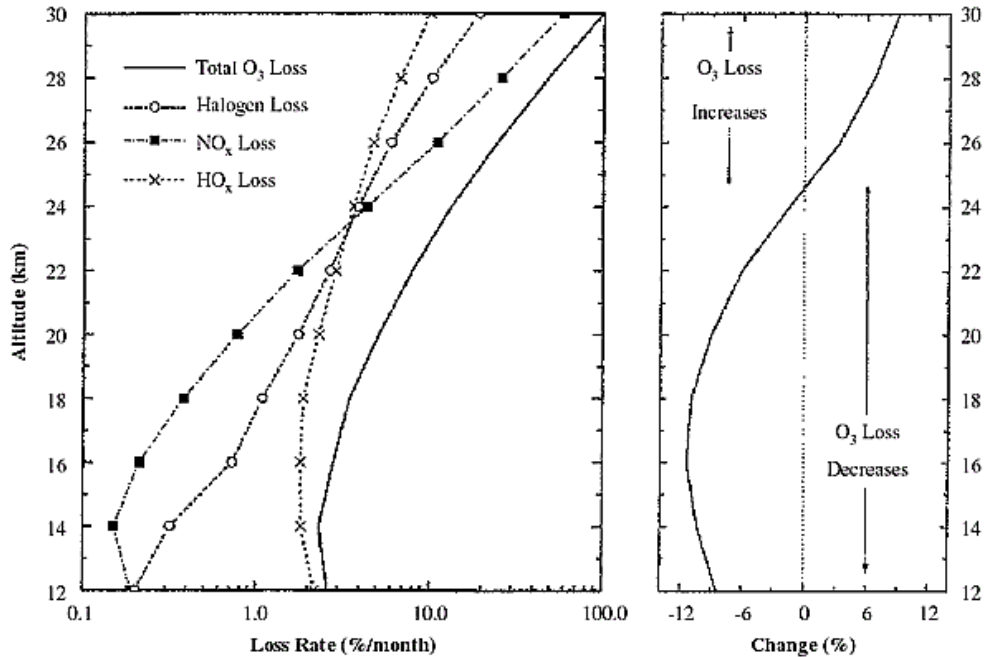
Figure 2. One-dimensional model results for the month of March at northern midlatitudes used to illustrate the relative roles of ozone-destroying radicals (left panel) and percentage change in the ozone destruction rate for a uniform 20% increase in NOx (right panel) as functions of altitude [IPCC, 1999].

of NOx on ozone will differ for subsonic and supersonic aircraft, which deposit their exhaust mainly in the UT and LS, respectively [IPCC, 1999]. Thus, in order to assess the impacts of aviation, the proportion of stratospheric (e.g., supersonic) and tropospheric (e.g., subsonic) emissions from a future fleet of aircraft (the so-called mixed fleet) must be known [Gauss et al., 2006]. What is important to note here is that assessments of the impact of emissions of a particular assumed fleet of aircraft on ozone have relied explicitly on the ability to accurately model this altitude dependence of the ozone response to changes in NOx, the vertical distribution of which depends not only on the flight altitude, but also upon knowledge of the vertical transport of NOx and possible redistribution by cloud and aerosol processes. These themes will become important later in this SSWP, as the implications are explored of new observations in the UT/LS that show a more important role for heterogeneous chemistry and possible redistribution of HNO_3 than was known at the time of the previous assessment.
The strong linkages between these three topics, especially heterogeneous chemistry and aerosol and cloud processes, couple various themes that are addressed in this and other chapters of this report, and require that we consider the direct impacts of the major aircraft combustion products, as well as the indirect effects of non-CO_2 emissions that participate in gas-phase and heterogeneous reactions (e.g., SOx, soot, NOx, and H_2O) with the background atmosphere.

308 **2.c. Advancements since the 1999 IPCC Report**
309 Since the publication of the 1999 IPCC report, there have been more than several
310 hundred studies that address important issues raised in that report. While it is not possible
311 to do justice to all of these studies in this SSWP, we summarize here where significant
312 advances have been made.
313
314 To help define the range of species and concentrations of important engine exhaust
315 emissions, new measurements have been obtained of soot and particle precursor gases
316 [Dakhel et al., 2007; Hays and Vander Wal, 2007; Karcher et al., 2007; Sorokin and
317 Arnold, 2004] such as chemi-ions [Arnold et al., 2000; Eichkorn et al., 2002; Haverkamp
318 et al., 2004; Miller et al., 2005; Sorokin and Arnold, 2006], sulfur and NOx [Herndon et
319 al, 2004; Schroder et al., 2000; Schumann et al., 2002; Tsague et al., 2006, 2007;
320 Wormhoudt et al., 2007], and volatile organic compounds (VOCs) and particles
321 [Anderson, et al., 2006; Herndon et al., 2006; Lobo et al., 2007; Knighton et al., 2007;
322 Nyeki et al., 2004; Sorokin et al., 2001; Wey et al., 2007; Wilson et al., 2004;
323 Yelvington et al., 2007], in the exhaust of engines or aircraft on the ground and at cruise
324 altitudes. In addition, new laboratory studies have further defined the reactivity of engine-
325 emitted soot, most importantly regarding uptake of water and reactivity to NOx, NOy,
326 and O_3 [Popovicheva et al., 2000, 2003, 2004, 2007; Shonija et al., 2007; Talukdar et al.,
327 2006; Wei et al., 2001]. These new studies help to constrain parameters that are critically
328 important for modeling the perturbations of reactive species (e.g., NOx and VOCs) and
329 particle evolution (e.g., chemi-ions, VOCs, and soot) emitted by aircraft in the UT/LS
330 [Ma and Zhao 2000; Petzold et al., 2005; Wei and Liu 2007]. Key new results and
331 implications of these studies are summarized in Section 2.c.I.
332
333 Evidence is mounting from more than a decade of in situ measurements and from new
334 satellite observations that air in the UT/LS is influenced considerably by convective
335 transport from the surface. In fact, there are more recent studies reporting on this issue
336 than for any of the other issues of this SSWP. In Section 2.C.II. some new results are
337 highlighted, in particular those that address some key uncertainties in NOx and HOx
338 budgets. Of particular interest to this SSWP are efforts to quantify lightning, biomass
339 burning, and convective PBL (planetary boundary layer) pollution sources of NOx to the
340 upper troposphere [Brunner et al, 2001; Decaria et al., 2005; Fehr et al., 2004; Hudman et
341 al., 2007; Koike et al., 2002; Lange et al., 2001; Leue et al., 2001; Levy et al., 1999; Ma
342 et al., 2002; Martin et al., 2006, 2007; Muhle et al., 2002; Parrish et al., 2004; Pierce et
343 al., 2003; Ridley et al., 2005; Sauvage et al., 2007; Schumann and Huntrieser, 2007;
344 Sioris et al., 2007; Smyshlyaev et al., 2003; Stohl et al., 2002; Thakur et al., 1999; van
345 Noije et al., 2006; Wang et al., 2000; Zhang et al., 2000; Ziereis et al., 1999, 2000],
346 fluxes that were highlighted in previous assessments as being poorly constrained. Not
347 only do these sources of NOx (and, hence, NOy) dominate the odd nitrogen budget in the
348 UT, thereby setting the background conditions upon which aircraft emissions represent a
349 small, but potentially significant, perturbation, incomplete knowledge of their magnitudes
350 and seasonal and geographic distributions make it difficult to directly attribute NOx
351 enhancements to aircraft operations except in highly localized plumes or heavily traveled
352 flight corridors [Brunner et al., 2005; Colette and Ancellet, 2005; Colette et al., 2005;
353 Grewe et al., 2002; Koike et al., 2000; Marecal et al., 2006; Mari et al., 2002; Meijer et

354 al., 2000; Park et al., 2004; Schlager et al., 1999; Tsai et al., 2001; Wang and Prinn,
355 2000]. New in situ observations with a larger suite of measurements of tracers for
356 biomass burning, human activities, lightning, and stratospheric fluxes [Bertram et al.,
357 2007; Singh et al., 2007], not only provide for attribution of sources other than aircraft
358 emissions, but also provide new clues into photochemical processes that transform
359 reactive NOx into species that serve as reservoirs or that can redistribute NOy (hence,
360 NOx) by condensation onto particles followed by sedimentation [Neuman et al., 2006].
361
362 The interactions of NOy species with particles [Gao et al., 2004; Popp et al., 2006;
363 Karcher and Voigt, 2006; Voigt et al., 2006, 2007] raise important new questions that
364 rely on the ability to model formation, composition, and reactivity of particles [Considine
365 et al., 2000; Meier and Hendricks, 2002; Meilinger et al., 2001; von Kuhlmann and
366 Lawrence; 2006]. Several key new modeling studies have shown that heterogeneous
367 chemistry involving NOx, HOx, and halogens, is extremely important in particle-rich
368 exhaust plumes and persistent contrails, and, depending on the subsequent behavior of
369 these species as these plumes and contrails disperse, can even have important
370 implications on the sign of ozone response to aircraft exhaust on hemispheric scales
371 [Meilinger et al., 2005; Sovde et al., 2007]. These results and their implications are
372 discussed in Section 2.c.III.
373
374 The importance of convective sources of HOx in the upper troposphere has been known
375 for many years [Collins et al., 1999; Crawford et al., 1999; Muller and Brasseur, 1999;
376 Reiner et al., 1999; Singh et al., 2000]. New observations of HOx and volatile organic
377 compounds in conjunction with modeling studies, continue to reinforce this view
378 [Colomb et al., 2006, Mari et al., 2002; Olson et al., 2004; Ravetta et al., 2001; Singh et
379 al., 2004; Snow et al., 2003, 2004; Stickler et al., 2006; Wang and Chen, 2006], and they
380 provide some important insights into the nature of previous disagreements between
381 modeled and measured HOx that seem to depend on NOx [Ren et al., 2008]   (the
382 previously referenced "coupled HOx/NOx discrepancy" [e.g., Faloona et al., 2000]). New
383 measurements of HO_2NO_2 [Murphy et al., 2004; Kim et al., 2007] could help to identify
384 important missing chemistry, while issues of resolution have been shown to be important
385 under some conditions [Olson et al., 2006].
386
387 Measurements of water vapor in the upper troposphere and the stratosphere, where the
388 naturally occurring humidities are the lowest found on Earth, have always been a source
389 of controversy [e.g., Kley et al., 2000]. Not only are emissions of water vapor from
390 aircraft critical for understanding radiative impacts of exhaust, accurate knowledge of
391 background water vapor distributions and temperatures, and the microphysics of water-
392 containing particles, are essential in order to accurately model heterogeneous chemistry,
393 HOx distributions, and possible redistribution of reactive species in the UT/LS by
394 sedimentation. Ongoing studies by a number of groups [Bencherif et al., 2006; Bortz et
395 al., 2006; Ferrare et al., 2004; Folkins et al., 2006; Gao et al., 2005; Gulstad and Isaksen,
396 2007; Helten et al., 1999; Kley et al., 2000; Luo et al., 2007; Marecal et al., 2007;
397 Miloshevich et al., 2006; Nedoluha et al., 2002; Park et al., 2004; Ramaswamy et al.,
398 2001; Spichtinger et al., 2002; Troller et al., 2006; Vaughan et al., 2005; Vay et al., 2000
399 that have improved our understanding of water vapor and supersaturation are summarized

400 in Section 2.c.IV. New studies addressing temperatures in the UT/LS are summarized in
401 Section 2.c.V.
402
403 In addition to results that have improved our understanding of key uncertainties outlined
404 in previous assessments, there have been some observations, some controversial, that
405 raise important new questions about our basic understanding of chemistry in the UT/LS
406 that could have major implications for the impacts of aviation. These will be presented in
407 Section 3 of this SSWP, and include new studies related to the bromine budget [Dorf, et
408 al., 2006a, 2006b; Salawitch, et al., 2005; Schauffler, et al., 1999; Sioris, et al., 2006;
409 Theys, et al., 2007], the unusual impacts of bromine on NOx chemistry [Sinnhuber and
410 Folkins, 2006; Hendricks, et al., 2000; Yang, et al., 2005], and new observations of
411 chlorine activation in the UT/LS [Thornton, et al., 2003, 2005, 2007] that call for a fresh
412 look at the potential impacts of heterogeneous reactions in the UT/LS, especially in
413 persistent contrails [Borrmann, et al., 1996; Lelieveld, et al., 1999; Bregman, et al.,
414 2002].
415

416 **2.c.I. Engine Emissions**
417 Although knowledge of the emissions of sulfate was identified as a key uncertainty in
418 previous assessments, the main issue was not so much the sulfate itself, as the impact of
419 fuel sulfur on particle nucleation. Since then, a number of studies have characterized
420 particulate emissions from a variety of aircraft engines. The most significant new result is
421 that particle production does not closely track fuel sulfur content [Wey et al., 2006;
422 Yelvington et al., 2007]. While studies have shown that ion nucleation is the probable
423 mechanism for volatile aerosol production in aircraft exhaust [e.g., Miller et al., 2005],
424 measurements of positive and negative chemiions have revealed a greater role for LVOCs
425 (low volatility VOCs) than previously believed [Eichkorn et al., 2002; Sorokin and
426 Arnold, 2006; Miller et al., 2005].
427
428 In a study of an on-wing commercial gas turbine engine, Lobo et al. [2007] recently
429 found little dependence of particulate emissions with varying fuel sulfur content,
430 although they did observe that the soluble mass fraction of particles increased with
431 distance from the engine exit plane and with increasing aromatic and sulfur content of the
432 fuel, consistent with increased uptake of water by hygroscopic particles. Recent
433 measurements of engine-generated soot [Shonija et al., 2007] found significant water
434 uptake due to the existence of impurities within the engine, with amounts of absorbed
435 water increasing with decreasing temperatures in the exhaust plume (reaching 18% by
436 weight at threshold conditions for contrail formation). In light of previous observations
437 of significant uptake of water by soot, these authors have inferred that to be hygroscopic,
438 soot does not have to be processed by reactions with sulfuric or nitric acids, as was
439 previously believed, and that impurities in engine-generated soot will play key roles in
440 the formation of CCN in aircraft plumes. These results are consistent with a laboratory
441 study of Talukdar et al. [2006], who found that uptake of nitric acid on aviation kerosene
442 soot is reversible, and not a significant source of NOx, as had been suggested previously.
443 They are also consistent with another study that found the characteristics of soot emitted

444 by engines are determined largely by combustor processes, and not by subsequent
445 reactions in the turbine/nozzle.
446
447 It is important to recognize that measurements of soot from combustors must be
448 considered carefully, as it may be chemically and physical unstable, as shown in a recent
449 study by Popovichava et al. [2003]. In addition, it is unclear whether ground level
450 measurements will apply under cruise conditions, where combustion is more complete
451 and LVOC emissions are likely to be significantly smaller. But from the majority of new
452 studies, it does appear that aircraft-generated particles are relatively hygroscopic, and
453 therefore are likely to be good CCN. A new particulate emission inventory developed
454 under the European PartEmis program should help reduce uncertainties in modeled
455 impacts of particulate emissions by aircraft [Petzold et al., 2005].
456
457 Important new measurements of the emissions of hydrocarbons and NOx, including
458 speciation, have been obtained in the exhaust plumes of a variety of aircraft types during
459 the APEX campaign [Herndon et al., 2004; Herndon et al. 2007; Knighton et al., 2007;
460 Wormhoudt et al., 2007]. To first order, the results are in good agreement with previous
461 studies, increasing confidence in the emissions databases used for modeling aircraft
462 impacts. Additional insights from these studies include the finding that fuel type and
463 plume age appear to have only minor effects on the emissions of hydrocarbons, including
464 speciation, whereas temperature appears to be an important factor. NOx emissions were
465 found to increase with thrust, while the fraction of NO_2/NOx decreased from 80% at
466 lowest thrust to below 7% at highest thrust. Nitrous acid (HONO) was found to be a
467 minor species (~7%) that increased with thrust, and also served as a good indicator for
468 predicting abundances of other trace species, such as oxides of sulfur.
469
470 In summary, new results indicate an increased role for hydrocarbons in formation of
471 particles in aircraft exhaust, a decreased tendency for reduction of HNO_3 to NOx on soot,
472 and, as will be discussed in a separate chapter, a general increase ice-forming activity for
473 aircraft emissions. This raises the importance of heterogeneous chemistry to reduce NOx,
474 and increase the importance of HOx and halogens, in persistent contrails.
475
476 **2.c.II. Sources of NOx and HOx in the Upper Troposphere**
477 Motivated by the dominant role placed on NOx and HOx by previous aircraft
478 assessments [Brasseur et al., 1998; IPCC 1999], the past decade has been witness to a
479 multitude of studies to attribute sources of these species in the upper troposphere,
480 especially those that could potentially be due to aircraft. A brief review of some
481 important new results is presented below.
482
483 *Sources of NOx*
484 The main source of NOx in the stratosphere is oxidation of N_2O, and based on tight
485 correlations that have been observed between NOy (the sum of reactive nitrogen species)
486 and N_2O, it is relatively straightforward to simulate the impact of an additional source of
487 NOx from direct injection of aircraft exhaust or parameterized transport from the
488 troposphere [IPCC 1999]. However, there are a number of potentially significant sources
489 of NOx to the upper troposphere, not just those from aircraft emissions, all of which must

490 be reasonably well understood in order to determine the perturbation of NOx due to
491 aircraft [IPCC 1999]. Of these non-aircraft sources, lightning and convective transport
492 from the boundary layer have stood out as dominant sources of NOx in the UT [Grewe et
493 al., 2002]. The studies are too numerous to describe here, but we summarize a few key
494 results that have emerged from these studies that significantly improve our understanding
495 of NOx sources.
496
497 Around the time of the 1999 IPCC assessment, lightning was estimated to represent a
498 source strength of about 3-5 Tg(N) yr^{-1}. In a comprehesive review of three decades of
499 research on this topic, Schumann and Huntrieser [2007] have concluded that the best
500 estimate for the annual lightning NOx source is 5 ± 3 Tg(N) yr^{-1}. Consistent with this, in
501 a recent study using a combination of space-based NO_2 observations from
502 SCIAMACHY, O_3 observations from OMI and MLS, and HNO_3 observations from
503 ACE-FTS, Martin et al. [2007] determine a range of 6 ± 2 Tg(N) yr^{-1} for the lightning
504 NOx sources. For reference, such a source-strength is about 8-10 times larger than the
505 estimated NOx source from aircraft emissions [Kraabol et al., 2002] but only about 1/8th
506 of the total NOx source strength assumed in state-of-the-art aircraft NOx emissions
507 impacts studies [e.g., Gauss et al., 2006].
508
509 It is important to note that aircraft emissions are more confined in altitude and to heavily
510 traveled corridors than these other sources, so they can still represent a large local
511 perturbation. What makes assessing aircraft contributions so difficult, then, is not only
512 the quantification of these larger global sources, but specifying their geographic
513 distributions with sufficient precision so that the contributions due to the highly localized
514 aircraft emissions can be quantified. In other words, the large, distributed sources
515 determine the broader background abundances of NOx into which the aircraft emissions
516 represent a highly localized perturbation. Thus, studies addressing the contributions of
517 various sources of NOx (or NOy) to the UT are critical for evaluating the significance of
518 that due to aircraft.
519
520 *Source Attribution of NOx in the Upper Troposphere*
521 Singh et al. [2007] analyzed observations of reactive nitrogen species in the UT over
522 North America in the summer of 2004, reporting that ~30% of the NOy in the UT is in
523 the form of NOx. PAN and HNO_3 were the dominant reservoirs of reactive nitrogen in
524 the UT and LS, respectively. Relying on tracers for biomass burning emissions (e.g.,
525 HCN) and anthropogenic pollution, they concluded that lightning represents a larger
526 source of NOx to that region than was believed previously. Model simulations based on
527 these observations [Hudson et al., 2005] imply that lightning was responsible for
528 approximately 75% of the NOx observed in this region. These results suggest that the
529 NOx observed in this region is relatively 'fresh', that is, it is undergoing photochemical
530 aging (e.g., oxidizing). Consistent with this, Sioris et al. [2007] reported large local NO_2
531 enhancements at ~10 km that they attributed to lightning, estimating that it is responsible
532 for 60% of the upper tropospheric NO_2 in the tropics.
533
534 Bertram et al. [2007] develop the idea of a 'photochemical clock', using the ratio of
535 observed NOx to that determined with a photochemical model with similar total NOy

536 (i.e., NOx_{obs}/NOx_{ss}) to estimate that ~17% of the air in the UT under the conditions
537 sampled was transported from the planetary boundary layer. Furthermore, they estimate a
538 turnover rate by convection of 0.1 day^{-1} for air in the UT (although it should be noted that
539 this is includes altitudes somewhat below typical aircraft cruise altitudes).
540
541 These results suggest that non-aircraft sources of NOx to the upper troposphere are more
542 important than previously believed, consistent with the observations of Klemm et al.,
543 [1998], who found that clear perturbations due to aircraft in the northest Atlantic corridor
544 were difficult to identify on scales larger than a few km due to natural variability,
545 whereas in 'fresh' plumes between 15 and 90 minutes in age, enhancements of up to 10
546 ppb were observed. Based on NOy/O_3 correlations, Koike et al. [2000] estimated that the
547 mean NOy enhancement in the North Atlantic corridor is of order 70 ppt at 11 km,
548 implying NOx enhancements of about 40% above backgrounds. They also found the
549 NOy enhancements to increase with increasing ozone (e.g., closer to the chemical
550 tropopause). Given the more recent observations of Singh et al. [2007] of significant
551 transport from the surface, Koike et al. [2000] may have significantly overestimated the
552 NOx contributions from aircraft.
553
554 *Sources of HOx*
555 Not only does OH largely determine the lifetime of methane, a greenhouse gas that plays
556 a key role in the Aircraft RF uncertainties framework (Figure 1, [Sausen et al., 2005]),
557 both OH and HO_2 participate in catalytic cycles that destroy ozone and are necessary for
558 ozone production. Therefore, models must be able to reproduce both total HOx
559 abundances and the partitioning within the HOx family (the generally preferred indicator
560 being the OH/HO_2 ratio) over a wide range of conditions found in the UT/LS.
561
562 Measurements of HOx carried out in the 1990s revealed significantly larger abundances
563 of this critical oxidizer than could be modeled with assumed sources [e.g., see Faloona et
564 al., 2000]. By the time of the 1999 IPCC assessment, it was well known that sources of
565 HOx in addition to H_2O/O_3 photochemistry were required to resolve this discrepancy,
566 especially in the upper troposphere [Collins et al., 1999; Crawford et al., 1999; Muller
567 and Brasseur, 1999; Reiner et al., 1999; Singh et al., 2000]. Since then, a number of
568 ongoing studies related to sources of HOx have been published, and models for assessing
569 aircraft impacts have used any available in situ observations to constrain
570 parameterizations of HOx, including measurements of species such as H_2O_2, whose
571 abundances serve as sensitive indicators of HOx chemistry [Brunner et al., 2005]. The
572 basic understanding of HOx chemistry seems to be relatively sound, in that it is widely
573 acknowledged that additional sources, generally gases transported from the PBL by

574
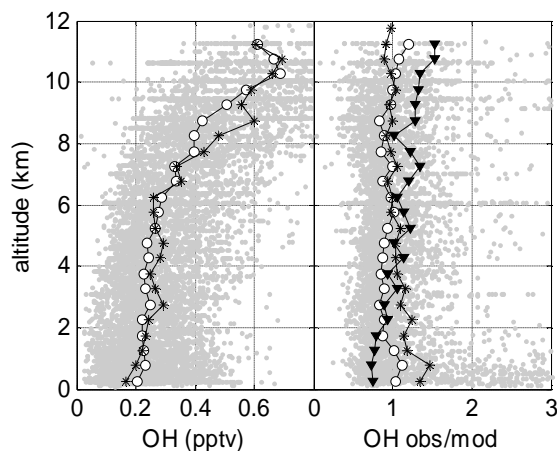
Figure 3. (left panel) Comparison of the median vertical profiles of measured (circles) and modeled (stars) of OH for INTEX-A. (right panel) Measured-to-modeled OH in INTEX-A (circles), TRACE-P (stars) and PEM Tropics B (triangles). Individual 1-minute measurements from INTEX-A are shown (gray dots) [from Ren et al., 2008].

convection (in agreement with the conclusions based on NOx partitioning described above), are required to fully explain HOx abundances. The partitioning between OH and HO_2 varies with NOx in a fashion that can be reproduced reasonably well by models [for example, see Brunner et al., 2005, Ren et al., 2008, and references therein]. Figure 3 shows comparison of OH measurements from recent missions with modeled OH abundances, indicating good agreement over a wide altitude range [Ren et al., 2008].

The results shown in Figure 3 indicate that there should be a firm basis for model simulations of OH distributions over a wide range of conditions, as is required to predict the lifetime of CH_4 to a reasonable degree of accuracy. However, important model-measurement discrepancies remain in modeling the partitioning of OH and HO_2 that are not well understood, as will be discussed in Section 3 [Hudman et al., 2006; Ren et al., 2008]. One of the challenges in comparing modeled and measured HOx is the inherent non-linearities in HOx chemistry; in essence, unless the photochemical conditions are highly uniform during sampling, some differences in modeled and measured total HOx or OH/HO_2 can be due simply to the coarse temporal resolution of the model. As shown by Olson et al. [2006], such errors are most problematic at high solar zenith angles and at high and variable NOx conditions. In light of the significant role that heterogeneous chemistry plays in the effect of NOx on ozone in the UT, this type of issue could become very important in future assessments of aircraft impacts.

There are several implications of the results highlighted above that are worth noting here. First, the increased role of convection from the PBL to sources of NOx and HOx to the upper troposphere reduces the significance of aircraft perturbations of these species or their precursors. Thus, it is likely that model simulations used in prior assessments, updated to reflect these new observations, would find the impacts of aircraft emissions to ozone and methane in the UT/LS to be diminished. However, increased transport of short-lived species from the PBL also implies increased production of aerosols in the UT

608   due to oxidation of these gases into less volatile products. Second, increased 'aging' of
609   UT air results in a shift in the partitioning from NOx to NOy. As discussed in the
610   following sections, this has important implications for the role of long-lived reservoirs of
611   nitrogen oxides in particle stability. Heterogeneous reactions are effective in denoxifying
612   cold, particle rich regions of the atmosphere, such as where persistent contrails are
613   formed. Thus, increased transport from the PBL implies a greater role for ozone-
614   destroying reactions of HOx and halogen radical species that are normally kept in lower
615   abundances by NOx.
616
617   **2.c.III. Conversion of NOx to NOy**
618   The laboratory finding that uptake of nitric acid on aircraft kerosene soot is reversible
619   [Talukdar et al., 2006] implies that emissions of soot will not shift the partitioning of
620   NOy to NOx in aircraft plumes, as was believed previously. This result, together with
621   new measurements of the hygroscopicity of soot and the subsequent formation of CCN
622   and emissions of particles from engines (e.g., see Section 2.c.I. and SSWPs III and IV),
623   implies, rather, that in plumes, contrails, and potentially even in heavily traveled flight
624   corridors, there will be more rapid conversion of NOx to NOy. Although the impacts of
625   these new findings have yet to be fully explored, results from recent modeling efforts
626   provide clues as to what might be the tendencies.
627
628
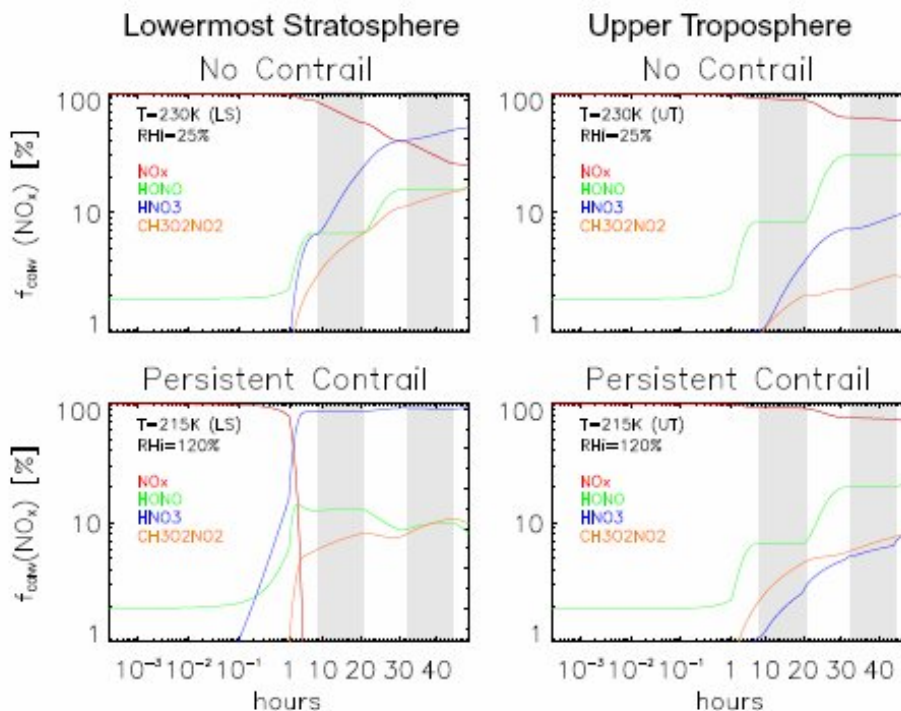
629

630   **Figure 4.** Model results from Meilinger et al. [2005] showing the impact of
631   heterogeneous processing of NOx in a persistent contrail in the lower stratosphere (left
632   panels) and in the upper troposphere (right panels). Shaded regions refer to nighttime.
633

634 A modeling study by Kraabol et al. [2002] found that reactions that form odd-nitrogen
635 reservoirs in aircraft plumes and persistent contrails reduce the magnitude of changes in
636 ozone as a result of the conversion of ~25-35% of the aircraft NOx to NOy. A subsequent
637 study by Meilinger et al. [2005] found that NOy formation depends very strongly on
638 heterogeneous reactions, especially in the lowermost stratosphere. Figure shows the shift
639 in NOy partitioning due to heterogeneous chemistry in a persistent contrail. In the
640 lowermost stratosphere, NOx is completely converted to HNO_3 in a matter of hours,
641 whereas without a contrail, even after a few days, conversion of NOx to NOy is only
642 50%. According to Meilinger et al., in the lower stratosphere, ozone destruction by
643 chlorine and bromine enhances that due to NO+O_3 in the early plume and dominates over
644 NOx-induced ozone production in the aged plume. This is the result of combined effects
645 of halogen activation and denoxification by heterogeneous reactions on contrail ice
646 particles. The situation in the upper troposphere is less clear, and the tendency of ozone
647 depends strongly on temperatures in the initial plume and persistent contrail. However,
648 reductions in net ozone production or shifts from ozone production to loss result from the
649 more complete treatment of heterogeneous chemistry. The recent modeling study of
650 Sovde et al. [2007] examines the global implications of heterogeneous reactions on the
651 ozone changes induced by aircraft exhaust products. Although they focus on the impacts
652 of a mixed fleet for the year 2050, there are some important new conclusions that extend
653 the results of Meilinger et al. [2005] to hemispheric scales. (It is also important to note
654 that even in a mixed fleet, operations of subsonic aircraft dominate the overall emissions
655 budget). As shown in Figure 5, the most significant implication of more rapid conversion
656
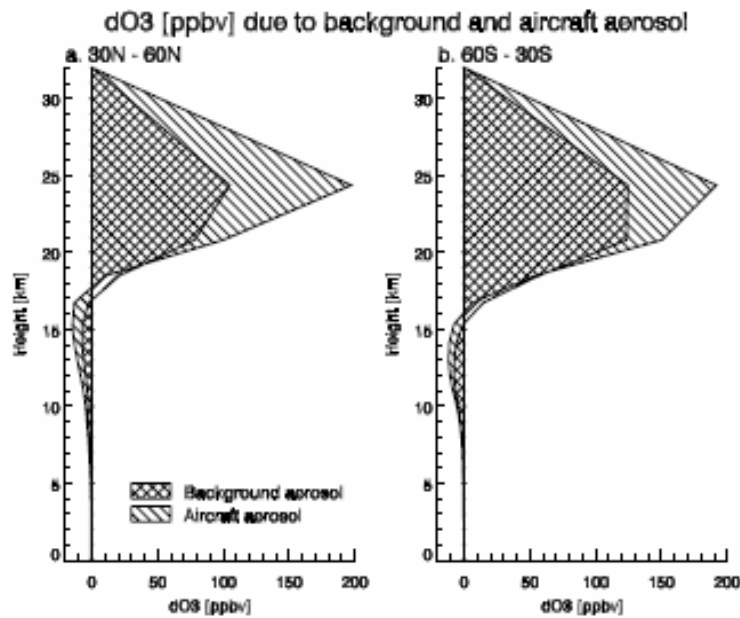
657

658 **Figure 5.** Vertical profile of the zonally averaged response of ozone to aircraft emissions
659 of NOx assuming background aerosols and aircraft aerosol perturbations for a 2050
660 Mixed Fleet, as described in Sovde et al. [2007].
661

662   of NOx to NOy is the complete reversal in the sign of the response of ozone to nitrogen
663   emissions (e.g., see Figure 2) from net production to net loss below 18 km (i.e., in the
664   upper troposphere) and from net loss to net production above 24 km. Although the two
665   ozone change curves shown in the right panel of Figure 2 and Figure 5 have similar
666   shapes, they are nearly mirror images of one another, as Figure 2 deals with the quantity
667   ozone loss, whereas Figure 5 shows ozone gain, with altitude. Using reasonable estimates
668   for an average vertical profile of ozone, the percent change in ozone near 25 km in Figure
669   5 is about +2 to +4%, whereas near the mid-latitude tropopause (12-16 km) the change is
670   of comparable magnitude, but opposite in sign. In essence, one could achieve similar
671   changes to those modeled in Figure 2 by *decreasing* NOx by ~10%.

672

673   It is worthwhile to consider how it is possible for the sign of the impacts of NOx
674   emissions to completely reverse since the last major reviews of aviation (and even the
675   2006 Workshop). Hints can be found in the study by Meilinger et al. [2005] discussed
676   above and one by Hendricks et al. [2000] who investigate the influence of naturally
677   occurring bromine on the chemistry of aircraft emissions in the UT/LS. First, the
678   partitioning of NOx emissions is shifted far more toward HNO_3 in the more recent studies
679   than in the model used to generate Figure 2 (and presumably the state-of-the-art models
680   used at the time of the 1999 IPCC Assessment). Second, (and largely a consequence of
681   this shift from NOx to HNO_3) the relative contributions of the NOx, HOx, and halogen
682   families to ozone loss in the UT/LS differ in the more recent model simulations from
683   those used for previous assessments.

684

685   Hendricks et al. [2000] found the somewhat surprising result that bromine radicals, even
686   at the minor abundances that are thought to be present in the UT/LS, efficiently convert
687   NOx to NOy by heterogeneous hydrolysis of $BrONO_2$ on background and aircraft-
688   produced aerosols. They showed that this process can even be an important pathway for
689   denoxification in the lowermost stratosphere. As noted by Meilinger et al. [2005], such
690   halogen chemistry becomes significantly more important in exhaust-influenced air in the
691   plumes of aircraft, in cirrus, and in persistent contrails. This issue will be addressed in
692   more detail in Section 3, since the role of halogens in aviation impacts has received little
693   attention and remains one of the major uncertainties in UT/LS chemistry.

694

695   Halogen chemistry may not be dominant throughout the UT/LS, but it is important to
696   note that even a few tens of parts per trillion, background abundances of halogens are
697   sufficient to compete with (and even dominate in some regions) HOx- and NOx-
698   catalyzed destruction of ozone in the UT/LS. The non-linear coupling between HOx,
699   NOx, and halogen oxides makes the assessment of the impacts of emissions of any specie
700   that influences abundances of just one of these families very difficult to assess unless we
701   have a solid quantitative understanding of each of the major ozone-destroying radical's
702   response to changes in the abundances of the others. Although such an understanding has
703   been achieved for the middle-to-upper stratosphere, the situation is less clear for the
704   lowermost stratosphere and upper troposphere, especially for the reactive halogen
705   species, abundances of which are so strongly modulated by heterogeneous processes.
706   Given the additional complication of non-linearities in particle formation, composition,
707   and heterogeneous reaction rates with respect to relative humidity, temperature, and

708   abundances of H_2O and HNO_3, the details of plume formation and dispersion, particle
709   growth, composition, and sedimentation, and the ability to predict the presence of ice
710   crystals in the UT/LS all become essential factors in assessing the chemistry of aircraft
711   exhaust. In light of the clearly dominant role played by water vapor in all of these issues,
712   the next section will examine progress in understanding water vapor in the UT/LS.
713
714   **2.c.IV. Water Vapor and Supersaturation**
715   H_2O abundances in the UT/LS are controlled by a combination of transport processes.
716   Both large- (e.g., Brewer-Dobson circulation) and small-scale (e.g., waves, convection)
717   processes are important [IPCC 1999; SPARC 2000]. Temperature, chemistry (e.g., CH_4
718   oxidation) and microphysics also play roles. Transport phenomena are key elements in
719   UT water distribution; these include such occurrences as horizontal transport from the
720   tropics to sub-tropics and midlatitudes and vertical motions associated with mesoscale
721   convection, midlatitude cyclones and downward transport from the stratosphere.
722
723   SPARC [2000] noted that there has been a 2 ppm increase of H_2O (~1%/yr) in the
724   stratosphere since the mid-1950s, about 0.55 ppm of which can be attributed to increases
725   in CH_4, while the source of the remaining ~1.5 ppm (75% of the total) remains unknown.
726   Trends in relative humidity in the upper troposphere have been found in some latitude
727   bands, but there is no apparent global trend; variability from ENSO, large-scale
728   circulation modes and temperature all contribute to the complexity of attributing trends.
729
730   Agreement amongst measurements of H_2O in the lower stratosphere (60-100 mb) has
731   always been problematic. Although typically clustering within 10% of each other, some
732   individual instruments have systematically differed from the mode of the measurements
733   by 25-30%. The source of this disagreement is under investigation.
734
735   Water measurements in the upper troposphere are less numerous than those in the
736   stratosphere, and they are less reliable overall. Radiosonde data are not sufficiently
737   accurate for determining trends at the level of importance for understanding perturbations
738   by aircraft. Measurements from TOVS are reasonable, on average, but very difficult to
739   validate because of the high temporal and spatial variability of H_2O vapor in the UT. The
740   measurement of tropospheric water vapor amounts via radio occultation of Global
741   Positioning Satellite (GPS) signals has become a fairly mature technique, and methods
742   for determining vertical profiles of water with high vertical resolution (a few hundred
743   meters) are under development [e.g., Troller et al., 2006].
744
745   Since the last water vapor assessment [SPARC 2000], a number of uncertainties relevant
746   to aircraft impacts have been addressed in some detail, as described below:
747   Intercomparison experiments and laboratory work for stratospheric water vapor
748   instruments have been ongoing; validation of satellite H_2O retrievals and numerous
749   correlative measurements have been conducted; improvements in radiosonde H_2O
750   measurements have been made; a number of process studies have been conducted to
751   investigate the role of convection and cloud microphysical properties in UT/LS H_2O
752   distributions and studies of stratosphere-troposphere exchange mechanisms.
753

754   *Intercomparison and Validation*
755   Detailed intercomparisons of lidar, radiosondes, and frost-point sensors (AFWEX)
756   revealed that the frost-point/chilled mirror measurements are "drier" (i.e., lower water
757   vapor) than the others by 10-25% in the UTLS [Ferrare et al., 2004]. During the 2003
758   AWEX-G campaign, (designed to validate the AIRS measurements from the A-train
759   satellites), six radiosonde-type sensors were flown against the University of Colorado
760   Cryogenic Frostpoint Hygrometer (CFH). With appropriate corrections for solar heating,
761   data from the Vaisala RS-90 sensor was found to be suitably accurate for use in
762   validation studies [Miloshevich et al., 2006].
763
764   Intercomparisons between the satellite-based POAM measurement (solar occulation) and
765   the in situ MOZAIC data set showed that POAM water vapor values are about 10%
766   higher than those determined with capacitive humidity sensors flown on several in-
767   service aircraft [Nedoluha et al., 2002]. Finally, based on comparisons made during the
768   SONEX and POLINAT campaigns in 1997, Tunable Diode Laser (TDL) and cryogenic
769   hygrometers were found to agree to within their stated instrumental accuracies of 10%
770   [Vay et al., 2000], whereas a similar intercomparison conducted between the POLINAT
771   and MOZAIC datasets found water vapor measurements to agree within 5% [Helten et
772   al., 1999]. However the agreement between measured values of relative humidity was
773   worse, potentially pointing to temperature measurement problems.
774
775   Perhaps of most significance for this White Paper will be the upcoming results from the
776   AquaVIT blind intercomparison that was carried out at the AIDA chamber in Karlsruhe
777   in Fall 2007 (http://imk-aida.fzk.de/campaigns/RH01/Water-Intercomparison-www.htm).
778   This formal program brought together more than twenty instruments that measure water
779   vapor and/or condensed water for a two-week measurement campaign. The results of a
780   formal blind intercomparison among a subset of the instruments are due out Spring 2008,
781   and should elucidate some of the reasons why water vapor measurements in the cold, dry
782   UTLS have disagreed to a level that is greater than their reported uncertainties.
783
784   *Observations in UT*
785   Observations of relative humidity over ice (RHi) and supersaturation in the upper
786   troposphere have been analyzed in detail, and both radiosonde measurements and those
787   derived from the chilled-mirror "SnowWhite" frost point hygrometer show frequent
788   supersaturation with respect to ice during wintertime (24% of time) [Vaughan et al.,
789   2005]. Data from MLS show occurrences of high supersaturations in only about 0.5% of
790   observations overall, with considerably larger frequencies of occurrence found over
791   Antarctica [Spichtinger et al., 2002]. Only one direct observation of RHi relevant for
792   assessing supersaturation in an aircraft-related contrail has been reported. Gao et al.
793   [2005] argued that the high supersaturations they observed might be due to co-
794   condensation of other species (e.g., HNO_3) in cloud particles.
795
796   *Climatology/Mechanistic Studies*
797   Ten years of MOZAIC data have been compiled to relate UT water to deep convection
798   and moisture transport [Luo et al., 2007]. Interannual variability is observed to correlate
799   in some cases with average temperature and/or ENSO, but is not fully explained by

800   either. Regional differences are well-explained by convective frequency. However, no
801   trend in H_2O abundances has been found in the MOZAIC data over the period Aug 1994
802   to Dec 2003 [Bortz et al., 2006].
803
804   Comparison of global or mechanistic model results with observations can also provide
805   insight into the significance of various transport processes for determining the water
806   vapor distribution. For example, MOZART model results and HALOE water vapor data
807   are in good agreement with respect to the seasonal cycle of vertical transport (the so-
808   called "tape recorder"), but some significant differences exist in distributions around the
809   tropopause [Park et al., 2004]. Much of this difference is attributed to the model's
810   treatment of moisture transport in the monsoon regions, as well as stratosphere-
811   troposphere exchange in those areas. Similar results were obtained when comparing
812   simulations from the NCAR Community Atmosphere Model (CAM 3.0) to HALOE
813   observations and reanalyses by ECMWF. Deficiencies in the calculation of stratospheric
814   water vapor are attributed to weaknesses in the model's core stratospheric dynamics, in
815   particular, the lack of a QBO and crude representation of planetary waves [Gulstad and
816   Isaksen, 2007]. The authors also note the importance of the model's temperature fields,
817   which continue to show a polar cold bias; this particularly affects water vapor
818   distributions in the southern hemisphere.
819
820   To date, mechanistic model simulations have focused on the representation of water
821   vapor in the tropics. For example, tropical climatologies of H_2O, CO, HNO_3 and O_3 are
822   compared to calculations of vertical profiles of the same species obtained from four
823   models with differing parameterizations of convection [Folkins et al., 2006]. No single
824   model/parameterization emerged as "best", with each having some failings in its ability
825   to reproduce observations. Comparisons of balloon-borne water vapor observations over
826   Brazil with profiles calculated by the Brazilian Regional Atmospheric Modeling System
827   (BRAMS) and ECMWF global analyses illustrate the importance of both model vertical
828   resolution and the treatment of microphysics in the ability to calculate realistic water
829   vapor profiles [Marécal et al., 2007].
830
831   **2.c.V. UT/LS Temperatures**
832   Atmospheric temperature is a fundamental quantity in all areas that this SSWP considers
833   – gas-phase and heterogeneous chemistry, the formation and persistence of condensed
834   matter (e.g., cirrus, contrails, polar stratospheric clouds), and transport processes. Thus
835   uncertainties in our knowledge of the mean temperature in the UT/LS, as well as its
836   natural variability, impact a wide range of processes important for understanding the
837   impacts of aircraft emissions on climate. Furthermore, the inability of models to
838   adequately simulate the temperatures in the atmospheric regions of interest may have
839   significant impacts on their treatment of heterogeneous processes and parameterizations
840   of microphysics (in addition to the role of temperature in model dynamics, such as the
841   classic GCM "cold pole" problem). A review of the temperature trends associated with
842   the broader climate change issue is beyond the scope of this document and controversies
843   surrounding the temperature record for the surface and mid-troposphere will not be
844   discussed.
845

846 A comprehensive review of temperature trends in the stratosphere was published in 2001
847 [Ramaswamy et al., 2001]. This work indicated that temperature trends in the lower
848 stratosphere were negative (-0.5 ± 0.25 $^{\circ}$C/decade) and consistent with known trends in
849 stratospheric ozone as well as other greenhouse gases. These authors noted, however, that
850 better knowledge of the vertical profiles of ozone and water vapor, and their changes,
851 throughout the upper troposphere and lower stratosphere were critical for proper
852 attribution of the observed temperature changes. Stratospheric temperature trends updated
853 through 2005 are presented in Chapter 5 of WMO [2006] and are consistent with those
854 reported earlier.
855
856 Similar exhaustive trend studies for the UT/LS have not been carried out, although data
857 for this region do exist (from radiosondes, satellites and even in-service aircraft). One
858 regional study [Bencherif et al., 2006] uses radiosonde data gathered over South Africa to
859 show that temperatures are decreasing throughout the UT/LS (200 hPa and altitudes
860 above) between 1980 and 2001. In that region, upper tropospheric temperatures have
861 decreased at a rate of -0.10 ± 0.18 $^{\circ}$C/decade, a value similar to that reported by Parker et
862 al. [1997] for an analysis based on globally gridded radiosonde observations.
863
864 Sensitivity of the rates of chemical processes to temperature can be significant. In general
865 an error of a degree or two makes little difference in the rate of a gas-phase process;
866 however, the same cannot be said for heterogeneous chemical transformations. The
867 composition of condensed phases is often a strong function of temperature, as is the
868 threshold for condensation. For example, at 200 K, a 1-K change in temperature changes
869 the saturation vapor pressure of water over ice by approximately 15%. When coupled to
870 uncertainties in water vapor measurements, errors in temperature observations or
871 calculations can have dramatic impacts on the determination of conditions such as
872 supersaturation or the presence of polar stratospheric clouds, and hence, chlorine
873 activation.
874
875 **2.d. Present State of Measurements and Data Analysis**
876 To understand the photochemistry of ozone in the UT/LS, it is important to know the
877 distributions of the major species that produce ozone (HOx, NOx, and hydrocarbons) and
878 those that destroy it (HOx, ClOx, BrOx, and NOx). Due to the strong coupling between
879 species within the radical families and between species from different families, it is not
880 necessary to measure all of the important species simultaneously. However, it is
881 important to have a good understanding of interrelationships between the major ozone-
882 forming/destroying radicals under the wide range of conditions that prevail where aircraft
883 emissions can be found. This includes temperatures that can range from ~190-240 K,
884 solar zenith angles from 0 degrees to greater than 90 degrees, and ozone abundances that
885 range from tens to thousands of ppb.
886
887 Not only is it a primary emission product of combustion, NOx has a controlling influence
888 on partitioning within the HOx and halogen families. Therefore, measurements of NOx in
889 the UT/LS are important for defining the range of variation of the other ozone-controlling
890 radicals. Results from a number of major aircraft campaigns, some designed to validate
891 new orbiting platforms, as well as routine measurements from   commercial airliners

892   equipped with instrumentation, have provided a wealth of information relevant for
893   understanding oxidation, as well as ozone formation and loss, in the UT/LS. The results
894   summarized in section 2.c for UT NOx and HOx chemistries have provided a strong
895   foundation for new modeling studies to address the impacts of NOx emissions on ozone
896   and methane in the broader upper troposphere and lower stratosphere. However, new
897   results pointing to a reversal in the impacts on ozone in aircraft contrails and cirrus
898   clouds raises important questions about the completeness of the measurements.
899   Unfortunately, observations in regions of low NOx have not been a major priority of
900   recent aircraft campaigns, and key satellite instruments do not have sufficient vertical or
901   horizontal resolution to examine these kinds of issues in narrow regions where
902   heterogeneous chemistry could play a dominant role .
903
904   Our understanding of the distribution of water vapor and the processes that control it
905   remains problematic. In the regions where heterogeneous chemistry would be most
906   important (i.e., at or near the tropopause), long-standing discrepancies between
907   measurements makes it extremely difficult to predict the chemical response to any
908   perturbation, let alone one that includes potential ice nuclei, water vapor and important
909   co-condensable species such as nitric acid, plus species that can inhibit ice formation
910   (such as volatile organic compounds). Although this issue is addressed in detail in
911   another SSWP in the context of cirrus and persistent contrail formation, the critical role
912   that these observations play in allowing for the prediction of the reactivities of particles
913   and, hence, their importance to this SSWP, cannot be understated. Resolution of this
914   problem is critical for assessing the impacts of aircraft emissions on particle formation,
915   heterogeneous chemistry, redistribution of condensable species, transport of emissions to
916   the stratosphere, and production of HOx. Currently, the reported differences of up to 30%
917   between widely respected measurements is unacceptable, especially when they imply
918   strange behavior for particles that could change our fundamental view of the nature of
919   aerosols and clouds [e.g., cubic ice, nitric acid antifreeze, and very large
920   supersaturations].
921
922   Important results on water vapor measurements are expected in 2008 from the recent
923   AquaVIT intercomparison discussed in Section 2.c.IV.; however, it is important to note
924   that laboratory intercomparisons of the same or similar instruments have been carried out
925   before, and while they have answered some questions, they have largely been
926   unsuccessful at resolving the major discrepancies in the atmospheric measurements
927   themselves. Consequently, the state of *agreement* among water vapor measurements
928   remains inadequate for assessing the key remaining aviation impacts issues, even though
929   the instruments themselves may be in a mature state.
930
931   A new approach to water vapor intercomparisons would be welcome. One approach that
932   could be promising - dedicated flights into the combustion plumes of rockets and aircraft
933   - is described in more detail below. In 2008, potentially important results will be
934   forthcoming from a small pilot program called "PUMA" (Plume Ultrafast Mesaurements
935   Acquisition) that explore the nature of the discrepancy between water vapor
936   measurements in the UT/LS and the implications of heterogeneity on interpretations of
937   non-linear processes (such as threshold behaviors for condensation and evaporation of

938 ice, HOx and halogen photochemistry, and redistribution of major species, such as H$_2$O
939 and NOx). Preliminary analyses of H$_2$O and particulate water data in evaporating plumes
940 are quite promising, and indicate that future measurements in these environments could
941 play a critical role in validating the accuracies of water vapor measurements. An
942 interesting question raised by these studies is whether the highly perturbed plumes
943 represent a realistic environment for investigating fundamental photochemical and
944 dynamical issues important in the UT/LS. From the point of view of the assessment of
945 aircraft emissions, it would seem that such environments, especially the plumes and
946 persistent contrails produced by aircraft themselves, would be ideal natural 'laboratories'
947 for studying important processes identified in these SSWPs. In addition, there are some
948 who argue that pushing measurements outside their normal dynamic range is one sure
949 way to find problems that might help in identifying those issues that are important under
950 more normal conditions.
951
952 Finally, it is important to note here that satellite observations, with a few noteworthy
953 exceptions, have not yet been a major driving force in refining our understanding of
954 aircraft impacts. However, following completion of validation activities, new results from
955 the AURA platform, as well as those from SCIAMACHY, ACE, etc., will be analyzed in
956 light of the issues raised here and in previous assessments. It is very likely that significant
957 new insights into convective sources of NOx and NOy, HOx, and aerosols will be
958 forthcoming from analyses of observations made from numerous satellite platforms. Such
959 results will be especially important in defining the basic state of the UT/LS into which
960 aircraft emissions represent a small, but important, perturbation.
961
962 **2.f. Current estimates of climate impacts and uncertainties**
963 Since the IPPC [1999] Assessment and the Sausen [2005] of the Brasseur et al. [1998]
964 European Report, there are no direct comparative model studies that address current
965 estimates of climate impacts and uncertainties. However, on the basis of the new results
966 presented above, some general conclusions can be drawn. First, on the basis of improved
967 understanding of upper tropospheric sources of NOx, in particular, due to lightning and
968 convection from the PBL, it can be interred that the climate impact of aircraft emissions
969 on regional and global scales will be reduced. Second, on the basis of studies showing an
970 increased sensitivity of NOx and NOy to heterogeneous chemistry, it is likely that for
971 subsonic emissions there will be regions of the atmosphere where aircraft NOx and
972 particles may, in fact, result in ozone losses, especially in the tropopause and LS regions.
973 On the basis of this result, one would expect the climate impacts of subsonic aircraft
974 emissions to be smaller than previously believed, and possibly reversed in sign relative to
975 previous evaluations (e.g., negative instead of positive), whereas the impacts of
976 supersonic emissions would be greater than previously believed, and positive instead of
977 negative. Third, the observation of nitric acid-containing particles in the UT/LS, along
978 with measurements indicating more vigorous transport of NOx from the surface, raises
979 the possibility that NOx and NOy are processed more rapidly in the UT/LS than
980 previously believed. Finally, the presence of reactive halogens in the UT/LS, species that,
981 at the abundances that have been observed, can only coexist with NOx if there is rapid
982 heterogeneous processing, raises the possibility for highly non-linear photochemistry that

983　can result in a net positive or net negative change in ozone with aircraft emissions of
984　NOx and particles.
985

986　It is likely that future studies of the climate impacts of subsonic aircraft emissions that
987　have more realistic treatments of lightning and convective sources of NOx, more
988　complete treatments of redistribution of NOy, especially in persistent contrails, and
989　heterogeneous halogen chemistry will find that the climate impacts are reduced, or even
990　reversed in sign (i.e. ozone losses due to aircraft) in the UT/LS. This possibility, calls into
991　question the uncertainties ascribed to the chemistry of NOx emissions by aircraft. Our
992　understanding probably remains as "fair", until new CTM studies can be carried out, but
993　the magnitudes of the error bar placed on the RF terms in Figure 1 may be too small, and
994　may need to accommodate a reverse in sign, at least until the implications of these new
995　results can be properly assessed with new model studies.
996

997　The growing body of HOx observations in the UT indicates that OH abundances are at
998　the high end of most model predictions, resulting in a lower lifetime for methane in the
999　UT. This implies that, at least in these regions, methane will have a greater sensitivity to
1000　perturbations on NOx and aerosols due to aircraft emissions. In addition, the potential for
1001　an increased role in halogen chemistry in cirrus and persistent contrails raises the
1002　possibility that aircraft perturbations to methane may currently be underestimated, as the
1003　reaction of methane with chlorine atoms is likely to be more important in the UT/LS than
1004　is currently believed.
1005

1006　**2.g Interconnectivity with other SSWP theme areas**
1007　As has been discussed earlier, the chemistry of aircraft emissions is highly non-linear and
1008　strongly coupled with important processes dealt with in other SSWPs, including
1009　formation of persistent contrails and cirrus. Furthermore, and potentially more
1010　problematic for assessing impacts, emissions of NOx could alter redistribution of NOy
1011　and water, not only from aircraft exhaust, but from the background atmosphere as well if
1012　the addition of NOx results in enhanced large-particle stability and sedimentation. It is
1013　also possible for NOx influences to impact transport of NOy and H_2O (although the latter
1014　may be too small to matter) from the UT into the LS. As noted in Section 2.d., the
1015　greatest uncertainty for this SSWP is due to the implications of continuing discrepancies
1016　in water vapor measurements in the cold and dry regions of the UT/LS. Thus, there is a
1017　strong interconnection between this SSWP and those on particle microphysics and
1018　contrail and cirrus cloud formation.
1019

1020　**3. Outstanding issues**
1021　Progress made in areas highlighted in Section 2.c., especially that relating to the
1022　importance of heterogeneous chemistry, raise new questions about the fundamental
1023　chemistries of NOx, HOx, and halogens, and the interactions of ice and nitric acid in the
1024　UT/LS, all which can have important consequences in future assessments of aviation
1025　impacts. Key new findings in these areas are summarized in Section 3.a. Although their
1026　impacts have not yet been adequately assessed, their tendency to push the effects of
1027　aviation emissions in the same general direction that has been found in model studies

1028 summarized in Section 2.c.III. is somewhat troublesome, in that they have the ability to
1029 offset some of the advances that have occurred over the past decade.
1030
1031 **3.a. Science**
1032 The key developments in UT chemistry summarized in Section 2.c. place considerably
1033 more emphasis on the role of heterogeneous chemistry of non-aircraft species, such as the
1034 halogens, on understanding the distributions of background H_2O and nitrogen oxides, and
1035 on the need for new studies that address chemical heterogeneities of the UT/LS.
1036 One of the interesting consequences of the increased importance of heterogeneous
1037 processes is the change in sign of ozone response with NOx perturbation described
1038 earlier. This section will highlight important issues listed in the 2006 Workshop
1039 [Wuebbles et al., 2006] that remain unresolved, and new findings that raise new questions
1040 about chemistry in the UT that must be understood before uncertainties in the impacts of
1041 aircraft emissions on chemistry in the UT/LS can be reduced further.
1042
1043 **3.a.I Discrepancies in Coupled HOx and NOx Chemistry**
1044 The ability to realistically simulate ozone production and loss and the coupling between
1045 CH_4, CO, OH, and O_3 relies upon an accurate model representation of the response of
1046 HOx (and, to a lesser extent, halogen radicals) to variations in NOx. There have been a
1047 significant number of campaigns where NO, NO_2, OH, HO_2, and ozone have been
1048 measured simultaneously, and the first-order linkages between the NOx and HOx
1049 families have been demonstrated. However, model comparisons with HOx observations
1050 have been somewhat problematic [Faloona et al., 2000]. Olson et al. [2006] show that
1051 most of the previous model-measurements discrepancies at high NOx (e.g. during
1052 SONEX) can be explained by non-linearities of HOx chemistry under highly variable
1053 conditions for NOx (i.e., the model timescales are too long, relative to the measurements,
1054 such that averages of derived quantities do not represent quantities derived from averages
1055 of the individual measurements – see also Wild and Prather [2006]).
1056
1057 Despite considerable progress that has been made in the area of tropospheric HOx
1058 chemistry, as noted in two very recent papers [Hudman et al., 2007; Ren et al., 2008],
1059 observations continue to highlight important discrepancies between models and
1060 measurements. Figure 6 taken from Ren et al. [2008] shows how well models agree with
1061 measurements of HOx during three recent major field campaigns for which there were
1062 comprehensive suites of measurements of sources of HOx. The agreement between
1063 modeled and measured OH is quite good over most of the range, except, perhaps, at the
1064 very highest NO where a slight underprediction develops for INTEX-A (where the
1065 highest NO values were observed). However, at high NO, measured HOx exceeds that
1066 from the model by as must as an order of magnitude at highest NO. Further insight into
1067 this issue is gained by examining the altitude dependence of the discrepancy, as shown in
1068 Figure 7. Clearly these results are problematic for assessments of the impacts of aviation,
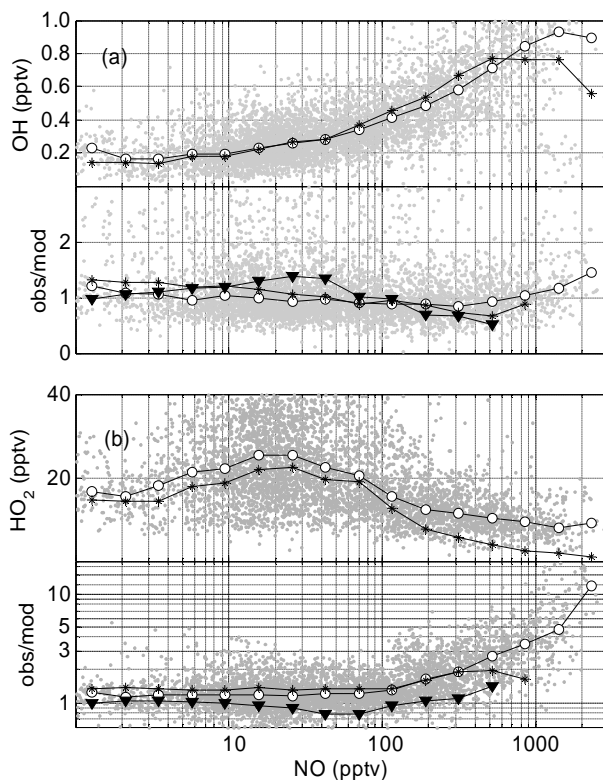
Figure 6. (a) Comparison of NO dependence for observations of OH (upper panel) and the ratio of measured-to-measured OH (lower panel). (b) Comparison of NO dependence for observations of HO_2 (upper panel) values and the ratio of measured-to-modeled HO_2 from INTEX-A (circles), TRACE-P (stars) and PEM Tropics B (triangles). Individual INTEX-A 1-minute measurements are shown (gray dots). All lines show the median profiles [from Ren et al., 2008].

since high NOx abundances can develop in heavily traveled flight corridors [e.g., see IPCC 1999]. The reasons for these discrepancies remain elusive. However, new observations of a critical species, pernitric acid (HO_2NO_2), whose abundance is determined by the coupled photochemistry of HOx and NOx, may help provide some answers [Murphy et al., 2002; Kim et al., 2007]. In a new report of simultaneous in situ observations of HO_2NO_2, NO_2, and HO_2, at aircraft cruise altitudes, Kim et al. [2007] found that abundances of HO_2NO_2 were about a factor-of-two low than those calculated with assumed photochemistry and observed abundances of HO_2 and NO_2. This discrepancy can be reconciled if one of the measurements (most likely HO_2NO_2 or HO_2) were in error (too small or too large,
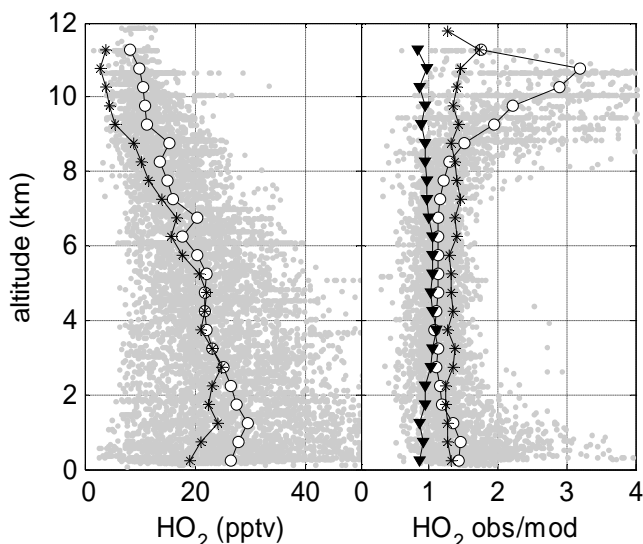
Figure 7. Similar to Figure 3, but for HO$_2$. (left panel) Comparison of the median vertical profiles of measured (circles) and modeled (stars) of OH for INTEX-A. (right panel) Measured-to-modeled OH in INTEX-A (circles), TRACE-P (stars) and PEM Tropics B (triangles). Individual 1-minute measurements from INTEX-A are shown (gray dots) [from Ren et al., 2008].

respectively). However, it is interesting to note that the trend in this discrepancy with altitude is similar to that of Figure 7, raising the possibility of missing or poorly understood chemistry coupling HOx to NOx in the relatively cold and dry upper troposphere. It is particularly problematic for assessments of aircraft emissions that the discrepancy is largest at cruising altitudes for most large subsonic aircraft.

3.a.II. Halogen Chemisty
In any modeling study of the impacts of a perturbation, it is important to start with a correct description of the composition of the background atmosphere. In previous aircraft assessments [Brasseur et al., 1998; IPCC 1999] it has been assumed that reactive halogens are not present in sufficient abundances to significantly impact ozone chemistry. Such a view was not based on observations, as there were few reliable observations of ClO and BrO in the UT/LS. Following the first observations of enhanced ClO in the lowermost stratosphere in 1991 [e.g., Avallone et al., 1993], ozone loss due to heterogeneous chemistry on cirrus clouds was proposed as a way to explain a gap between modeled and measured ozone trends in the midlatitude LS [e.g., Borrmann et al., 1996; Solomon et al., 1997]. A detailed examination of water vapor and ClO measurements in the UT/LS found no evidence for heterogeneous activation of chlorine [Smith et al., 2001]. However, subsequent measurements of ClO in the Arctic and examination of measurements over the continental US, both near the tropopause, found
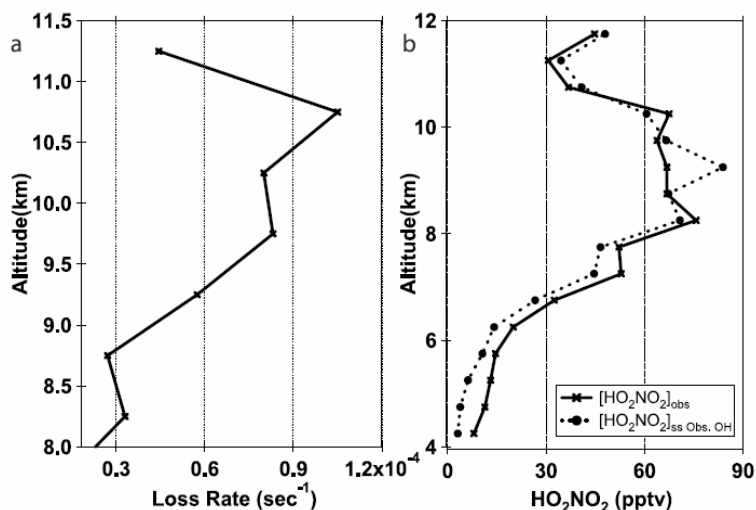
Figure 8. Implications of new observations reported by Kim et al. [2007] revealed an imbalance of production minus loss representing 50% of the magnitude of the production rate calculated from observed abundances of HO_2 and NO_2 (left panel). HO_2NO_2 abundances were in good agreement with steady-state calculations based on observed abundances of OH (right panel), suggesting a problem with coupled HO_2/NO_2 chemistry or one of the observations.

evidence for widespread chlorine activation in regions of high particulate loading [Thornton et al., 2003, Thornton et al., 2007]. The diurnal behavior of reactive chlorine was very suggestive of rapid in situ processing by aerosols [Thornton, 2005].

As noted in Section 2.c.III., modeling studies that included heterogeneous processing of NOx found significant changes in the response of ozone to aircraft emissions. In one case [Meilinger et al., 2005], it was the consideration of heterogeneous reactions on ice in persistent contrails that led to important changes in ozone response. In the case of the study by Hendricks et al. [2000], simply including heterogeneous reactions of bromine nitrate, significant denoxification occurred in some regions with important consequences on ozone. Finally, in the very recent study by Sovde et al. [2007], properly accounting for known heterogeneous reactions on aircraft-perturbed aerosol particles resulted in a complete reversal in sign of the ozone response to increased emissions in the UT. Based on these results alone, a reexamination of the role of heterogeneous reactions on background aerosols and in persistent contrails and cirrus using updated photochemical parameters is warranted.

Adding to the complexity of this issue, over the past decade there have been a number of reports (more than will be referred to here – see Salawitch et al. [2005]) of larger-than-expected abundances of BrO in the upper. Salawitch et al. [2005] make a strong case for the need to add upwards of 2-4 ppt of bromine to the stratospheric budget, either by transport of inorganic species (such as BrO, $BrONO_3$, and HOBr) or short-lived organic sources. In light of the increased number of surface sources required to explain recent NOx and HOx measurements in the UT, it seems reasonable that both types of species could contribute to this ~10-20% enhancement in the total bromine budget by short-lived

1152 species [e.g., Sinnhuber and Folkins, 2006]. However, there are some important caveats.
1153 First, it is only the remotely sensed observations of BrO that point to a need to increase
1154 the bromine budget beyond what measurements of organic source gases seem to suggest
1155 – in other words, beyond about 4 ppt of bromine from short-lived compounds [e.g., Dorf
1156 et al. 2006a]. Second, even the remote sensing observations of BrO do not agree; they
1157 split roughly 50/50 in number between those that agree [Schofield et al., 2004];
1158 Sinnhuber et al., 2005] with a budget based on measurements of source gases and some
1159 short-lived compounds near the tropopause [e.g., Schauffler et al., 1999] and those that
1160 suggest missing nearly double those short-lived sources of bromine [e.g., Sioris et al.,
1161 2006; Theys et al., 2007].
1162
1163 This issue is treated in great detail in the recent WMO Ozone Report [2006], so will not
1164 be discussed further here, other than to note that due to the importance of bromine in
1165 some regions of the UT/LS (e.g., Hendricks et al., 2000), new observations of BrO with
1166 high spatial resolution, and in conjunction with observations of NOx and HOx, may be
1167 required to resolve this issue.
1168
1169 **3.a.III. Potential Surprises**
1170 "Our vision is often more obstructed by what we think we know than by our lack of
1171 knowledge." These words of Krister Stehdahl, the Harvard Professor of Divinity, apply
1172 well to this problem. It is important to remember the lessons of the 1985 WMO Ozone
1173 Assessment, where the consensus view at the time was that the ClO dimer and
1174 heterogeneous reactions would not play important roles in stratospheric ozone chemistry.
1175 This lesson seems relevant to this White Paper, and the authors view several issues that
1176 fall in this category as the most important in terms of limiting our ability to accurately
1177 assess the current impacts of aviation on UT/LS chemistry and predict future impacts.
1178
1179 *Scavenging of NOy*
1180 Another important series of new observations are those related to the formation of nitric-
1181 acid containing ice particles in the UT/LS [Voigt et al. 2007, Voigt et al. 2007, and Popp
1182 et al. 2006]. The fact that such particles are larger, and less abundant than other particles
1183 suggests that their sedimentation could impact distributions of reactive nitrogen and
1184 water in the UT/LS. Redistribution and/or removal of NOy and H_2O from the UT/LS
1185 could result in important non-linearities that are presently not treated adequately in
1186 models. For example, it is possible that addition of aircraft NOx, followed by enhanced
1187 sedimentation of nitric acid-containing particles, could denitrify a narrow layer centered
1188 about the flight corridor. In the tropics, such a process could even mean that aircraft
1189 emissions 'seed' the removal of NOy and water, thereby decreasing transport of these
1190 species to the stratosphere (i.e. a negative feedback loop). Recent observations of
1191 significant chlorine activation in broad region near the polar tropopause where NOy-
1192 containing particles were also observed [Thornton et al., 2003] suggest that such a
1193 feedback is possible. Thus, it is important to understand better uptake of NOy species on
1194 ice particles and the role of temperature and water vapor (i.e. RHi) on such processes.
1195 Key to such an understanding will be the accuracies of measurements of water vapor and
1196 condensed water in the UT/LS.
1197

1198 *Non-linear Processes – Feedbacks and Plume Dispersion*
1199 The issue of potential surprises due to a lack of understanding of plume dispersion must
1200 be examined in greater detail. One of the ubiquitous features of in situ measurements of
1201 many types is their high degree of heterogeneity to very small scales [Richard et al. 2006,
1202 and Lovejoy et al. 2007]. In fact, for reactive species, this can translate down to sub-
1203 meter scales [unpublished results from the PUMA campaign]. Therefore, it is insufficient
1204 to assume simple gaussian plume dispersion when it is known that constituents exhibit a
1205 high degree of variability, even hours after they are emitted. This is especially the case
1206 when differences between vertical mixing and horizontal shear forces result in
1207 filamentary structures [e.g Fairley et al., 2007] that are difficult to describe with a simple
1208 gaussian parameterization.
1209
1210 We also lack a basic understanding of non-linear processes that can occur in the
1211 heterogeneous environment of an aircraft plume and persistent contrail. With the likely
1212 addition presence of solid or liquid mixtures of HNO_3 and H_2O (e.g. nitric acid
1213 trihydrate), in which the stability is proportional to the density of the plume raised to a
1214 power as large as four, and where heterogeneous reaction rates are strong non-linear
1215 functions of relative humidity and composition, this problem has only become more
1216 difficult to handle following observations of nitric acid-containing particles in the UT/LS.
1217 In a sense, this issue, along with the non-linear coupling between HOx, ClOx, BrOx, and
1218 NOx, is reminiscent of the ozone hole. While the effects will not be as severe, their role
1219 in the aircraft emissions assessment process is only now being addressed in sufficient
1220 detail.
1221
1222 **3.b. Measurements and analysis**
1223 New and improved measurements and analysis of existing data should help to address
1224 some of the outstanding issues highlighted above. As noted previously, reanalysis of HOx
1225 measurements may help to resolve some discrepancies between models and
1226 measurements that have been noted previously. It is also possible, perhaps likely, that
1227 such analyses will raise new questions. In addition, ongoing observations of HOx, along
1228 with NOx, source gases, and tracers of transport from the PBL and stratosphere, as are
1229 planned for major campaigns such as ARCTAS in 2008 are critical for efforts to map out
1230 seasonal and regional variations of this critical oxidizer. Such observations will provide
1231 important constraints for models used to assess the role of HOx chemistry, especially tat
1232 related to methane oxidation.
1233
1234 New, fast response, in situ measurements in aircraft plumes, including particles, water
1235 vapor, several good tracers of combustion and mixing (e.g. CO_2 and CO), ice water
1236 content, HOx, NOx, and at least one halogen radical would go far toward reducing
1237 uncertainties resulting from non-linear processes. The capability exists for such
1238 measurements, although to date, they have not been carried out downstream of an aircraft
1239 or in aircraft flight corridors (the potential to rectify this situation exists during
1240 ARCTAS).
1241
1242 Continued analyses of satellite data, particularly those with sufficient horizontal
1243 resolution to identify regions of interesting chemistry (e.g. in persistent contrails, the

1244 North Atlantic Flight Corridor, or in the tropopause region), may shed light on the
1245 importance of potential non-linearities that may be difficult to examine by in situ
1246 methods. Of particular value would be studies of correlative measurements of clouds and
1247 trace constituents (e.g. TES, MLS, SCIAMACHY, OMI, AIRS, MODIS) that might
1248 reveal linkages between cloud occurrences and constituent abundances.
1249
1250 Efforts should continue to understand bromine and chlorine chemistry in the UT/LS, in
1251 particular the variations of abundances of BrO and ClO. Of particular interest would be
1252 high-resolution correlative measurements of these species with HO_2, OH, and NOx, along
1253 with their respective source gases. Observations in aircraft plumes and flight corridors
1254 would be especially helpful for constraining plume dispersion models. Finally, it will
1255 likely be necessary to carry out frequent water vapor measurements intercomparisons to
1256 continue to refine our understanding of the factors that influence the discrepancies that
1257 have been observed between various techniques.
1258
1259 **4.a. Prioritization of Issues Based on Impact**
1260 The outstanding issues identified above can be prioritized on the basis of the level of
1261 scientific understanding and the magnitude of the terms each represents in the most
1262 recent IPCC "Radiative Forcing"-like representation of aviation effects on climate.
1263 Referring to Figure 1, this would suggest that improvements in understanding of the
1264 processes that impact the distribution of ozone (28 mW m^{-2} and "fair") and the lifetime of
1265 methane (20 mW m^{-2} and "fair") will be most significant. Of lesser importance are the
1266 impacts on direct radiative forcings due to emissions of CO_2, H_2O, sulfate and soot.
1267 Finally, of least importance would be investigation of issues that were not considered in
1268 detail in previous impacts assessments.
1269
1270 However, it is also worthwhile to consider prioritization of issues on the basis of the
1271 extent to which they may represent a dramatic shift in our basic understanding of the
1272 impacts of aviation. In this case, those issues deemed of least importance using the
1273 present framework of the IPCC Forcings, as outlined above, could be considered of
1274 highest priority from the point of view of uncertainty or "surprise". For example, if a
1275 proper treatment of heterogeneous chemistry on aircraft-produced particles or of aircraft
1276 emissions of NOx and H_2O on background aerosols results in a reversal of the sign of
1277 ozone change in the UT/LS, this would essentially render as moot the prioritization of
1278 issues based on the previous IPCC-like forcings. That is, because the sign for the
1279 radiative impact of aircraft-induced ozone changes could, in fact, be negative, a result
1280 that is outside the present estimate of uncertainty for that particular term in Figure 1.
1281 While the possibility of this type of "surprise" is relatively small, given recent
1282 observations that raise questions about our understanding of heterogeneous chemistry in
1283 the UT/LS, it is prudent to examine the potential consequences of previously unknown
1284 processes before expending much effort toward reducing the uncertainties of processes
1285 that were previously believed to be the most important.
1286
1287 In the section that follows, we approach the prioritization from these different
1288 perspectives, beginning first with the conventional approach of prioritizing the issues on

1289 the basis of reducing the current list of uncertainties. We then follow with a prioritization
1290 of issues based on the potential for a major shift in our understanding of the impacts.
1291
1292 *Priority 1 – Water Vapor Measurements*
1293 Long-standing discrepancies among water vapor measurements (both in situ and remote)
1294 in the coldest and driest regions in the UT/LS continue to limit efforts to accurately
1295 quantify the role of heterogeneous chemistry in conversion of NOx to NOy, to model
1296 HOx production and loss, to predict the frequency and extent of halogen activation, and
1297 to model the distribution of exhaust emissions (in particular, sedimentation of NOx and
1298 H_2O) in the UT/LS. Of critical importance is the characterization of the role of
1299 supersaturation (i.e., RHi) in particle formation and growth, both highly non-linear
1300 processes.
1301
1302 One method for assessing the accuracy of water vapor measurements is to examine
1303 observations from different pairs of instruments in a series of informal intercomparisons.
1304 From such opportunities, it is known that particular instruments report data that is
1305 consistently as much as 40% larger than all other techniques under the driest conditions
1306 in the UT/LS. These data have led researchers to conclude that large supersaturations
1307 (well over 150% in some cases) exist. Because all of the in situ instruments have been
1308 characterized separately in the laboratory, it has been argued that carefully designed and
1309 executed laboratory intercomparisons will help to resolve outstanding differences. A
1310 recent formal (double-blind) intercomparison (AquaVIT) has revealed some issues that
1311 may help to reduce the discrepancy among instruments. However, it will still be
1312 necessary to demonstrate consistent agreement amongst instruments under a wide range
1313 of conditions in actual atmospheric observations before this problem can be considered to
1314 be resolved.
1315
1316 Unfortunately, few, if any, dedicated intercomparison campaigns are being planned that
1317 will adequately address this critical issue. In part, this is due to the high costs that would
1318 be associated with a multi-platform, multi-instrument campaign which would be required
1319 to demonstrate good agreement over the wide range of conditions found in the UT/LS.
1320 For example, a month-long dedicated WB57F campaign based in Houston, designed to
1321 sample across a wide range of latitudes in order to encounter a reasonable dynamic range
1322 of water vapor values would involve over $1 million in aircraft operating costs and
1323 adequate funds for participant travel and post-mission analysis. In addition, it is unclear
1324 how new measurements obtained in this manner would resolve outstanding issues from
1325 previous campaign involving similar flight tactics. From many perspectives, a new
1326 approach aimed at clearly identifying instrument performance issues is required to make
1327 significant progress in this area, and to lend credibility to the results.
1328
1329 A promising new approach that could be taken to identify key areas of disagreement
1330 between instruments is to deploy them into combustion plumes in the UT/LS, both those
1331 laid down by aircraft and those laid down by rockets. The validity of this approach has
1332 been demonstrated recently in a pilot mission called PUMA (Plume Ultrafast
1333 Measurements Acquisition). In 2004, 2005, and 2006, exhaust emissions from three
1334 rockets (Atlas IIAS and two Space Shuttles) were sampled for particle size distributions,

1335   ice water content, water vapor, temperature, and carbon dioxide. The advantage to this
1336   approach is that a significant range of abundances of H_2O (from ambient levels near 4
1337   ppm to over 30 ppm) are encountered at each altitude where the plumes are sampled,
1338   providing for a slope/intercept analysis for each instrument. Such an approach can reveal
1339   whether measurement differences are due to differences in calibration or to offsets, the
1340   latter of which can be significant for water vapor in the dry UT/LS. One of the
1341   interesting results from PUMA is the demonstration that the contrail evaporation point
1342   (when RHi drops below 100%) serves as an important independent validation of the H2O
1343   vapor pressure measurement – that is, independent of the CO_2/H_2O emission index,
1344   which constrains the slope of a calibration (the "span" or response function), the instant
1345   when RHi drops below 100%, which can be identified unambiguously by an enhanced
1346   total water measurement such as CLH, is a powerful constraint on the accuracy of a total
1347   water measurement to a level that cannot be achieved in any laboratory calibration based
1348   on water vapor alone.
1349
1350   *Priority 2 – Temperature measurements*
1351   As shown above, in the context of defining RHi, measurements of temperature on most
1352   platforms agree to a level that is better than the agreement amongst water vapor
1353   measurements. However, making accurate temperature measurements is a non-trivial
1354   process, especially on a fast-moving platform, such as the WB57F, ER-2, or HIAPER.
1355   For example, near 200 K, a difference of 1 ^{o}C translates into an uncertainty of 10% in
1356   RHi. Thus, any program designed to address water vapor accuracies (especially one that
1357   relies on the vapor-ice transition such as that described above) must also address the
1358   accuracy of temperature measurements. It is the correction from observed to static
1359   temperatures using the "recovery temperature" equation that is most uncertain, as the
1360   correction involves quadratic terms for air speed that rely on highly accurate
1361   measurements of static and dynamic pressure. Consequently, accurate knowledge of the
1362   air flow around the aircraft surface where temperature probes are mounted is critical in
1363   order to determine recovery temperature to better than 1 ^{o}C.
1364
1365   One issue that has been raised when different temperature measurements from the
1366   WB57F aircraft have been compared is that placement of inlets can have profound effects
1367   on water vapor measurements in clouds (or at RHi near 100%) due to possible inertial
1368   enhancement of particulate water. It is recommended here that to avoid ambiguities (such
1369   as pressure perturbations near blunt surfaces or under wings), it would be quite useful to
1370   install temperature probes in various locations around the aircraft, especially on wing
1371   pods or under the wings near where water vapor instruments are deployed in any
1372   campaign that has a focus on accuracies of water vapor measurements. Good agreement
1373   between such measurements (say one located on a wing pod and one on the nose) serves
1374   to provide increased confidence that differences between measurements of water vapor
1375   are not due to perturbations of the temperature/pressure field around an instrument. This
1376   approach was used successfully during the PUMA campaign. As shown below, such
1377   measurements represent a very small cost compared to the time that could be lost in post-
1378   mission analyses that must account for potential consequences due to placement of
1379   temperature and pressure measurements.
1380

1381 *Priority 3. HOx Measurements*
1382 Critical to the modeling effort that is required to determine the impact of aircraft
1383 emissions on the global methane budget (and hence the radiative forcing term that is
1384 labeled by "CH_4" in Figure 1) is the ability for the models to accurately simulate global
1385 OH distributions. Not only does the abundance of OH determine the tropospheric lifetime
1386 of methane and the rate of conversion of NOx to NOy, OH and HO_2 are important ozone
1387 destroying radicals. In addition, the ability to model the sources of HOx in the UT/LS
1388 improves knowledge of the surface convective sources that also contribute the budget of
1389 NOx in the UT/LS. Finally, measurements of OH and the OH/HO2 ratio provide
1390 constraints on NOx and halogen chemistries.
1391
1392 A substantial heritage of measurements of OH and HO_2 in the UT/LS has been
1393 established as a result of numerous campaigns involving the ER-2 and DC-8 aircraft.
1394 Because HOx abundances are fundamental to a number of important processes in models
1395 used to assess aircraft impacts, continuing to add to the current database of HOx
1396 measurements will serve to reduce important uncertainties in those models. Frequent
1397 intercomparisons between measurements of OH and HO2 using different techniques will
1398 also help investigators reduce their measurement uncertainties, and should be
1399 encouraged.
1400
1401 *Priority 4 – Coupled HOx/NOx Chemistry*
1402 Possible discrepancies between modeled and measured HO_2NO_2, a compound that
1403 provides a critical link between the photochemistries of HOx and NOx families, should
1404 be investigated further. The current discrepancy points out a potential problem with the
1405 new measurements of HO_2NO_2 or one or more of the species that produces it, an error in
1406 a critical photochemical parameter, or missing chemistry that could be important in
1407 determining abundances of NOx or NOy in the UT/LS. Efforts to reduce uncertainties in
1408 the measurements of HO_2NO_2 and modeling investigations of potential errors in sources
1409 or sinks of HO_2NO_2 should be encouraged.
1410
1411 *Prioritization based on potential impacts that are currently unknown*
1412 Although important uncertainties remain in the processes listed in the section above, for
1413 all of these it is possible to estimate the likely bounds of their impacts with investigations
1414 that are constrained by known uncertainties in existing measurements. For example,
1415 impacts could be assessed with a model that assumes ice particle formation in the UT/LS
1416 at supersaturations consistent with the low end (i.e., driest) of the water vapor
1417 measurements and with those consistent with the high end of the measurements. Based on
1418 the resulting range of impacts, the need to resolve the discrepancies in water vapor
1419 measurements could be quantified (for example, a range of 10%, rather than 30%, is
1420 required for adequate assessment of this term). However, for several processes, the
1421 observations may be too limited to provide a reliable estimate of the impacts of aircraft
1422 emissions. In this section, these processes are given high priority based on the possibility
1423 that they could be significant, but reasonable bounds cannot yet be placed on their
1424 potential impacts due to lacking observational constraints (e.g., the situation, although
1425 probably not as dramatic, can be likened to that of 1985 when it was believed that

1426 heterogeneous reactions were not significant for ozone balance and that CFC-related
1427 ozone loss would occur in the middle stratosphere at mid-latitudes).
1428
1429 *Priority 1 – Investigations of non-linear effects*
1430 Recent observations of nitric acid-containing particles [Popp, et al.,] and enhancements
1431 in reactive chlorine [Thornton et al.,] in the UT/LS outside the polar regions have raised
1432 the possibility that heterogeneous reactions could lead to conversion of NOx to NOy, and
1433 activation of chlorine, in persistent contrails or cirrus occurring in flight corridors. It is
1434 even possible that NOy could be redistributed by sedimentation of particles if they grow
1435 large enough in these regions. Such processes are strongly non-linear in plumes or
1436 exhaust-influenced regions, due to the threshold nature of particle formation and strong
1437 water dependence of heterogeneous reactions involving halogens and NOy. To
1438 understand the role of such processes in UT/LS chemistry, details of the dispersion of
1439 exhaust become extremely important.
1440
1441 At the present time, there are few observations of the variability of constituents in and
1442 subsequent dispersion to the background atmosphere of exhaust plumes. In addition, the
1443 chemical composition of particles in exhaust plumes has only recently begun to be
1444 studied, and measurements of reactive halogens in the UT/LS with instruments sensitive
1445 enough to observe their small-scale (e.g., plume scale) variability have been ignored.
1446 Given the recent model results shown in Sections 2.C.II and 2.C.IV above, it is important
1447 to investigate the potential impacts of dispersion processes on the chemistry of plumes.
1448 Significant progress toward setting possible limits on the importance of such processes
1449 would be possible with modeling efforts that consider extreme cases, such as complete
1450 removal of NOy by sedimentation in persistent contrails, slow dispersion of plumes, and
1451 rapid heterogeneous reactions. Such studies could then serve to guide observations of
1452 species such as HNO_3, particles, ClO, and BrO that would constrain the impacts of these
1453 processes on the chemistry of ozone in the UT/LS.
1454
1455 *Priority 2 – The Role of Halogen Oxides in Background UT/LS Ozone Chemistry*
1456 Although it is believed that the importance of halogen oxides is limited by excess
1457 abundances of NOx in the UT/LS, recent observations of widespread, low levels (~1-2
1458 ppt) of BrO throughout the UT/LS and narrow regions with significant enhancements of
1459 ClO raise important questions about our understanding of halogen chemistry in the
1460 altitude region where aircraft emissions have the greatest impact on ozone abundances.
1461 Because coupled NOx/HC/HOx (i.e. "smog") chemistry tends to produce ozone in the
1462 upper troposphere, whereas halogens solely (and rapidly) destroy ozone, a better
1463 understanding of the distributions of halogen radicals is necessary to accurately simulate
1464 the impact of aircraft NOx and H_2O emissions on ozone in the UT/LS. Of particular
1465 concern is the possibility that NOx serves as a catalyst for production of halogen oxides
1466 via rapid heterogeneous reactions in the presence of sunlight. This situation is somewhat
1467 the reverse of that in the winter polar stratosphere, where NOx serves to deactivate the
1468 halogen radicals via formation of relatively stable reservoirs. In the UT/LS at lower
1469 latitudes, however, rapid heterogeneous conversion of inorganic halogen acids (e.g.,
1470 HOBr, HBr, HOCl, and HCl) is limited by availability of oxidants such as $ClNO_3$ and
1471 $BrNO_3$, such that addition of NOx serves as a catalyst for halogen activation, so long as

particulate surface areas are sufficient. With recent studies showing a reversal in sign of the impact of aircraft emissions on ozone abundances due to more rapid heterogeneous chemistry and halogen activation, it is important that the issue of distributions of halogen oxides be revisited.

There are several cost-effective ways that this issue could be approached. First, because abundances of ClO and BrO are quite small in this region, it would be useful for a team of investigators composed of modelers and measurements experts to model the impact on ozone of extreme scenarios involving halogen radicals in the UT/LS using the few existing observations. The calculated ranges of ozone could then be used to reexamine the radiative impacts of aircraft emissions. In addition, new high-resolution in situ measurements of halogen oxides in the UT/LS could be obtained in conjunction with measurements of NOx and HOx as part of larger campaigns designed to study the oxidative state of the UT/LS. Such measurements in the upper troposphere have had a very low priority on previous missions, except for the 1998 WB-57F Aerosol Mission (WAM) and the 2000 SOLVE campaign, results of which have shown that active forms of chlorine are more prevalent than was believed previously, provided that ample aerosol surface area abundances ($> 3 \, \mu m \, cm^{-3}$) are available. There are cost-effective ways to pursue this line of investigation, such as redeploying atomic resonance fluorescence (RF) instruments that have been used for over two decades for stratospheric measurements and that were previously flown on the WB-57F and DC-8 aircraft, in this case reconfigured for improved sensitivity under tropospheric conditions, or by adapting instruments that use an alternative detection technique (e.g., chemical ionization mass spectrometry - CIMS). In either case, there will be modest costs (see below) associated with the laboratory efforts required to optimize the existing stratospheric instruments for use in the UT/LS or those required to develop new calibrations and to develop a heritage of reliable observations, in the case of a new measurement technique, such as CIMS.

Laboratory measurements of key rate parameters at low temperatures of the UT/LS will continue to refine our understanding the sensitivities of NOx and heterogeneous chemistries to temperature, relative humidity and pressure, variables that can be important in the UT/LS.

4.b. Ability to Reduce Uncertainties
Given the wealth of new information regarding UT/LS chemistry that has become available in recent years, the ability to reduce uncertainties in estimates of the climate impacts of aviation is quite good. Significant progress can be made on nearly all of the topics presented in this SSWP within 3 to 5 years. The most problematic of the issues, those involving accuracies of water vapor measurements, plume dispersion, and heterogeneous chemistry, may require a longer timeframe to achieve the level of confidence that is associated with attribution of cause-and-effect for ozone destruction in the stratosphere, but given the level of knowledge already attained in the atmospheric chemistry community, it is not unreasonable to expect that an effort that is more focused on resolving the key issues outlined above can see significant progress within the time frame of 2 three-year grant cycles.

1518   First, and most critical, will be detailed studies with models that can treat plume
1519   chemistry and dispersion to scope out the range of possible impacts of non-linear particle
1520   formation processes and heterogeneous chemistry. Coupled with this knowledge, field
1521   and laboratory studies can be carried out to reduce the uncertainties in the most critical
1522   parameters that are revealed in these model studies. Of particular significance will be
1523   those fields studies that can address plume processes directly with the powerful suite of
1524   instruments and platforms that are currently in the atmospheric sciences arsenal. With
1525   few exceptions (such as better instruments for measuring halogens at part-per-trillion
1526   abundances and new or improved instruments to measure oxygenated source gases for
1527   HOx), the instruments and platforms required to provide critical observations to constrain
1528   these process models already exist, and the investment in the investigations needed to
1529   answer the critical questions will be valuable for issues that reach beyond the impacts of
1530   aircraft (for example, alternative energy production, changing climate, new technologies,
1531   etc.).
1532
1533   **4.c. Practical Use**
1534   Addressing all of the key issues above will have important practical applications,
1535   including improvements in measurements that address a broad range of atmospheric
1536   issues. Additional model development, especially an accurate and validated plume
1537   dispersion model can be quite useful for studying a number of issues related to climate
1538   change, including source apportionment of CO_2, an issue that will be of major importance
1539   in the future if CO_2 trading schemes become prevalent.
1540
1541   **4.d. Achievability**
1542   As noted in Section 4.b., important results are clearly achievable in all areas outlined in
1543   this SSWP. In most cases, cost will be the primary limiting issue, as some instruments or
1544   platforms that may be required for the most definitive studies will require significant
1545   modifications or deployment costs. Improvements in models that will be necessary to
1546   assimilate the results from new observations may require the development of new codes
1547   (for example, a high-resolution plume dispersion model). However, to date technology
1548   does not seem to be what has limited the development of such a model.
1549
1550   **4.e. Cost**
1551   Addressing the water vapor measurements issue will probably be the most productive use
1552   of funds at this point in time in terms of reducing uncertainties in aircraft climate impacts.
1553   However, due to the high level of interest for other programs (e.g., satellite validation and
1554   climate change studies in general), significant leveraging of funds should be possible, and
1555   should immediately be pursued. However, a business-as-usual approach is very likely not
1556   going to foster significant progress in this area, such that a new and creative program will
1557   be required. It would be helpful to develop clear milestones with broad community
1558   support, with implications for failure of PIs to meet stated accuracies. New and
1559   innovative approaches to validating water vapor (and condensed water) measurements in
1560   the cold and dry UT/LS, such as periodic direct flights in exhaust plumes to calibrate
1561   individual instruments, to reveal discrepancies between instruments, and to monitor
1562   instrumental drift, would be particularly useful. Such efforts that could also build on
1563   recent efforts, such as AquaVIT, to maintain a traceable set of intercomparisons, should

1564   be monitored regularly by a group of scientists who are both knowledgeable in the field,
1565   and outsiders who have an expertise in measurement intercomparisons and validations. It
1566   would be particularly helpful to develop a water vapor standard for calibrations and
1567   traceability, just as was done for ozone measurements, thereby reducing the reliance on
1568   costly large-scale laboratory intercomparisons.

1569

1570   It would be very useful to carry out an in-flight intercomparison of water vapor
1571   measurements in the UT/LS from a common platform, such as the DC-8 or WB-57, one
1572   that involves frequent sampling in aircraft plumes (both wet and dry). Not all instruments
1573   would have to participate in such an intercomparison, but it would be essential to have
1574   sufficient variety of existing instruments that span the range of current measurements
1575   (e.g., from those that are on the low side of the intercomparisons, such as frost point
1576   hygrometers, to those that are on the high side, such as the JPL TDL). Results in dry
1577   plumes can be traced to an absolute value using simultaneous measurements of CO_2,
1578   since the stoichiometry of combustion of aviation fuel is well known.

1579

1580   Overall, a ~$1-2 million program over five years, with funds provided from a variety of
1581   sources, would catalyze significant progress on this issue, and get away from the
1582   business-as-usual approach of providing limited funding for smaller, term efforts that
1583   piggy-back off larger projects, and end up suffering from too little funding without a
1584   guarantee of continued funds to thoroughly investigate the causes for discrepancies. A
1585   Water Vapor Campaign, whose chief focus is on reducing the uncertainties in
1586   measurements and maintaining a long-term, traceable record, should be a top priority for
1587   an aircraft impacts program, as well as a general world-wide program to monitor climate
1588   change.

1589

1590   With a clear focus on water vapor, other issues can be dealt with on an 'add-value' basis.
1591   For example, studies of non-linear processes in plumes would be a natural add-on to
1592   missions that use combustion plumes as a way to investigate instrument differences and,
1593   potentially, as a way to maintain a long-term calibration standard (assuming that
1594   combustion of kerosene will remain the method of choice for aircraft propulsion for
1595   many decades. Issues that require some instrument development (e.g., halogen and
1596   oxygenated organic compound measurements) should be initiated as soon as possible to
1597   reduce the long lead times that are associated with integration and demonstration of new
1598   instruments on research aircraft. Funding for these developments could be leveraged with
1599   funding agencies like NSF and DOE, insofar as other programs will benefit from the use
1600   of such instruments in other environments (e.g., halogens in the polar boundary layer,
1601   oxygenated compounds in urban pollution/source attribution studies, etc.). International
1602   cooperation would also help to reduce development time and cost, especially where there
1603   are common interests for measurement capabilities (i.e., it is cheaper per unit to build
1604   more than one).

1605

1606   Addition of increments of ~$300-500 K in a few key areas would likely result in
1607   important progress for most of the issues highlighted in this SSWP. A total program of $5
1608   million, including the water vapor project mentioned above, would probably reduce most
1609   of the remaining climate uncertainties in aviation operations by half, and change the level

1610 of understanding from poor or fair to good for most, if not all, chemical terms in the
1611 climate forcing framework.
1612
1613 **4.f. Timeline**
1614 Significant progress could be made on all of the issues discussed above within 3-5 years
1615 with an adequately resourced project. The expertise exists in the community and there
1616 would be limited need for development of new techniques. In fact, waiting longer could
1617 inadvertently result in significant additional expenses to carry out similar work, as
1618 experts in some areas retire or become involved in other projects. In the worst case, it is
1619 possible for an opportunity to be lost altogether. Because time is a factor, heritage should
1620 be a major factor in consideration of projects to fund. The cost of missed opportunities is
1621 difficult to estimate, but it vastly exceeds the cost of starting from scratch. instrument to
1622 service. (for example, it would be highly desirable to bring the NOAA-lyman alpha water
1623 instrument back into service, and waiting much longer may preclude this, and
1624 resurrecting this capability from scratch would be prohibitively costly, especially given
1625 the extraordinarily long record of measurements for this instrument) .
1626
1627 *Immediate*
1628 A water vapor program should be developed immediately. This issue will be around for a
1629 long time, and waiting longer will only serve to up the overall cost. Development and
1630 integration of new (or modified) instruments designed to address key 'missing terms' or
1631 resolve discrepancies between measurements should also begin as soon as possible. Far
1632 too often, such measurements are missing from major campaigns due to lack of planning
1633 and preparation.
1634
1635 **5. Best Way to Assess Uncertainties with Current Knowledge**
1636 In the absence of improvements in our understanding of the outstanding issues presented
1637 in Section 4.a., there are studies that can be undertaken now to assess the impacts of
1638 aviation on chemistry of the UT/LS that will represent a significant advance since the
1639 1999 IPCC Report. Before recommending such studies, it is important to note that such
1640 an advance does not necessarily imply that all of the specific uncertainties reported in
1641 previous assessments will be improved. It is possible that new observations reported
1642 above may reveal gaps in our understanding that were not foreseen a decade ago.
1643
1644 As noted above, resolving the water vapor measurements discrepancy in the cold, dry
1645 UT/LS is crucial in order to improve our understanding of the climate impacts of aviation
1646 that are linked to chemistry. Therefore, it would be extremely useful to use the best
1647 available 3D global chemical transport models to study the sensitivity of climate impacts
1648 to the two extreme possibilities that are represented in the literature. Based on
1649 uncertainties described in SSWPs dealing with clouds and aerosols, it is unclear whether
1650 the models sufficiently capture the complexities of condensation and dehydration, so it
1651 may not be straightforward to study these extreme cases from 'first principles.' That is, a
1652 realistic treatment of particle formation, composition, reactivity, and sedimentation, as a
1653 function of supersaturation on the scales of individual plumes and persistent contrails
1654 may not yet be possible. In this case, it would still be very useful to use some statistical
1655 representation of occurrences of cirrus, contrails, and persistent contrails as a basis for

1656 estimating the frequency of heterogeneous chemistry events [e.g., Bregman et al., 2002;
1657 Meilinger et al., 2005] and their contribution to the $d[O_3]$ and $d[CH_3]$ terms in the
1658 radiative forcing framework (e.g., Figure 1).
1659
1660 It is imperative that the recent results of Sovde et al. [2007] be examined in detail over
1661 the possible ranges of critical parameters such as lightning and convective fluxes of NOx,
1662 sources of HOx, microphysics of mixtures of HNO_3 and H_2O, and background
1663 abundances of halogens. Sensitivity tests of regional and global ozone and methane
1664 responses to aircraft emissions would help to narrow down the list of parameters to those
1665 that contribute to the bulk of the uncertainty in the aircraft RF terms. (This approach is
1666 similar to one taken several decades ago to define which rate parameters were most
1667 critical in determining ozone loss due to chlorine buildup, for example.)
1668
1669 New sensitivity studies should be carried out to address the role of processes that are
1670 highly scale-dependent, such as denoxification, sedimentation, and mixing. Processes that
1671 are important in persistent contrails, for example, may have very different impacts if they
1672 are modeled as being severe, but highly localized, versus moderate and more widespread.
1673 Effects such as redistribution of NOy by sedimentation are likely to be more severe,
1674 whereas those such as ozone loss due to chlorine activation may be less severe, in the
1675 former case (i.e., highly localized assumption).
1676
1677 Due to the large and growing body of HOx observations, it would be extremely useful to
1678 reevaluate the "CH_4" radiative forcing term with a CTM that is either constrained by or
1679 validated with observed OH fields.
1680
1681 Finally, it could be useful to carry out a series of focused observational studies to
1682 quantify the uncertainties in temperature and pressure measurements from aircraft. Not
1683 only will such studies improve our understanding of the uncertainties in past
1684 determinations of supersaturation, they will serve as the basis for much improved
1685 measurements of temperature in the UT/LS for future studies. Of particular value will be
1686 the development of ultra-fast (~100 Hz or faster) temperature probe for research aircraft
1687 such as HIAPER, the ER-2, the WB57F and Global Hawk, all of which can play
1688 important roles in defining thermodynamic variables in the UT/LS, but also for
1689 commercial aircraft that could be used to carry out long-term measurements in the
1690 UT/LS.
1691
1692 **6. Summary**
1693 Aircraft emit a variety of species that can alter climate and the chemistry of Earth's
1694 atmosphere. In this context, the most important are emissions of NOx, particles, and
1695 water vapor, all of which interact to determine ozone distributions in the UT/LS, a region
1696 where radiatively active gases have a strong influence on temperature and dynamics.
1697 Previous assessments pointed to increases in ozone columns and reductions in methane
1698 (from the influence of NO on the OH/HO_2) as the two chemical impacts that were likely
1699 to have the largest impact on climate (aircraft radiative forcing, RF). It was found that
1700 these two terms were of roughly equal magnitude, but opposite sign, so that the net
1701 climate impact of aircraft emissions chemistry was approximately neutral. However, the

understanding of the processes that determine these quantities was considered poor to fair. In the view that UT/LS chemistry is controlled by NOx, these two terms will always cancel, because the processes that result in ozone production will lead to methane destruction.

New observations and modeling efforts undertaken over the past decade have raised important questions about the basis for earlier assessments. In particular, NOx in the UT/LS is found to be partitioned in long-lived reservoirs to a larger extent than previously believed, presumably by heterogeneous reactions. Convective and lightning sources of NOx to the upper troposphere have also been found to be more important than previously believed. In addition, reactive bromine and chlorine radicals have been observed in the UT or LS, implying a greater role for these species in partitioning of HOx. Finally, large particles containing nitric acid have been observed in the UT/LS. Models that include more vigorous heterogeneous chemistry in the UT/LS indicate that emissions of particles from aircraft may actually reduce ozone in the UT and increase ozone in the lower stratosphere, the opposite of what was reported in the previous assessments.

Given that the climate impacts from ozone changes are partially offset by those of methane changes (assuming that the inverse relationship between NOx and OH is maintained under these new conditions), the impact to climate overall may not change dramatically with this sign reversal in ozone changes. However, if these changes are confirmed, strategies for reducing the impacts of aircraft emissions on atmospheric chemistry and climate would be very different than those based on work summarized in previous assessments. Therefore, it is important that these new findings and their implications be explored in more detail before designing mitigation strategies.

Significant progress toward reducing the uncertainties in UT/LS chemistry identified here can be made with modest investments in key areas. The observational and modeling tools are largely available, thanks to the high priority that has been placed on understanding UT/LS chemistry. Several high priority studies are recommended here. Of greatest priority would be supporting efforts to resolve long-standing discrepancies among measurements of water vapor, including establishment of a water vapor standard that is appropriate for UT/LS conditions, and carrying out high-resolution measurements of water vapor, particles, and CO_2 in and around aircraft plumes with a platform such as the DC-8, WB-57, or HIAPER. Augmentations of measurements of key species to address coupled radical chemistry to the payloads for major campaigns could reduce uncertainties in basic ozone loss chemistry.

With added importance of aerosols and clouds to ozone chemistry in the UT/LS, it will be important to assess the importance of heterogeneous chemistry and aerosol formation and evolution in aircraft plumes, persistent contrails, and cirrus clouds. Models that treat plume dispersion with some realism may be necessary, although our knowledge of the potential range of impacts of plume processes can probably be improved by simple sensitivity tests that assume extreme bounds for processes such as denoxification and redistribution of species such as NOy and H_2O. It would be reasonable to expect that

1748 significant new results to improve our understanding of the impacts of aircraft exhaust on
1749 atmospheric chemistry and climate would be forthcoming within three to five years of
1750 formulation of a focused program to address the major uncertainties presented in this
1751 White Paper for a total expenditure of under $10 million, including funds from all
1752 sources. There are significant opportunities for synergistic studies that are currently in the
1753 planning stages or underway, with strategic placement of new funds to target particular
1754 elements that are critical for specifically assessing the impacts of aircraft.

7. References

Anderson, B. E., et al. (2006), Hydrocarbon emissions from a modern commercial airliner, *Atmospheric Environment*, *40*(19), 3601-3612.

Arnold, F., A. Kiendler, et al. (2000), Chemiion concentration measurements in jet engine exhaust at the ground: Implications for ion chemistry and aerosol formation in the wake of a jet aircraft, *Geophysical Research Letters,* 27(12), 1723-1726.

Avallone, L. M., D. W. Toohey, et al. (1993), Balloon-Borne In-Situ Measurements of ClO and Ozone - Implications for Heterogeneous Chemistry and Midlatitude Ozone Loss, *Geophysical Research Letters,* 20(17), 1795-1798.

Bertram, T. H., A. E. Perring, et al. (2007), Direct measurements of the convective recycling of the upper troposphere, *Science,* 315(5813), 816-820.

Bencherif, H., R. D. Diab, T. Portafaix, B. Morel, P. Keckhut, and A. Moorgawa (2006), Temperature climatology and trend estimates in the UTLS region as observed over a southern subtropical site, Durban, South Africa, *Atmospheric Chemistry and Physics*, 6, 5121–5128.

Borrmann, S., S. Solomon, et al. (1996), The potential of cirrus clouds for heterogeneous chlorine activation, *Geophysical Research Letters,* 23(16), 2133-2136.

Bortz, S. E., et al. (2006), Ozone, water vapor, and temperature in the upper tropical troposphere: Variations over a decade of MOZAIC measurements, *Journal of Geophysical Research-Atmospheres*, *111*(D5), doi:10.1029/2005JD006512

Brasseur, G.P., R.A. Cox, et al. (1998), European scientific assessment of the atmospheric effects of aircraft emissions, *Atmospheric Environment*, 32 (13), 2329-2418.

Bregman, B., Wang, P. H., and Lelieveld, J. (2002), Chemical ozone loss in the tropopause region on subvisible ice clouds, calculated with a chemistry-transport model, *Journal of Geophysical Research-Atmospheres,* 107(D3), doi:10.1029/2001JD000761.

Brunner, D., et al. (2001), Nitrogen oxides and ozone in the tropopause region of the Northern Hemisphere: Measurements from commercial aircraft in 1995/1996 and 1997, *Journal of Geophysical Research-Atmospheres*, *106*(D21), 27673-27699.

Brunner, D., et al. (2005), An evaluation of the performance of chemistry transport models - Part 2: Detailed comparison with two selected campaigns, *Atmospheric Chemistry and Physics, 5*, 107-129.

Carslaw, D. C., et al. (2006), Detecting and quantifying aircraft and other on-airport contributions to ambient nitrogen oxides in the vicinity of a large international airport, *Atmospheric Environment, 40*(28), 5424-5434.

Chughtai, A. R., et al. (2003), The effect of temperature and humidity on the reaction of ozone with combustion soot: Implications for reactivity near the tropopause, *Journal of Atmospheric Chemistry*, *45*(3), 231-243.

Colette, A., and G. Ancellet (2005), Impact of vertical transport processes on the tropospheric ozone layering above Europe. Part II: Climatological analysis of the past 30 years, *Atmospheric Environment*, *39*(29), 5423-5435.

Colette, A., et al. (2005), Impact of vertical transport processes on the tropospheric ozone layering above Europe. Part I: Study of air mass origin using multivariate analysis, clustering and trajectories, *Atmospheric Environment*, *39*(29), 5409-5422.

1801 Colette, A., and G. Ancellet (2006), Variability of the tropospheric mixing and of
1802   streamer formation and their impact on the lifetime of observed ozone layers,
1803   *Geophysical Research Letters*, *33*(9), doi:10.1029/2006GL025793.
1804 Collins, W. J., et al. (1999), Role of convection in determining the budget of odd
1805   hydrogen in the upper troposphere, *Journal of Geophysical Research-Atmospheres*,
1806   *104*(D21), 26927-26941.
1807 Colomb, A., et al. (2006), Airborne measurements of trace organic species in the upper
1808   troposphere over Europe: the impact of deep convection, *Environmental Chemistry*,
1809   *3*(4), 244-259.
1810 Considine, D. B., et al. (2000), A polar stratospheric cloud parameterization for the
1811   global modeling initiative three-dimensional model and its response to stratospheric
1812   aircraft, *Journal of Geophysical Research-Atmospheres*, *105*(D3), 3955-3973.
1813 Cooper, O. R., et al. (2006), Large upper tropospheric ozone enhancements above
1814   midlatitude North America during summer: In situ evidence from the IONS and
1815   MOZAIC ozone measurement network, *Journal of Geophysical Research-
1816   Atmospheres*, *111*(D24), doi:10.1029/2006JD007306.
1817 Cox, V. (2007), *NextGen and Its Impact on Performance Worldwide Symposium on
1818   Performance of the Air Navigation System*, Presentation to the ICAO, Montreal,
1819   Quebec, Canada, March 26-30, 2007.
1820 Crawford, J., et al. (1999), Assessment of upper tropospheric HOx sources over the
1821   tropical Pacific based on NASA GTE/PEM data: Net effect on HOx and other
1822   photochemical parameters, *Journal of Geophysical Research-Atmospheres*,
1823   *104*(D13), 16255-16273.
1824 Dakhel, P. M., et al. (2007), Postcombustion evolution of soot properties in an aircraft
1825   engine, *Journal of Propulsion and Power 23*(5), 942-948.
1826 DeCaria, A. J., et al. (2005), Lightning-generated NOx and its impact on tropospheric
1827   ozone production: A three-dimensional modeling study of a Stratosphere-
1828   Troposphere Experiment: Radiation, Aerosols and Ozone (STERAO-A)
1829   thunderstorm, *Journal of Geophysical Research-Atmospheres*, *110*(D14),
1830   doi:10.1029/2004JD005556.
1831 Dessens, O. and P. Simon (2002), The importance of dynamics/chemistry coupling in the
1832   evaluation of aircraft emission impact studies, *Meteorologische Zeitschrift 11*(3),
1833   161-175.
1834 Dorf, M., et al. (2006), Balloon-borne stratospheric BrO measurements: comparison with
1835   Envisat/SCIAMACHY BrO limb profiles, *Atmospheric Chemistry and Physics 6*,
1836   2483-2501.
1837 Dorf, M., et al. (2006), Long-term observations of stratospheric bromine reveal slow
1838   down in growth, *Geophysical Research Letters 33*(24), doi:10.1029/2006GL027714.
1839 Eichkorn, S., et al. (2002), Massive positive and negative chemiions in the exhaust of an
1840   aircraft jet engine at ground-level: mass distribution measurements and implications
1841   for aerosol formation, *Atmospheric Environment 36*(11), 1821-1825.
1842 Esler, J. G., Roelofs, G. J., Kohler, M. O., and O'Connor, F. M., (2004), A quantitative
1843   analysis of grid-related systematic errors in oxidising capacity and ozone production
1844   rates in chemistry transport models. *Atmospheric Chemistry and Physics 4*, 1781.
1845 Fairlie, T. D., et al. (2007), Impact of multiscale dynamical processes and mixing on the
1846   chemical composition of the upper troposphere and lower stratosphere during the

1847   Intercontinental Chemical Transport Experiment-North America, *Journal of*
1848   *Geophysical Research-Atmospheres 112*(D16), doi:10.1029/2006JD007923.
1849   Faloona, I., et al. (2000), Observations of HOx and its relationship with NOx in the upper
1850   troposphere during SONEX, *Journal of Geophysical Research-Atmospheres 105*(D3):
1851   3771-3783.
1852   Farias, F. and H. ApSimon (2006), Relative contributions from traffic and aircraft NOx
1853   emissions to exposure in West London, *Environmental Modelling & Software 21*(4):
1854   477-485.
1855   Fehr, T., et al. (2004), Model study on production and transport of lightning-produced
1856   NOx in a EULINOX supercell storm, *Journal of Geophysical Research-Atmospheres,*
1857   *109*(D9), doi:10.1029/2003JD003935.
1858   Ferrare, R. A., et al. (2004), Characterization of upper-troposphere water vapor
1859   measurements during AFWEX using LASE, *Journal of Atmospheric and Oceanic*
1860   *Technology, 21*(12), 1790-1808.
1861   Folkins, I., et al. (2006), Testing convective parameterizations with tropical
1862   measurements of HNO_3, CO, H_2O, and O_3: Implications for the water vapor budget,
1863   *Journal of Geophysical Research-Atmospheres, 111*(D23), 10.1029/2006JD007325
1864   Forster, C., et al. (2003), The residence times of aircraft emissions in the stratosphere
1865   using a mean emission inventory and emissions along actual flight tracks, *Journal of*
1866   *Geophysical Research-Atmospheres 108*(D12), doi:10.1029/2002JD002515.
1867   Gao, R. S., et al. (2004), Evidence that nitric acid increases relative humidity in low-
1868   temperature cirrus clouds, *Science 303*(5657): 516-520.
1869   Gao, R. S., et al. (2006), Measurements of relative humidity in a persistent contrail,
1870   *Atmospheric Environment, 40*(9), 1590-1600.
1871   Gauss, M., et al. (2003), Impact of H_2O emissions from cryoplanes and kerosene aircraft
1872   on the atmosphere, *Journal of Geophysical Research-Atmospheres, 108*(D10),
1873   doi:10.1029/2002JD002623.
1874   Gauss, M., et al. (2006), Impact of aircraft NOx emissions on the atmosphere - tradeoffs
1875   to reduce the impact, *Atmospheric Chemistry and Physics 6*, 1529-1548.
1876   Grewe, V., et al. (2002), Impact of aircraft NOx emissions. Part 1: Interactively coupled
1877   climate-chemistry simulations and sensitivities to climate-chemistry feedback,
1878   lightning and model resolution, *Meteorologische Zeitschrift 11*(3): 177-186.
1879   Giannakopoulos, C., et al. (2003), Modelling the impacts of aircraft traffic on the
1880   chemical composition of the upper troposphere, *Proceedings of the Institution of*
1881   *Mechanical Engineers Part G-Journal of Aerospace Engineering 217*(G5): 237-243.
1882   Gulstad, L. and I. S.A. Isaksen, (2007), Modeling water vapor in the upper troposphere
1883   and lower stratosphere, *Terrestrial, Atmospheric and Oceanic Science, 18,* 415-436.
1884   Haag, W., et al. (2003), Freezing thresholds and cirrus cloud formation mechanisms
1885   inferred from in situ measurements of relative humidity, *Atmospheric Chemistry and*
1886   *Physics, 3*, 1791-1806.
1887   Haverkamp, H., et al. (2004), Positive and negative ion measurements in jet aircraft
1888   engine exhaust: concentrations, sizes and implications for aerosol formation,
1889   *Atmospheric Environment 38*(18), 2879-2884.
1890   Hays, M. D. and R. L. Vander Wal (2007), Heterogeneous soot nanostructure in
1891   atmospheric and combustion source aerosols, *Energy & Fuels 21*(2), 801-811.

Helten, M., et al. (1999), In-flight comparison of MOZAIC and POLINAT water vapor measurements, *Journal of Geophysical Research-Atmospheres*, *104*(D21), 26087-26096.

Hendricks, J., et al. (2000), Implications of subsonic aircraft NOx emissions for the chemistry of the lowermost stratosphere: Model studies on the role of bromine, *Journal of Geophysical Research-Atmospheres 105*(D5), 6745-6759.

Herndon, S. C., et al. (2004), NO and NO_2 emission ratios measured from in-use commercial aircraft during taxi and takeoff, *Environmental Science & Technology 38*(22), 6078-6084.

Herndon, S. C., et al. (2006), Hydrocarbon emissions from in-use commercial aircraft during airport operations, *Environmental Science & Technology 40*(14), 4406-4413.

Hudman, R. C., et al. (2007), Surface and lightning sources of nitrogen oxides over the United States: Magnitudes, chemical evolution, and outflow, *Journal of Geophysical Research-Atmospheres 112*(D12), doi:10.1029/2006JD007912.

Immler, F., et al. (2007), Cirrus clouds, humidity, and dehydration in the tropical tropopause layer observed at Paramaribo, Suriname (5.8 ^{o}N, 55.2 ^{o}W), *Journal of Geophysical Research-Atmospheres 112*(D3), doi:10.1029/2006JD007440.

Intergovernmental Panel on Climate Change (1999). Aviation and the Global Atmosphere, Special Report of IPCC Working Groups I and III, Cambridge University Press, Cambridge, UK.

Jaegle, L., et al. (1999), Ozone production in the upper troposphere and the influence of aircraft during SONEX: Approach of NOx-saturated conditions, *Geophysical Research Letters*, *26*(20), 3081-3084.

Karcher, B., et al. (2007), Insights into the role of soot aerosols in cirrus cloud formation, *Atmospheric Chemistry and Physics*, *7*(16), 4203-4227.

Karcher, B. and C. Voigt (2006), Formation of nitric acid/water ice particles in cirrus clouds, *Geophysical Research Letters 33*(8), doi:10.1029/2006GL025927.

Kim, S., L. et al., (2007), Measurement of HO_2NO_2 in the free troposphere during the Intercontinental Chemical Transport Experiment–North America 2004, *Journal of Geophysical Research - Atmospheres, 112*, doi:10.1029/2006JD007676.

Klemm, O., et al. (1998), Measurements of nitrogen oxides from aircraft in the northeast Atlantic flight corridor, *Journal of Geophysical Research-Atmospheres 103*(D23): 31217-31229.

Kley, D., J. M. Russell III, and C. Phillips, eds., SPARC Assessment of Upper Tropospheric and Stratospheric Water Vapour, World Climate Research Programme, WCRP-113, Dec 2000.

Knighton, W. B., et al. (2007), Quantification of aircraft engine hydrocarbon emissions using proton transfer reaction mass spectrometry, *Journal of Propulsion and Power 23*(5): 949-958.

Koike, M., et al. (2000), Impact of aircraft emissions on reactive nitrogen over the North Atlantic Flight Corridor region, *Journal of Geophysical Research-Atmospheres 105*(D3): 3665-3677.

Koike, M., et al. (2002), Reactive nitrogen over the tropical western Pacific: Influence from lightning and biomass burning during BIBLE A, *Journal of Geophysical Research-Atmospheres*, *108*(D3), doi:10.1029/2001JD000823.

1937 Kraabol, A. G., et al. (2002), Impacts of NOx emissions from subsonic aircraft in a global
1938   three-dimensional chemistry transport model including plume processes, *Journal of*
1939   *Geophysical Research-Atmospheres 107*(D22), .
1940 Labrador, L. J., et al. (2004), Strong sensitivity of the global mean OH concentration and
1941   the tropospheric oxidizing efficiency to the source of NOx from lightning,
1942   *Geophysical Research Letters*, *31*(6), doi:10.1029/2003GL019229.
1943 Lange, L., et al. (2001), Detection of lightning-produced NO in the midlatitude upper
1944   troposphere during STREAM 1998, *Journal of Geophysical Research-Atmospheres*,
1945   *106*(D21), 27777-27785.
1946 Law, K. S., et al. (2000), Comparison between global chemistry transport model results
1947   and Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft
1948   (MOZAIC) data, *Journal of Geophysical Research-Atmospheres*, *105*(D1), 1503-
1949   1525.
1950 Lelieveld, J., et al. (1999), Chlorine activation and ozone destruction in the northern
1951   lowermost stratosphere, *Journal of Geophysical Research-Atmospheres*, *104*(D7),
1952   8201-8213.
1953 Leue, C., et al. (2001), Quantitative analysis of NOx emissions from Global Ozone
1954   Monitoring Experiment satellite image sequences, *Journal of Geophysical Research-*
1955   *Atmospheres*, *106*(D6), 5493-5505.
1956 Levy, H., et al. (1999), Simulated tropospheric NOx: Its evaluation, global distribution
1957   and individual source contributions, *Journal of Geophysical Research-Atmospheres*,
1958   *104*(D21), 26279-26306.
1959 Li, Q. B., et al. (2005), North American pollution outflow and the trapping of
1960   convectively lifted pollution by upper-level anticyclone, *Journal of Geophysical*
1961   *Research-Atmospheres*, *110*(D10), doi:10.1029/2004JD005039.
1962 Lobo, P., et al. (2007), Physical characterization of aerosol emissions from a commercial
1963   gas turbine engine, *Journal of Propulsion and Power 23*(5): 919-929.
1964 Longfellow, C. A., et al. (1999), Reactive uptake on hydrocarbon soot: Focus on NO_2,
1965   *Journal of Geophysical Research-Atmospheres*, *104*(D11), 13833-13840.
1966 Lopez, J. P., et al. (2006), CO signatures in subtropical convective clouds and anvils
1967   during CRYSTAL-FACE: An analysis of convective transport and entrainment using
1968   observations and a cloud-resolving model, *Journal of Geophysical Research-*
1969   *Atmospheres*, *111*(D9), doi:10.1029/2005JD006104.
1970 Lovejoy, S., et al. (2007), Is isotropic turbulence relevant in the atmosphere?,
1971   *Geophysical Research Letters 34*(15), doi:10.1029/2007GL029359.
1972 Luo, Z. Z., et al. (2007), Ten years of measurements of tropical upper-tropospheric water
1973   vapor by MOZAIC. Part I: Climatology, variability, transport, and relation to deep
1974   convection, *Journal of Climate*, *20*(3), 418-435.
1975 Ma, J. Z., and X. J. Zhou (2000), Development of a three-dimensional inventory of
1976   aircraft NOx emissions over China, *Atmospheric Environment*, *34*(3), 389-396.
1977 Ma, J. Z., et al. (2002), Summertime tropospheric ozone over China simulated with a
1978   regional chemical transport model. 2. Source contributions and budget, *Journal of*
1979   *Geophysical Research-Atmospheres*, *107*(D22), doi:10.1029/2001JD001355.
1980 Marecal, V., et al. (2006), Modelling study of the impact of deep convection on the utls
1981   air composition - Part I: Analysis of ozone precursors, *Atmospheric Chemistry and*
1982   *Physics*, *6*, 1567-1584.

Marécal, V., G. Durry, K. Longo, S. Freitas, E. D. Rivière, and M. Pirre (2007), Mesoscale modelling of water vapour in the tropical UTLS: two case studies from the HIBISCUS campaign, *Atmospheric Chemistry and Physics 7*, 1471-1489.

Mari, C., et al. (2002), Sources of upper tropospheric HOx over the South Pacific Convergence Zone: A case study, *Journal of Geophysical Research-Atmospheres*, *108*(D2), doi:10.1029/2000JD000304.

Mari, C., et al. (2002), On the relative role of convection, chemistry, and transport over the South Pacific Convergence Zone during PEM-Tropics B: A case study, *Journal of Geophysical Research-Atmospheres*, *108*(D2), doi:10.1029/2001JD001466.

Martin, R. V., et al. (2006), Evaluation of space-based constraints on global nitrogen oxide emissions with regional aircraft measurements over and downwind of eastern North America, *Journal of Geophysical Research-Atmospheres*, *111*(D15), doi:10.1029/2005JD006680.

Martin, R. V., et al. (2007), Space-based constraints on the production of nitric oxide by lightning, *Journal of Geophysical Research-Atmospheres*, *112*(D9), doi:10.1029/2006JD007831.

Meijer, E. W., et al. (2000), Model calculations of the impact of NOx from air traffic, lightning, and surface emissions, compared with measurements, *Journal of Geophysical Research-Atmospheres*, *105*(D3), 3833-3850.

Meier, A. and J. Hendricks (2002), Model studies on the sensitivity of upper tropospheric chemistry to heterogeneous uptake of HNO_3 on cirrus ice particles, *Journal of Geophysical Research-Atmospheres 107*(D23), doi:10.1029/2001JD000735.

Meilinger, S. K., et al. (2001), On the impact of heterogeneous chemistry on ozone in the tropopause region, *Geophysical Research Letters*, *28*(3), 515-518.

Meilinger, S. K., et al. (2005), Microphysics and heterogeneous chemistry in aircraft plumes - high sensitivity on local meteorology and atmospheric composition, *Atmospheric Chemistry and Physics 5:* 533-545.

Miller, T. M., et al. (2005), Mass distribution and concentrations of negative chemiions in the exhaust of a jet engine: Sulfuric acid concentrations and observation of particle growth, *Atmospheric Environment 39*(17): 3069-3079.

Miloshevich, L. M., et al. (2006), Absolute accuracy of water vapor measurements from six operational radiosonde types launched during AWEX-G and implications for AIRS validation, *Journal of Geophysical Research-Atmospheres*, *111*(D9), doi:10.1029/2005JD006083.

Morris, G. A., et al. (2003), Potential impact of subsonic and supersonic aircraft exhaust on water vapor in the lower stratosphere assessed via a trajectory model, *Journal of Geophysical Research-Atmospheres*, *108*(D3), doi:10.1029/2002JD002614.

Muhle, J., et al. (2002), Biomass burning and fossil fuel signatures in the upper troposphere observed during a CARIBIC flight from Namibia to Germany, *Geophysical Research Letters*, *29*(19).

Muller, J. F., and G. Brasseur (1999), Sources of upper tropospheric HOx: A three-dimensional study, *Journal of Geophysical Research-Atmospheres*, *104*(D1), 1705-1715.

Murphy, J. G., et al. (2004), Measurements of the sum of HO_2NO_2 and $CH_3O_2NO_2$ in the remote troposphere, *Atmospheric Chemistry and Physics*, *4*, 377-384.

Nedoluha, G. E., et al. (2002), Polar Ozone and Aerosol Measurement III measurements of water vapor in the upper troposphere and lowermost stratosphere, *Journal of Geophysical Research-Atmospheres*, *107*(D10), doi: 10.1029/2001JD000793.

Neuman, J. A., et al. (2006), Reactive nitrogen transport and photochemistry in urban plumes over the North Atlantic Ocean, *Journal of Geophysical Research-Atmospheres*, *111*(D23), doi:10.1029/2005JD007010.

Nyeki, S., et al. (2004), Properties of jet engine combustion particles during the PartEmis experiment: Particle size spectra (d > 15 nm) and volatility, *Geophysical Research Letters*, *31*(18), doi:10.1029/2004GL020569.

Olson, J. R., et al. (2004), Testing fast photochemical theory during TRACE-P based on measurements of OH, HO_2, and CH_2O, *Journal of Geophysical Research-Atmospheres*, *109*(D15), doi:10.1029/2003JD004278.

Olson, J. R., et al. (2006), A reevaluation of airborne HOx observations from NASA field campaigns, *Journal of Geophysical Research-Atmospheres 111*(D10), doi:10.1029/2005JD006617.

Park, M., et al. (2004), Seasonal variation of methane, water vapor, and nitrogen oxides near the tropopause: Satellite observations and model simulations, *Journal of Geophysical Research-Atmospheres*, *109*(D3), doi:10.1029/2003JD003706.

Parker, D. E., M. Gordon, D. P. N. Cullum, D.M. H. Sexton, C. K. Folland, and N. Rayner (1997), A new global gridded radiosonde temperature database and recalculated temperature trends, *Geophysical Research Letters 24*, 1499–1502.

Parrish, D. D., et al. (2004), Fraction and composition of NOy transported in air masses lofted from the North American continental boundary layer, *Journal of Geophysical Research-Atmospheres*, *109*(D9), doi:10.1029/2003JD004226.

Peace, H., et al. (2006), Identifying the contribution of different airport related sources to local urban air quality, *Environmental Modelling & Software 21*(4), 532-538.

Petzold, A., et al. (2005), Particle emissions from aircraft engines - a survey of the European project PartEmis, *Meteorologische Zeitschrift*, *14*(4), 465-476.

Pierce, R. B., et al. (2007), Chemical data assimilation estimates of continental US ozone and nitrogen budgets during the Intercontinental Chemical Transport Experiment-North America, *Journal of Geophysical Research-Atmospheres*, *112*(D12), doi:10.1029/2006JD007722.

Pison, I. and L. Menut (2004), Quantification of the impact of aircraft traffic emissions on tropospheric ozone over Paris area, *Atmospheric Environment 38*(7), 971-983.

Pitari, G., et al. (2002), Deep convective transport in a two-dimensional model: Effects on lower stratospheric aerosols and ozone, *Meteorologische Zeitschrift*, *11*(3), 187-196.

Popp, P. J., et al. (2006), The observation of nitric acid-containing particles in the tropical lower stratosphere, *Atmospheric Chemistry and Physics 6*, 601-611.

Popovicheva, O. B., et al. (2004), Water adsorption and crystallization on soot particles, *Izvestiya Atmospheric and Oceanic Physics*, *40*(2), 193-201.

Popovicheva, O. B., and A. M. Starik (2007), Aircraft-generated soot aerosols: Physicochemical properties and effects of emission into the atmosphere, *Izvestiya Atmospheric and Oceanic Physics*, *43*(2), 125-141.

Popovicheva, O. B., et al. (2003), Microstructure and water adsorbability of aircraft combustor soots and kerosene flame soots: Toward an aircraft-generated soot

laboratory surrogate, *Journal of Physical Chemistry A 107*(47),10046-10054.

Popovitcheva, O. B., et al. (2000), Experimental characterization of aircraft combustor soot: Microstructure, surface area, porosity and water adsorption, *Physical Chemistry Chemical Physics 2*(19), 4421-4426.

Ravetta, F., et al. (2001), Experimental evidence for the importance of convected methylhydroperoxide as a source of hydrogen oxide (HOx) radicals in the tropical upper troposphere, *Journal of Geophysical Research-Atmospheres*, *106*(D23), 32709-32716.

Ramaswamy, V., et al., (2001), Stratospheric Temperature Trends: Observations and Model Simulations, *Reviews of Geophysics*, *39*, 61-122.

Reiner, T., et al. (1999), Measurements of acetone, acetic acid, and formic acid in the northern midlatitude upper troposphere and lower stratosphere, *Journal of Geophysical Research-Atmospheres*, *104*(D11), 13943-13952.

Richard, E. C., et al. (2006), High-resolution airborne profiles of CH_4, O_3, and water vapor near tropical Central America in late January to early February 2004, *Journal of Geophysical Research-Atmospheres 111*(D13), doi:10.1029/2005JD006513.

Ridley, B. A., et al. (2005), Comments on the parameterization of lightning-produced NO in global chemistry-transport models, *Atmospheric Environment*, *39*(33), 6184-6187.

Salawitch, R. J., et al. (2005), Sensitivity of ozone to bromine in the lower stratosphere, *Geophysical Research Letters*, *32*(5), doi:10.1029/2004GL021504.

Sauvage, B., et al. (2007), Remote sensed and in situ constraints on processes affecting tropical tropospheric ozone, *Atmospheric Chemistry and Physics*, *7*, 815-838.

Sausen, R., et al. (2005), Aviation radiative forcing in 2000: An update on IPCC (1999), *Meteorologische Zeitschrift 14* (4), 555-561.

Schauffler, S. M., et al. (1999), Distributions of brominated organic compounds in the troposphere and lower stratosphere, *Journal of Geophysical Research-Atmospheres*, *104*(D17), 21513-21535.

Schlager, H., et al. (1999), Regional nitric oxide enhancements in the North Atlantic flight corridor observed and modeled during POLINAT 2 - a case study, *Geophysical Research Letters*, *26*(20), 3061-3064.

Schoeberl, M. R. and G. A. Morris (2000), A Lagrangian simulation of supersonic and subsonic aircraft exhaust emissions, *Journal of Geophysical Research-Atmospheres 105*(D9): 11833-11839.

Schofield, R., et al. (2004), Retrieved tropospheric and stratospheric BrO columns over Lauder, New Zealand, Journal Of Geophysical Research-Atmospheres, 109 (D14): D14304.

Schroder, F., et al. (2000), In situ studies on volatile jet exhaust particle emissions: Impact of fuel sulfur content and environmental conditions on nuclei mode aerosols, *Journal of Geophysical Research-Atmospheres*, *105*(D15), 19941-19954.

Schumann, U., et al. (2002), Influence of fuel sulfur on the composition of aircraft exhaust plumes: The experiments SULFUR 1-7, *Journal of Geophysical Research-Atmospheres*, *107*(D15), doi:10.1029/2001JD000813.

Schumann, U. and H. Huntrieser (2007), The global lightning-induced nitrogen oxides source, *Atmospheric Chemistry and Physics 7*(14), 3823-3907.

Shonija, N. K., et al. (2007), Hydration of aircraft engine soot particles under plume conditions: Effect of sulfuric and nitric acid processing, *Journal of Geophysical*

Research-Atmospheres 112(D2), doi:10.1029/2006JD007217.

Simpson, I. J., et al. (2003), Airborne measurements of cirrus-activated C_2Cl_4 depletion in the upper troposphere with evidence against Cl reactions, *Geophysical Research Letters*, *30*(20), doi:10.1029/2003GL017598.

Singh, H., et al. (2000), Distribution and fate of selected oxygenated organic species in the troposphere and lower stratosphere over the Atlantic, *Journal of Geophysical Research-Atmospheres*, *105*(D3), 3795-3805.

Singh, H. B., et al. (2004), Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P, *Journal of Geophysical Research-Atmospheres*, *109*(D15), doi:10.1029/2003JD003883.

Singh, H. B., L. Salas, et al. (2007), Reactive nitrogen distribution and partitioning in the North American troposphere and lowermost stratosphere, *Journal of Geophysical Research-Atmospheres 112*(D12), doi:10.1029/2006JD007664.

Sinnhuber, B.M., et al. (2005), Global observations of stratospheric bromine monoxide from SCIAMACHY, *Geophysical Research Letters 32*(20): L20810.

Sinnhuber, B. M., and I. Folkins (2006), Estimating the contribution of bromoform to stratospheric bromine and its relation to dehydration in the tropical tropopause layer, *Atmospheric Chemistry and Physics*, *6*, 4755-4761.

Sioris, C. E., et al. (2006), Latitudinal and vertical distribution of bromine monoxide in the lower stratosphere from Scanning Imaging Absorption Spectrometer for Atmospheric Chartography limb scattering measurements, *Journal of Geophysical Research-Atmospheres 111*(D14), doi:10.1029/2005JD006479.

Sioris, C. E., et al. (2007), Vertical profiles of lightning-produced NO_2 enhancements in the upper troposphere observed by OSIRIS, *Atmospheric Chemistry and Physics 7*(16), 4281-4294.

Smith, J. B., et al. (2001), Mechanisms for midlatitude ozone loss: Heterogeneous chemistry in the lowermost stratosphere?, *Journal of Geophysical Research-Atmospheres 106*(D1): 1297-1309.

Smyshlyaev, S. P., et al. (2003), Model study of the impact of convective processes on the gas composition of the upper troposphere and lower stratosphere, *Izvestiya Atmospheric and Oceanic Physics*, *39*(4), 432-443.

Snow, J. A., et al. (2003), Winter-spring evolution and variability of HOx reservoir species, hydrogen peroxide, and methyl hydroperoxide, in the northern middle to high latitudes, *Journal of Geophysical Research-Atmospheres*, *108*(D4), doi:10.1029/2002JD002172.

Snow, J. A., et al. (2007), Hydrogen peroxide, methyl hydroperoxide, and formaldehyde over North America and the North Atlantic, *Journal of Geophysical Research-Atmospheres*, *112*(D12), doi:10.1029/2006JD007746.

Sorokin, A., et al. (2001), On volatile particle formation in aircraft exhaust plumes, *Physics and Chemistry of the Earth Part C-Solar-Terrestial and Planetary Science*, *26*(8), 557-561.

Solomon, S., et al. (1997), Heterogeneous chlorine chemistry in the tropopause region, *Journal of Geophysical Research-Atmospheres 102*(D17): 21411-21429.

Sorokin, A., and F. Arnold (2004), Electrically charged small soot particles in the exhaust of an aircraft gas-turbine engine combustor: comparison of model and experiment,

Atmospheric Environment, 38(17), 2611-2618.

Sorokin, A. and F. Arnold (2006), Organic positive ions in aircraft gas-turbine engine exhaust, *Atmospheric Environment 40*(32): 6077-6087.

Sovde, O. A., et al. (2007), Aircraft pollution - a futuristic view, Atmospheric *Chemistry and Physics 7*(13), 3621-3632.

Spichtinger, P., et al. (2002), The statistical distribution law of relative humidity in the global tropopause region, *Meteorologische Zeitschrift, 11*(2), 83-88.

Stendahl, K. (1976): Paul Among Jews and Gentiles, and Other Essays, Fortress Press, p7.

Stevenson, D. S., et al. (2004), Radiative forcing from aircraft NOx emissions: Mechanisms and seasonal dependence, *Journal of Geophysical Research-Atmospheres* 109(D17), doi:10.1029/2004JD004759.

Stevenson, D. S., et al. (2006), Multimodel ensemble simulations of present-day and near-future tropospheric ozone, *Journal of Geophysical Research-Atmospheres, 111*(D8), doi:10.1029/2005JD006338.

Stickler, A., et al. (2006), Influence of summertime deep convection on formaldehyde in the middle and upper troposphere over Europe, *Journal of Geophysical Research-Atmospheres, 111*(D14), doi:10.1029/2005JD007001.

Stohl, A., et al. (2002), Export of NOy from the North American boundary layer during 1996 and 1997 North Atlantic Regional Experiments, *Journal of Geophysical Research-Atmospheres, 107*(D11), doi:10.1029/2001JD000519.

Stohl, A., et al. (2003), A new perspective of stratosphere-troposphere exchange, *Bulletin of the American Meteorological Society 84*(11), 1565.

Talukdar, R. K., et al. (2006), Uptake of HNO_3 on hexane and aviation kerosene soots, *Journal of Physical Chemistry A 110*(31), 9643-9653.

Theys, N., et al. (2007), Retrieval of stratospheric and tropospheric BrO columns from multi-axis DOAS measurements at Reunion Island (21 degrees S, 56 degrees E), *Atmospheric Chemistry and Physics 7*(18), 4733-4749.

Thornton, B. F., et al. (2003), In situ observations of ClO near the winter polar tropopause, *Journal of Geophysical Research-Atmospheres 108*(D8), doi:10.1029/2002JD002839.

Thornton, B. F., et al. (2005), Variability of active chlorine in the lowermost Arctic stratosphere, *Journal of Geophysical Research-Atmospheres 110*(D22) doi:10.1029/2004JD005580.

Thornton, B. F., et al. (2007), Chlorine activation near the midlatitude tropopause, *Journal of Geophysical Research-Atmospheres 112*(D18), doi:10.1029/2006JD007640.

Thakur, A. N., et al. (1999), Distribution of reactive nitrogen species in the remote free troposphere: data and model comparisons, *Atmospheric Environment, 33*(9), 1403-1422.

Troller, M., A. Geiger, E. Brockmann and H.-G. Kahle, (2006), Determination of the spatial and temporal variation of tropospheric water vapour using CGPS networks**, *Geophysical Journal International**, 167**, 509–520.

Tsague, L., et al. (2006), Prediction of the production of nitrogen oxide (NOx) in turbojet engines, *Atmospheric Environment, 40*(29), 5727-5733.

2211 Tsague, L., et al. (2007), Prediction of emissions in turbojet engines exhausts:
2212   relationship between nitrogen oxides emission index (EINOx) and the operational
2213   parameters, *Aerospace Science and Technology 11*(6), 459-463.
2214 Tsai, F. J., et al. (2001), A composite modeling study of civil aircraft impacts on ozone
2215   and sulfate over the Taiwan area, *Terrestrial Atmospheric and Oceanic Sciences*
2216   *12*(1), 109-135.
2217 Vaughan, G., et al. (2005), Water vapour and ozone profiles in the midlatitude upper
2218   troposphere, *Atmospheric Chemistry and Physics*, *5*, 963-971.
2219 van Noije, T. P. C., et al. (2006), Multi-model ensemble simulations of tropospheric NO_2
2220   compared with GOME retrievals for the year 2000, *Atmospheric Chemistry and*
2221   *Physics*, *6*, 2943-2979.
2222 Vay, S. A., et al. (2000), Tropospheric water vapor measurements over the North Atlantic
2223   during the Subsonic Assessment Ozone and Nitrogen Oxide Experiment (SONEX),
2224   *Journal of Geophysical Research-Atmospheres*, *105*(D3), 3745-3755.
2225 Voigt, C., et al. (2006), Nitric acid in cirrus clouds, *Geophysical Research Letters 33*(5).
2226 Voigt, C., et al. (2007), In-situ observations and modeling of small nitric acid-containing
2227   ice crystals, *Atmospheric Chemistry and Physics 7*(12), 3373-3383.
2228 von Kuhlmann, R. and M. G. Lawrence (2006), The impact of ice uptake of nitric acid on
2229   atmospheric chemistry, *Atmospheric Chemistry and Physics 6*, 225-235.
2230 Wang, C., and R. G. Prinn (2000), On the roles of deep convective clouds in tropospheric
2231   chemistry, *Journal of Geophysical Research-Atmospheres*, *105*(D17), 22269-22297.
2232 Wang, Y., et al. (2000), Evidence of convection as a major source of condensation nuclei
2233   in the northern midlatitude upper troposphere, *Geophysical Research Letters*, *27*(3),
2234   369-372.
2235 Wang, Y. H., et al. (2000), Influence of convection and biomass burning outflow on
2236   tropospheric chemistry over the tropical Pacific, *Journal of Geophysical Research-*
2237   *Atmospheres*, *105*(D7), 9321-9333.
2238 Wang, C. X., and Z. M. Chen (2006), Effect of CH_3OOH on the atmospheric
2239   concentration of OH radicals, *Progress in Natural Science*, *16*(11), 1141-1149.
2240 Wei, C. F., et al. (2001), Modeling of ozone reactions on aircraft-related soot in the upper
2241   troposphere and lower stratosphere, *Atmospheric Environment*, *35*(35), 6167-6180.
2242 Weisenstein, D.K., et al. (1993), Effects On Stratospheric Ozone From High-Speed Civil
2243   Transport - Sensitivity To Stratospheric Aerosol Loading, *Journal of Geophysical*
2244   *Research-Atmospheres, 98*(D12), 23133-23140.
2245 Wey, C.C., et al. (2007), Overview on the aircraft particle emissions experiment, *Journal*
2246   *of Propulsion and Power 23*(5), 898-905.
2247 Wey, T. and N. S. Liu (2007), Modeling jet engine aerosols in the postcombustor flow
2248   path and sampling system, *Journal of Propulsion and Power 23*(5), 930-941.
2249 Wild, O. and M. J. Prather (2006), Global tropospheric ozone modeling: Quantifying
2250   errors due to grid resolution, *Journal of Geophysical Research-Atmospheres*
2251   *111*(D11), doi:10.1029/2005JD006605.
2252 Wilson, C. W., et al. (2004), Measurement and prediction of emissions of aerosols and
2253   gaseous precursors from gas turbine engines (PartEmis): an overview, *Aerospace*
2254   *Science and Technology 8(*2), 131-143.

2255 World Meteorological Organization (2006), Scientific Assessment of Ozone Depletion
2256   2006 (WMO/UNEP), World Meteorological Organization Global Ozone Research
2257   and Monitoring Project—Report No. 50.
2258 Wormhoudt, J., et al., (2007), Nitrogen oxide (NO/NO$_2$/HONO) emissions measurements
2259   in aircraft exhausts, *Journal of Propulsion and Power* 23(5), 906-911.
2260 Wuebbles, D., et al. (2006): A report of findings and recommendations, Workshop on the
2261   Impacts of Aviation on Climate Change, June 7-9, Boston, MA.
2262 Yang, X., et al. (2005), Tropospheric bromine chemistry and its impacts on ozone: A
2263   model study, *Journal of Geophysical Research-Atmospheres*, *110*(D23),
2264   doi:10.1029/2005JD006244.
2265 Yelvington, P. E., et al. (2007), Chemical speciation of hydrocarbon emissions from a
2266   commercial aircraft engine, *Journal of Propulsion and Power 23*(5), 912-918.
2267 Zhang, R. Y., et al. (2000), Enhanced NOx by lightning in the upper troposphere and
2268   lower stratosphere inferred from the UARS global NO$_2$ measurements, *Geophysical*
2269   *Research Letters*, *27*(5), 685-688.
2270 Ziereis, H., et al. (1999), In situ measurements of the NOx distribution and variability
2271   over the eastern North Atlantic, *Journal of Geophysical Research-Atmospheres*,
2272   *104*(D13), 16021-16032.
2273 Ziereis, H., et al. (2000), Distributions of NO, NOx, and NOy in the upper troposphere
2274   and lower stratosphere between 28 degrees and 61 degrees N during POLINAT 2,
2275   *Journal of Geophysical Research-Atmospheres*, *105*(D3), 3653-3664.