

**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/updated February, 2008

Table of Contents

Title Page	1
Table of Contents	2
Executive Summary	3
1. Introduction and Background	6
2. Processes that Impact Climate	
2.a. Current State of the Science	6
2.b. The Role of UT/LS Chemistry	8
2.c. Advancements since the 1999 IPCC Report	11
2.c.I. Engine Emissions	13
2.c.II. Sources of NO _x in the Upper Troposphere	14
2.c.III. Conversion of NO _x to NO _y	18
2.c.IV. Water Vapor and Supersaturation	21
2.c.V. UT/LS Temperatures	23
2.d. Present State of Measurements and Data Analysis	24
2.e. Current Estimates of Climate Impacts and Uncertainties	26
2.f. Interconnectivity with Other Themes	27
3. Outstanding issues	
3.a. Science	27
3.a.I. Discrepancies in Coupled HO _x /NO _x Chemistry	28
3.a.II. Halogen Chemistry	30
3.a.III. Potential Surprises	32
3.b. Measurements and Analysis	33
4. Prioritization of issues	
4.a. Prioritization of Issues Based on Impact	34
4.b. Ability to Reduce Uncertainties	39
4.c. Practical Use	40
4.d. Achievability	40
4.e. Cost	40
4.f. Timeline	42
5. Best Way to Assess Uncertainties with Current Knowledge	42
6. Summary	43
7. References	46

Executive Summary

Aircraft emissions of particles, particle precursors, NO_x, 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 HO_x and NO_x radical species involved in ozone formation and destruction.
- Poor understanding of the sources of NO_x in the upper troposphere, especially due to lightning.
- Incomplete knowledge of the evolution of NO_x and NO_y in aircraft plumes during the first ~24 hours following emission.
- Incomplete understanding of, and potential non-linearities in, the coupling among CH₄, CO, OH and O₃ in the troposphere.
- Potential scavenging and removal of NO_x 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, NO_x, and trace organic species from aircraft engines.
- Observations constraining the lightning and convective fluxes of NO_x to the upper troposphere.
- Measurements of HO_x, its precursors, and coupled NO_x/HO_x chemistries in the UT.
- Rates and extent of conversion of NO_x to NO_y 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 be 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

- 47 predict formation and persistence of cirrus clouds and, hence, their impact on the
48 budgets of trace species that control ozone abundances in the UT/LS.
- 49 • Important discrepancies between modeled and observed HO_x species (primarily
50 HO₂) at high NO values in the region where subsonic aircraft emissions represent
51 the most significant perturbation to chemistry.
 - 52 • New observations of heterogeneous activation of chlorine in the tropopause
53 region.
 - 54 • Observations that indicate greater abundances of inorganic bromine than
55 previously believed, presumably due to more efficient transport of short-lived
56 bromine sources to the UT.
 - 57 • Observations of significant uptake of nitric acid in ice particles and an increased
58 role for HNO₃ in the stability of ice in the UT/LS.
- 59

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

65

66 These results, if studied with the best modeling tools available, should help constrain the
67 role of aircraft emissions on chemistry in the UT/LS. It is expected that the new result
68 will imply a diminished enhancement of ozone due to NO_x/hydrocarbon chemistry in the
69 UT, and possibly ozone losses in some regions where aircraft emissions enhance the
70 production of particulate surfaces areas or the lifetimes of cirrus clouds. Constraints on
71 OH abundances throughout the troposphere should reduce the uncertainties in modeled
72 impacts of aircraft emissions on the lifetime of methane, which is currently believed to
73 have a negative forcing on climate. Finally, modeling studies of the sensitivity of ozone
74 and HO_x to heterogeneous processes, including sedimentation of particles that contain
75 HNO₃ and halogen activation, should help to define the range of possible impacts these
76 processes could have.

77

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

83

- 84
- 85
- 86
- 87
- 88
- 89
- 90
- 91
- 92
- 93
- 94
- 95
- 96
- 97
- 98
- 99
- 100
- 101
- 102
- 103
- 104
- 105
- 106
- 107
- 108
- 109
- 110
- 111
- 112
- 113
- 114
- 115
- 116
- 117
- 118
- 119
- 120
- 121
- 122
- 123
- 124
- 125
- 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.
 - 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.
 - 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 HO_x/NO_x chemistry, errors in water vapor and supersaturation).
 - Guided by results from studies of the above issues, new questions should be developed to help guide measurement programs (dedicated or flights of opportunity).
 - Convene annual meetings of investigators participating in aviation impacts-related activities to foster frequent exchange of ideas. Rather than a comprehensive meeting, 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.

126 **1. Introduction and Background**

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

139
140 The goals of this White Paper are to summarize the ways in which aircraft emissions
141 impact atmospheric chemistry in the UT/LS, to examine what has been learned since the
142 last major assessments, and to prioritize future scientific studies that can reduce the most
143 important uncertainties that remain and that address new problems that have arisen.

144
145 **2. Processes that Impact Climate**

146
147 **2.a. Current State of the Science**

148 Two previous assessments have thoroughly reviewed the important properties of
149 emission products that are thought to be the most relevant to atmospheric chemistry
150 [IPCC, 1999; Brasseur et al., 1998]. Based on these reports, the most important products
151 of combustion of aircraft fuel (e.g., kerosene) are CO₂, H₂O, NO_x, soot, and oxides of
152 sulfur. All of these species interact strongly with infrared or visible light, serving to
153 directly warm or cool the planet. Some can alter the nature and radiative properties of
154 particulate matter (e.g., aerosols and clouds) or can promote formation of new particles
155 by changing the extent of supersaturation through influence on temperature and water
156 vapor abundances. Some, such as NO_x and soot, can also have important indirect impacts
157 on the atmosphere, including subtle shifts in chemical balance that can alter the natural
158 abundances of radiatively important gases such as O₃ and CH₄, or cause the redistribution
159 of naturally occurring species such as H₂O and HNO₃ via sedimentation of large
160 particles. Finally, through influences on radiation balance, these emissions can impact
161 atmospheric transport, especially between the troposphere and stratosphere.

162
163 These different, and in some cases offsetting, effects have been studied before in some
164 detail. IPCC [1999] identified warming due to enhancements of CO₂, contrails and cirrus,
165 and O₃ (which is thought to be increased by NO_x chemistry), and cooling by CH₄ (which
166 is thought to decrease as a result of enhancements of OH by NO_x chemistry), as the most
167 likely to have significant impacts on climate. It was believed that only one of these
168 processes, warming by CO₂, was well understood, whereas the relative scientific
169 understanding of the others was listed as fair to poor. An update of this assessment by
170 Sausen et al. [2005], recognized that work published since the turn of the century reduced
171 some of the key uncertainties. Nevertheless, the limited understanding of those processes

172 continues to represent a major hurdle to reducing the overall uncertainties in aviation
173 impacts [Wuebbles et al., 2006]. Of particular interest are impacts of NO_x on the
174 chemistry of ozone and on the budget of methane, which together could represent more
175 than half of the total impact of aircraft emissions on climate. If aviation transport
176 continues to grow, it is estimated that the number of flights will double from present rates
177 by about 2025 [Cox, 2007]. Unless major changes to combustion systems can be
178 implemented, aircraft emissions can also be expected to nearly double by 2025.
179 Consequently, the impacts of aviation operations on climate and the oxidative capacity of
180 the atmosphere are of great interest.

181

182 Both the IPCC [1999] and the Workshop on the Impacts of Aviation on Climate Change
183 [Wuebbles et al., 2006, hereafter called the “2006 Workshop”] concluded that the
184 following processes that influence NO_x chemistry contributed most to uncertainties in
185 assessments of the impact of the chemistry of aircraft exhaust on Earth’s climate:

- 186 (1) Incomplete knowledge of exhaust emissions of gases (primarily sulfur oxides) and
187 particles (e.g., soot) and their geographic and altitudinal distributions.
- 188 (2) Important discrepancies between modeled and measured distributions of key HO_x
189 and NO_x radical species involved in ozone formation and destruction.
- 190 (3) Poor understanding of the sources of NO_x in the upper troposphere, especially
191 lightning.
- 192 (4) Incomplete knowledge of the evolution of NO_x and NO_y in aircraft plumes
193 during the first ~24 hours following emission.
- 194 (5) Incomplete understanding of, and potential non-linearities in, the coupling among
195 CH₄, CO, OH and O₃ in the troposphere.
- 196 (6) Potential scavenging and removal of NO_x by aerosols and cirrus.
- 197 (7) Limited understanding of atmospheric transport, especially that between the
198 stratosphere and troposphere.

199

200 In addition, we note the critical nature of understanding the processes controlling water
201 vapor in the UT/LS [see IPCC 1999]. Water vapor is important not only because it is a
202 greenhouse gas that is directly emitted by aircraft but also because it is a significant
203 source of odd-hydrogen (HO_x) in the UT/LS. Species in the HO_x family produce and
204 destroy ozone, largely determine the lifetimes of CH₄ and CO, and also influence NO_x
205 chemistry under the conditions that prevail in the UT/LS. Finally, H₂O is the major
206 condensable species, playing a key role in the formation of ice particles and polar
207 stratospheric clouds in the UT/LS (see SSWP’s III and IV). As discussed in detail in a
208 separate SSWP, the relative humidity variable, RH_i, is the critical quantity for
209 understanding formation, growth, and evaporation of ice-containing particles in the
210 UT/LS. Therefore, direct emissions of water vapor to the atmosphere, as well as indirect
211 influences of other trace combustion products on water vapor distributions and
212 temperatures in the UT/LS, can have major impacts on the chemistry of the atmosphere.

213

214 Due to the strong non-linear coupling between NO_y, particles, and water/ice
215 precipitation, all of these factors are influenced by processes discussed in other SSWP’s,
216 most importantly, that on clouds and aerosols. Thus, the discussion here will overlap
217 strongly with other SSWP topics that address uncertainties in water vapor measurements

218 and parameterizations of aerosol properties and clouds. Of particular interest to UT/LS
219 chemistry are factors that limit the ability to predict the presence of ice and the extent of
220 uptake of nitric acid. The rates of heterogeneous reactions that repartition NO_x into NO_y
221 and that release active forms of chlorine vary by several orders of magnitude, depending
222 on the abundances of condensed HNO₃, a quantity that itself is non-linear with respect to
223 temperature and relative humidity (essentially a threshold with temperature or RH_i) [e.g.,
224 see WMO 2006 and references therein]. In addition, a significant confounding factor is
225 that heterogeneous reactions between halogens and temporary NO_x reservoirs can release
226 photolytic sources of HO_x, which, in turn, destroy methane and accelerate the gas-phase
227 formation of HNO₃. Enhancements of reactive chlorine also alter methane abundances. It
228 is safe to say that highly accurate measurements of water vapor are critical for any
229 assessment of atmospheric chemistry that is influenced by heterogeneous chemistry.

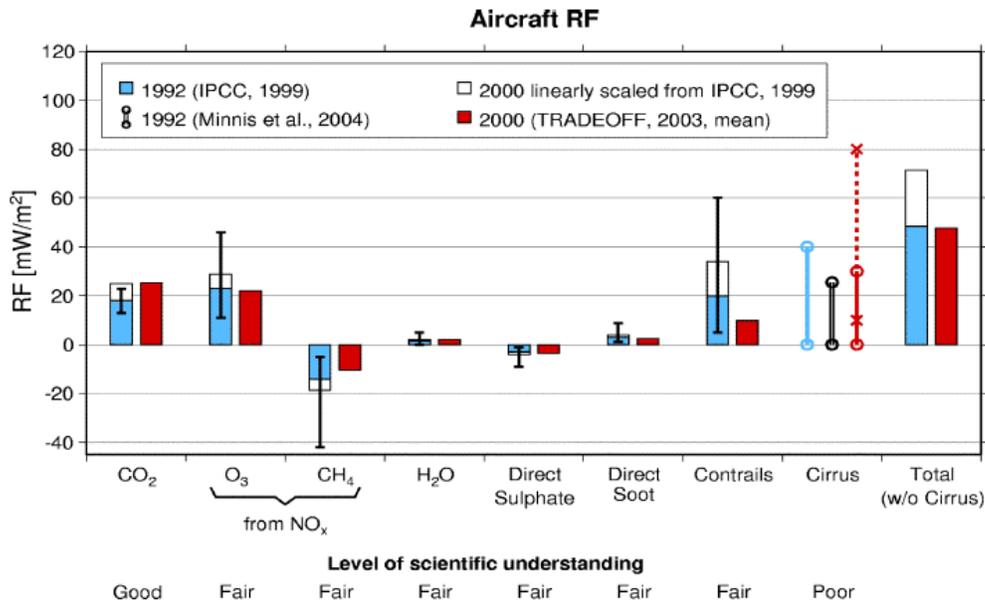
230

231 These issues are explored in detail in the following two major sections. The remainder of
232 Section 2 will summarize studies that have led to significant improvements in our
233 understanding of aircraft impacts on chemistry in the UT/LS. Section 3 will report on
234 recent observations that raise important new questions about chemical processes in the
235 UT/LS; new modeling efforts will be necessary to determine their proper roles in future
236 aviation impacts assessments.

237

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

239 The 2006 Workshop considered the combined impacts of NO_x emissions on ozone
240 abundances and, through perturbations to HO_x chemistry, on methane abundances, to
241 comprise the bulk of the total uncertainty in climate forcing due to aviation [Wuebbles et
242 al., 2006]. This SSWP examines recent results that address the various aspects of UT/LS
243 chemistry that were identified in the 1999 IPCC and 2006 Workshop reports and listed in
244 the previous section. Figure 1, reproduced from Sausen et al. [2005], updates a similar
245 figure from IPCC [1999]. It shows the Global Radiative Forcing (RF) framework that has
246 largely informed the bulk of recent scientific research into the impacts of aviation on
247 climate. As is clear from Figure 1, terms relating to chemistries of NO_x and HO_x are
248 among the three largest contributors to the aircraft RF, and, as will be shown in Section 3
249 below, the third term related to contrails is itself influenced by NO_x chemistry via the
250 role of HNO₃ in ice stability and contrail evolution. Consequently, uncertainties in the
251 chemistry of aircraft emissions in the UT/LS dominate the overall uncertainty in climate
252 forcing due to aviation.

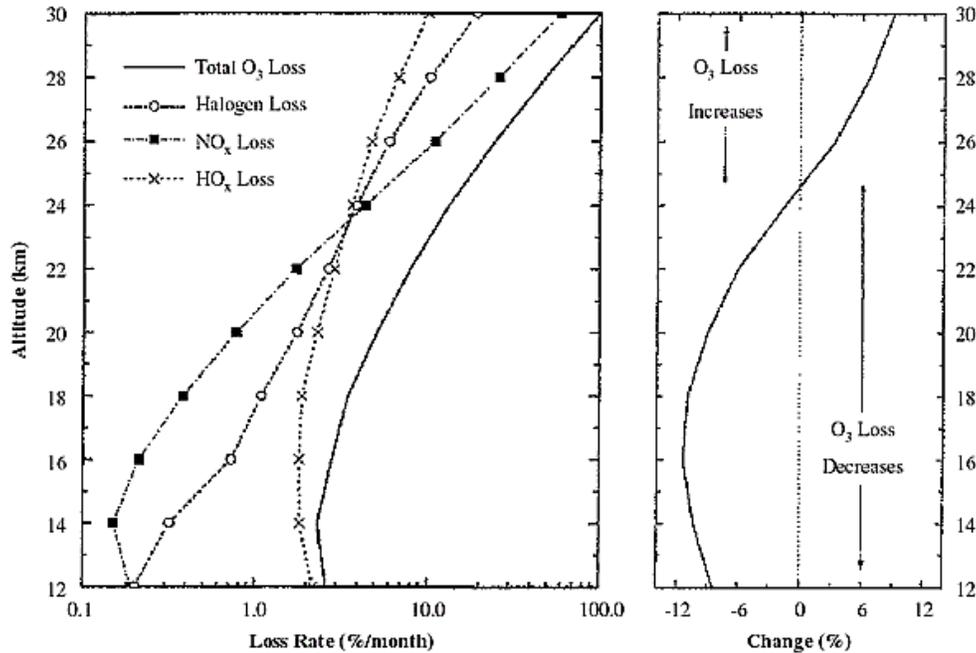


253
254

255 **Figure 1.** Global radiative forcing (RF) [mW m^{-2}] from aviation for 1992 and 2000,
256 based on IPCC (1999) and TRADEOFF results. The whiskers denote the 2/3 confidence
257 intervals of the IPCC (1999) values. The lines with the circles at the end display different
258 estimates for the possible range of RF from aviation-induced cirrus clouds. In addition
259 the dashed line with the crosses at the end denotes an estimate of the range for RF from
260 Sausen et al., [2005].

261

262 A key result of research conducted in the 1990s and summarized in Chapter 2 of IPCC
263 [1999] was that the response of ozone to changes in NO_x reverses sign in the lower
264 stratosphere. Formation of ozone by photochemistry initiated by oxidation of volatile
265 organic compounds dominates in the upper troposphere, whereas catalytic destruction of
266 ozone by NO_x dominates in the middle stratosphere. The discovery in the early 1990s of
267 a shift in the relative roles of halogens and NO_x in the lower stratosphere due to
268 heterogeneous conversion of N₂O₅ to HNO₃, lead to reexamination of the impacts of
269 emissions from supersonic aircraft. Model studies soon found that NO_x enhancements
270 near 20 km due to supersonic aircraft (or upward transport of subsonic aircraft emissions)
271 would lead to increases in ozone, thereby reducing reactive halogens [e.g., Weisenstein et
272 al., 1993]. Figure 2, taken from the 1999 IPCC Report, reveals this dual nature, and
273 illustrates why transport and mixing processes are critical in determining the response of
274 ozone to aircraft NO_x emissions. Although the simulation shown in Figure 2 was
275 designed simply to illustrate the sensitivity of ozone to a change in NO_x, and not to
276 predict the true response of ozone to a specific perturbation due to aviation, it still serves
277 to frame the discussion of impacts and uncertainties that follows. For example, it is easy
278 see that emissions that remain in the upper troposphere will lead to an increase in ozone,
279 whereas those that reach the stratosphere will increase ozone below 24 km, but decrease
280 it above. The net impact of NO_x emissions thus depends strongly upon the vertical
281 distribution of the resultant perturbation to background levels. Consequently, the impact



282

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

287

288 of NOx on ozone will differ for subsonic and supersonic aircraft, which deposit their
 289 exhaust mainly in the UT and LS, respectively [IPCC, 1999]. Thus, in order to assess the
 290 impacts of aviation, the proportion of stratospheric (e.g., supersonic) and tropospheric
 291 (e.g., subsonic) emissions from a future fleet of aircraft (the so-called mixed fleet) must
 292 be known [Gauss et al., 2006]. What is important to note here is that assessments of the
 293 impact of emissions of a particular assumed fleet of aircraft on ozone have relied
 294 explicitly on the ability to accurately model this altitude dependence of the ozone
 295 response to changes in NOx, the vertical distribution of which depends not only on the
 296 flight altitude, but also upon knowledge of the vertical transport of NOx and possible
 297 redistribution by cloud and aerosol processes. These themes will become important later
 298 in this SSWP, as the implications are explored of new observations in the UT/LS that
 299 show a more important role for heterogeneous chemistry and possible redistribution of
 300 HNO₃ than was known at the time of the previous assessment.

301

302 The strong linkages between these three topics, especially heterogeneous chemistry and
 303 aerosol and cloud processes, couple various themes that are addressed in this and other
 304 chapters of this report, and require that we consider the direct impacts of the major
 305 aircraft combustion products, as well as the indirect effects of non-CO₂ emissions that
 306 participate in gas-phase and heterogeneous reactions (e.g., SOx, soot, NOx, and H₂O)
 307 with the background atmosphere.

308

309

310

311 **2.c. Advancements since the 1999 IPCC Report**

312 Since the publication of the 1999 IPCC report, there have been more than several
313 hundred studies that address important issues raised in that report. While it is not possible
314 to do justice to all of these studies in this SSWP, we summarize here where significant
315 advances have been made.

316

317 To help define the range of species and concentrations of important engine exhaust
318 emissions, new measurements have been obtained of soot and particle precursor gases
319 [Dakhel et al., 2007; Hays and Vander Wal, 2007; Karcher et al., 2007; Sorokin and
320 Arnold, 2004] such as chemi-ions [Arnold et al., 2000; Eichkorn et al., 2002; Haverkamp
321 et al., 2004; Miller et al., 2005; Sorokin and Arnold, 2006], sulfur and NO_x [Herndon et
322 al., 2004; Schroder et al., 2000; Schumann et al., 2002; Tsague et al., 2006, 2007;
323 Wormhoudt et al., 2007], and volatile organic compounds (VOCs) and particles
324 [Anderson, et al., 2006; Herndon et al., 2006; Lobo et al., 2007; Knighton et al., 2007;
325 Nyeki et al., 2004; Sorokin et al., 2001; Wey et al., 2007; Wilson et al., 2004;
326 Yelvington et al., 2007], in the exhaust of engines or aircraft on the ground and at cruise
327 altitudes. In addition, new laboratory studies have further defined the reactivity of engine-
328 emitted soot, most importantly regarding uptake of water and reactivity to NO_x, NO_y,
329 and O₃ [Popovicheva et al., 2000, 2003, 2004, 2007; Shonija et al., 2007; Talukdar et al.,
330 2006; Wei et al., 2001]. These new studies help to constrain parameters that are critically
331 important for modeling the perturbations of reactive species (e.g., NO_x and VOCs) and
332 particle evolution (e.g., chemi-ions, VOCs, and soot) emitted by aircraft in the UT/LS
333 [Ma and Zhao 2000; Petzold et al., 2005; Wei and Liu 2007]. Key new results and
334 implications of these studies are summarized in Section 2.c.I.

335

336 Evidence is mounting from more than a decade of in situ measurements and from new
337 satellite observations that air in the UT/LS is influenced considerably by convective
338 transport from the surface. In fact, there are more recent studies reporting on this issue
339 than for any of the other issues of this SSWP. In Section 2.C.II. some new results are
340 highlighted, in particular those that address some key uncertainties in NO_x and HO_x
341 budgets. Of particular interest to this SSWP are efforts to quantify lightning, biomass
342 burning, and convective PBL (planetary boundary layer) pollution sources of NO_x to the
343 upper troposphere [Brunner et al., 2001; Decaria et al., 2005; Fehr et al., 2004; Hudman et
344 al., 2007; Koike et al., 2002; Lange et al., 2001; Leue et al., 2001; Levy et al., 1999; Ma
345 et al., 2002; Martin et al., 2006, 2007; Muhle et al., 2002; Parrish et al., 2004; Pierce et
346 al., 2003; Ridley et al., 2005; Sauvage et al., 2007; Schumann and Huntrieser, 2007;
347 Sioris et al., 2007; Smyshlyaev et al., 2003; Stohl et al., 2002; Thakur et al., 1999; van
348 Noije et al., 2006; Wang et al., 2000; Zhang et al., 2000; Ziereis et al., 1999, 2000],
349 fluxes that were highlighted in previous assessments as being poorly constrained. Not
350 only do these sources of NO_x (and, hence, NO_y) dominate the odd nitrogen budget in the
351 UT, thereby setting the background conditions upon which aircraft emissions represent a
352 small, but potentially significant, perturbation, incomplete knowledge of their magnitudes
353 and seasonal and geographic distributions make it difficult to directly attribute NO_x
354 enhancements to aircraft operations except in highly localized plumes or heavily traveled
355 flight corridors [Brunner et al., 2005; Colette and Ancellet, 2005; Colette et al., 2005;

356 Grewe et al., 2002; Koike et al., 2000; Marecal et al., 2006; Mari et al., 2002; Meijer et
357 al., 2000; Park et al., 2004; Schlager et al., 1999; Tsai et al., 2001; Wang and Prinn,
358 2000]. New in situ observations with a larger suite of measurements of tracers for
359 biomass burning, human activities, lightning, and stratospheric fluxes [Bertram et al.,
360 2007; Singh et al., 2007], not only provide for attribution of sources other than aircraft
361 emissions, but also provide new clues into photochemical processes that transform
362 reactive NO_x into species that serve as reservoirs or that can redistribute NO_y (hence,
363 NO_x) by condensation onto particles followed by sedimentation [Neuman et al., 2006].
364

365 The interactions of NO_y species with particles [Gao et al., 2004; Popp et al., 2006;
366 Karcher and Voigt, 2006; Voigt et al., 2006, 2007] raise important new questions that
367 rely on the ability to model formation, composition, and reactivity of particles [Conside
368 et al., 2000; Meier and Hendricks, 2002; Meilinger et al., 2001; von Kuhlmann and
369 Lawrence; 2006]. Several key new modeling studies have shown that heterogeneous
370 chemistry involving NO_x, HO_x, and halogens, is extremely important in particle-rich
371 exhaust plumes and persistent contrails, and, depending on the subsequent behavior of
372 these species as these plumes and contrails disperse, can even have important
373 implications on the sign of ozone response to aircraft exhaust on hemispheric scales
374 [Meilinger et al., 2005; Sovde et al., 2007]. These results and their implications are
375 discussed in Section 2.c.III.
376

377 The importance of convective sources of HO_x in the upper troposphere has been known
378 for many years [Collins et al., 1999; Crawford et al., 1999; Muller and Brasseur, 1999;
379 Reiner et al., 1999; Singh et al., 2000]. New observations of HO_x and volatile organic
380 compounds in conjunction with modeling studies, continue to reinforce this view
381 [Colomb et al., 2006, Mari et al., 2002; Olson et al., 2004; Ravetta et al., 2001; Singh et
382 al., 2004; Snow et al., 2003, 2004; Stickler et al., 2006; Wang and Chen, 2006], and they
383 provide some important insights into the nature of previous disagreements between
384 modeled and measured HO_x that seem to depend on NO_x [Ren et al., 2008] (the
385 previously referenced “coupled HO_x/NO_x discrepancy” [e.g., Faloona et al., 2000]). New
386 measurements of HO₂NO₂ [Murphy et al., 2004; Kim et al., 2007] could help to identify
387 important missing chemistry, while issues of resolution have been shown to be important
388 under some conditions [Olson et al., 2006].
389

390 Measurements of water vapor in the upper troposphere and the stratosphere, where the
391 naturally occurring humidities are the lowest found on Earth, have always been a source
392 of controversy [e.g., Kley et al., 2000]. Not only are emissions of water vapor from
393 aircraft critical for understanding radiative impacts of exhaust, accurate knowledge of
394 background water vapor distributions and temperatures, and the microphysics of water-
395 containing particles, are essential in order to accurately model heterogeneous chemistry,
396 HO_x distributions, and possible redistribution of reactive species in the UT/LS by
397 sedimentation. Ongoing studies by a number of groups [Bencherif et al., 2006; Bortz et
398 al., 2006; Ferrare et al., 2004; Folkins et al., 2006; Gao et al., 2005; Gulstad and Isaksen,
399 2007; Helten et al., 1999; Kley et al., 2000; Luo et al., 2007; Marecal et al., 2007;
400 Miloshevich et al., 2006; Nedoluha et al., 2002; Park et al., 2004; Ramaswamy et al.,
401 2001; Spichtinger et al., 2002; Troller et al., 2006; Vaughan et al., 2005; Vay et al., 2000]

402 that have improved our understanding of water vapor and supersaturation are summarized
403 in Section 2.c.IV. New studies addressing temperatures in the UT/LS are summarized in
404 Section 2.c.V.

405

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

417

418 **2.c.I. Engine Emissions**

419 Although knowledge of the emissions of sulfate was identified as a key uncertainty in
420 previous assessments, the main issue was not so much the sulfate itself, as the impact of
421 fuel sulfur on particle nucleation. Since then, a number of studies have characterized
422 particulate emissions from a variety of aircraft engines. The most significant new result is
423 that particle production does not closely track fuel sulfur content [Wey et al., 2006;
424 Yelvington et al., 2007]. While studies have shown that ion nucleation is the probable
425 mechanism for volatile aerosol production in aircraft exhaust [e.g., Miller et al., 2005],
426 measurements of positive and negative chemiions have revealed a greater role for LVOCs
427 (low volatility VOCs) than previously believed [Eichkorn et al., 2002; Sorokin and
428 Arnold, 2006; Miller et al., 2005].

429

430 In a study of an on-wing commercial gas turbine engine, Lobo et al. [2007] recently
431 found little dependence of particulate emissions with varying fuel sulfur content,
432 although they did observe that the soluble mass fraction of particles increased with
433 distance from the engine exit plane and with increasing aromatic and sulfur content of the
434 fuel, consistent with increased uptake of water by hygroscopic particles. Recent
435 measurements of engine-generated soot [Shonija et al., 2007] found significant water
436 uptake due to the existence of impurities within the engine, with amounts of absorbed
437 water increasing with decreasing temperatures in the exhaust plume (reaching 18% by
438 weight at threshold conditions for contrail formation). In light of previous observations
439 of significant uptake of water by soot, these authors have inferred that to be hygroscopic,
440 soot does not have to be processed by reactions with sulfuric or nitric acids, as was
441 previously believed, and that impurities in engine-generated soot will play key roles in
442 the formation of CCN in aircraft plumes. These results are consistent with a laboratory
443 study of Talukdar et al. [2006], who found that uptake of nitric acid on aviation kerosene
444 soot is reversible, and not a significant source of NO_x, as had been suggested previously.
445 They are also consistent with another study that found the characteristics of soot emitted

446 by engines are determined largely by combustor processes, and not by subsequent
447 reactions in the turbine/nozzle.

448

449 It is important to recognize that measurements of soot from combustors must be
450 considered carefully, as it may be chemically and physical unstable, as shown in a recent
451 study by Popovichava et al. [2003]. In addition, it is unclear whether ground level
452 measurements will apply under cruise conditions, where combustion is more complete
453 and LVOC emissions are likely to be significantly smaller. But from the majority of new
454 studies, it does appear that aircraft-generated particles are relatively hygroscopic, and
455 therefore are likely to be good CCN. A new particulate emission inventory developed
456 under the European PartEmis program should help reduce uncertainties in modeled
457 impacts of particulate emissions by aircraft [Petzold et al., 2005].

458

459 Important new measurements of the emissions of hydrocarbons and NO_x, including
460 speciation, have been obtained in the exhaust plumes of a variety of aircraft types during
461 the APEX campaign [Herndon et al., 2004; Herndon et al. 2007; Knighton et al., 2007;
462 Wormhoudt et al., 2007]. To first order, the results are in good agreement with previous
463 studies, increasing confidence in the emissions databases used for modeling aircraft
464 impacts. Additional insights from these studies include the finding that fuel type and
465 plume age appear to have only minor effects on the emissions of hydrocarbons, including
466 speciation, whereas temperature appears to be an important factor. NO_x emissions were
467 found to increase with thrust, while the fraction of NO₂/NO_x decreased from 80% at
468 lowest thrust to below 7% at highest thrust. Nitrous acid (HONO) was found to be a
469 minor species (~7%) that increased with thrust, and also served as a good indicator for
470 predicting abundances of other trace species, such as oxides of sulfur.

471

472 In summary, new results indicate an increased role for hydrocarbons in formation of
473 particles in aircraft exhaust, a decreased tendency for reduction of HNO₃ to NO_x on soot,
474 and, as will be discussed in a separate chapter, a general increase in ice-forming activity
475 for aircraft emissions. This raises the importance of heterogeneous chemistry to reduce
476 NO_x, and increase the importance of HO_x and halogens, in persistent contrails.

477

478 **2.c.II. Sources of NO_x and HO_x in the Upper Troposphere**

479 Motivated by the dominant role placed on NO_x and HO_x by previous aircraft
480 assessments [Brasseur et al., 1998; IPCC 1999], the past decade has been witness to a
481 multitude of studies to attribute sources of these species in the upper troposphere,
482 especially those that could potentially be due to aircraft. A brief review of some
483 important new results is presented below.

484

485 *Sources of NO_x*

486 The main source of NO_x in the stratosphere is oxidation of N₂O, and based on tight
487 correlations that have been observed between NO_y (the sum of reactive nitrogen species)
488 and N₂O, it is relatively straightforward to simulate the impact of an additional source of
489 NO_x from direct injection of aircraft exhaust or parameterized transport from the
490 troposphere [IPCC 1999]. However, there are a number of potentially significant sources
491 of NO_x to the upper troposphere, not just those from aircraft emissions, all of which must

492 be reasonably well understood in order to determine the perturbation of NO_x due to
493 aircraft [IPCC 1999]. Of these non-aircraft sources, lightning and convective transport
494 from the boundary layer have stood out as dominant sources of NO_x in the UT [Grewe et
495 al., 2002]. The studies are too numerous to describe here, but we summarize a few key
496 results that have emerged from these studies that significantly improve our understanding
497 of NO_x sources.

498
499 Around the time of the 1999 IPCC assessment, lightning was estimated to represent a
500 source strength of about 3-5 Tg(N) yr⁻¹. In a comprehensive review of three decades of
501 research on this topic, Schumann and Huntrieser [2007] have concluded that the best
502 estimate for the annual lightning NO_x source is 5 ± 3 Tg(N) yr⁻¹. Consistent with this, in
503 a recent study using a combination of space-based NO₂ observations from
504 SCIAMACHY, O₃ observations from OMI and MLS, and HNO₃ observations from
505 ACE-FTS, Martin et al. [2007] determine a range of 6 ± 2 Tg(N) yr⁻¹ for the lightning
506 NO_x sources. For reference, such a source-strength is about 8-10 times larger than the
507 estimated NO_x source from aircraft emissions [Kraabøl et al., 2002] but only about 1/8th
508 of the total NO_x source strength assumed in state-of-the-art aircraft NO_x emissions
509 impacts studies [e.g., Gauss et al., 2006].

510
511 It is important to note that aircraft emissions are more confined in altitude and to heavily
512 traveled corridors than these other sources, so they can still represent a large local
513 perturbation. What makes assessing aircraft contributions so difficult, then, is not only
514 the quantification of these larger global sources, but specifying their geographic
515 distributions with sufficient precision so that the contributions due to the highly localized
516 aircraft emissions can be quantified. In other words, the large, distributed sources
517 determine the broader background abundances of NO_x into which the aircraft emissions
518 represent a highly localized perturbation. Thus, studies addressing the contributions of
519 various sources of NO_x (or NO_y) to the UT are critical for evaluating the significance of
520 that due to aircraft.

521 *Source Attribution of NO_x in the Upper Troposphere*

522 Singh et al. [2007] analyzed observations of reactive nitrogen species in the UT over
523 North America in the summer of 2004, reporting that ~30% of the NO_y in the UT is in
524 the form of NO_x. PAN and HNO₃ were the dominant reservoirs of reactive nitrogen in
525 the UT and LS, respectively. Relying on tracers for biomass burning emissions (e.g.,
526 HCN) and anthropogenic pollution, they concluded that lightning represents a larger
527 source of NO_x to that region than was believed previously. Model simulations based on
528 these observations [Hudson et al., 2005] imply that lightning was responsible for
529 approximately 75% of the NO_x observed in this region. These results suggest that the
530 NO_x observed in this region is relatively ‘fresh’, that is, it is undergoing photochemical
531 aging (e.g., oxidizing). Consistent with this, Sioris et al. [2007] reported large local NO₂
532 enhancements at ~10 km that they attributed to lightning, estimating that it is responsible
533 for 60% of the upper tropospheric NO₂ in the tropics.

534
535
536 Bertram et al. [2007] develop the idea of a ‘photochemical clock’, using the ratio of
537 observed NO_x to that determined with a photochemical model with similar total NO_y

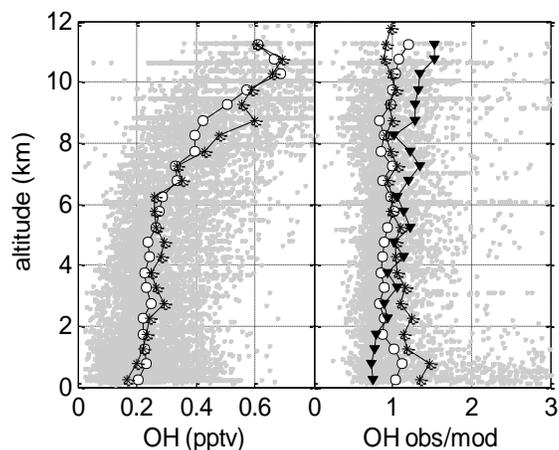
538 (i.e., $\text{NOx}_{\text{obs}}/\text{NOx}_{\text{ss}}$) to estimate that ~17% of the air in the UT under the conditions
539 sampled was transported from the planetary boundary layer. Furthermore, they estimate a
540 turnover rate by convection of 0.1 day^{-1} for air in the UT (although it should be noted that
541 this includes altitudes somewhat below typical aircraft cruise altitudes).

542
543 These results suggest that non-aircraft sources of NOx to the upper troposphere are more
544 important than previously believed, consistent with the observations of Klemm et al.,
545 [1998], who found that clear perturbations due to aircraft in the northeast Atlantic
546 corridor were difficult to identify on scales larger than a few km due to natural
547 variability, whereas in ‘fresh’ plumes between 15 and 90 minutes in age, enhancements
548 of up to 10 ppb were observed. Based on NOy/O_3 correlations, Koike et al. [2000]
549 estimated that the mean NOy enhancement in the North Atlantic corridor is of order 70
550 ppt at 11 km, implying NOx enhancements of about 40% above backgrounds. They also
551 found the NOy enhancements to increase with increasing ozone (e.g., closer to the
552 chemical tropopause). Given the more recent observations of Singh et al. [2007] of
553 significant transport from the surface, Koike et al. [2000] may have significantly
554 overestimated the NOx contributions from aircraft.

555 556 *Sources of HOx*

557 Not only does OH largely determine the lifetime of methane, a greenhouse gas that plays
558 a key role in the Aircraft RF uncertainties framework (Figure 1, [Sausen et al., 2005]),
559 both OH and HO_2 participate in catalytic cycles that destroy ozone and are necessary for
560 ozone production. Therefore, models must be able to reproduce both total HOx
561 abundances and the partitioning within the HOx family (the generally preferred indicator
562 being the OH/ HO_2 ratio) over a wide range of conditions found in the UT/LS.

563
564 Measurements of HOx carried out in the 1990s revealed significantly larger abundances
565 of this critical oxidizer than could be modeled with assumed sources [e.g., see Faloon et
566 al., 2000]. By the time of the 1999 IPCC assessment, it was well known that sources of
567 HOx in addition to $\text{H}_2\text{O}/\text{O}_3$ photochemistry were required to resolve this discrepancy,
568 especially in the upper troposphere [Collins et al., 1999; Crawford et al., 1999; Muller
569 and Brasseur, 1999; Reiner et al., 1999; Singh et al., 2000]. Since then, a number of
570 ongoing studies related to sources of HOx have been published, and models for assessing
571 aircraft impacts have used any available in situ observations to constrain
572 parameterizations of HOx, including measurements of species such as H_2O_2 , whose
573 abundances serve as sensitive indicators of HOx chemistry [Brunner et al., 2005]. The
574 basic understanding of HOx chemistry seems to be relatively sound, in that it is widely
575 acknowledged that additional sources, generally gases transported from the PBL by



576

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

581

582 convection (in agreement with the conclusions based on NO_x partitioning described
 583 above), are required to fully explain HO_x abundances. The partitioning between OH and
 584 HO₂ varies with NO_x in a fashion that can be reproduced reasonably well by models [for
 585 example, see Brunner et al., 2005, Ren et al., 2008, and references therein]. Figure 3
 586 shows comparison of OH measurements from recent missions with modeled OH
 587 abundances, indicating good agreement over a wide altitude range [Ren et al., 2008].

588

589 The results shown in Figure 3 indicate that there should be a firm basis for model
 590 simulations of OH distributions over a wide range of conditions, as is required to predict
 591 the lifetime of CH₄ to a reasonable degree of accuracy. However, important discrepancies
 592 remain in between the modeled and measured partitioning of OH and HO₂ that are not
 593 well understood, as will be discussed in Section 3 [Hudman et al., 2006; Ren et al., 2008].
 594 One of the challenges in comparing modeled and measured HO_x is the inherent non-
 595 linearities in HO_x chemistry; in essence, unless the photochemical conditions are highly
 596 uniform during sampling, some differences in modeled and measured total HO_x or
 597 OH/HO₂ can be due simply to the coarse temporal resolution of the model. As shown by
 598 Olson et al. [2006], such errors are most problematic at high solar zenith angles and at
 599 high and variable NO_x conditions. In light of the significant role that heterogeneous
 600 chemistry plays in the effect of NO_x on ozone in the UT, this type of issue could become
 601 very important in future assessments of aircraft impacts.

602

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

610 due to oxidation of these gases into less volatile products. Second, increased ‘aging’ of
 611 UT air results in a shift in the partitioning from NO_x to NO_y. As discussed in the
 612 following sections, this has important implications for the role of long-lived reservoirs of
 613 nitrogen oxides in particle stability. Heterogeneous reactions are effective in denoxifying
 614 cold, particle rich regions of the atmosphere, such as where persistent contrails are
 615 formed. Thus, increased transport from the PBL implies a greater role for ozone-
 616 destroying reactions of HO_x and halogen radical species that are normally held to lower
 617 abundances by reactions with NO_x.

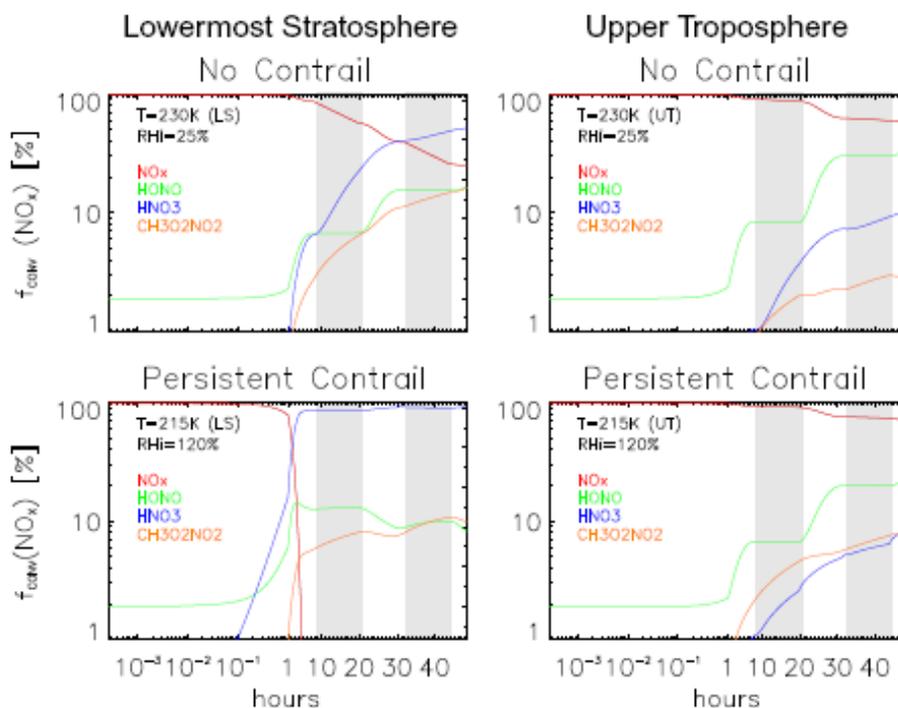
618

619 2.c.III. Conversion of NO_x to NO_y

620 The laboratory finding that uptake of nitric acid on aircraft kerosene soot is reversible
 621 [Talukdar et al., 2006] implies that emissions of soot will not shift the partitioning of
 622 NO_y to NO_x in aircraft plumes, as was believed previously. This result, together with
 623 new measurements of the hygroscopicity of soot and the subsequent formation of CCN
 624 and emissions of particles from engines (e.g., see Section 2.c.I. and SSWPs III and IV),
 625 implies, rather, that in plumes, contrails, and potentially even in heavily traveled flight
 626 corridors, there will be more rapid conversion of NO_x to NO_y. Although the impacts of
 627 these new findings have yet to be fully explored, results from recent modeling efforts
 628 provide clues as to what might be the tendencies.

629

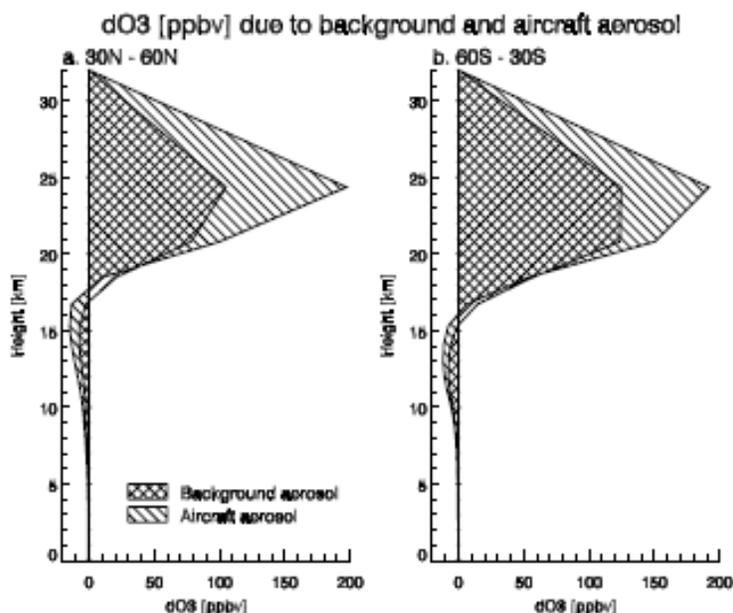
630



631

632 **Figure 4.** Model results from Meilinger et al. [2005] showing the impact of
 633 heterogeneous processing of NO_x in a persistent contrail in the lower stratosphere (left
 634 panels) and in the upper troposphere (right panels). Shaded regions refer to nighttime.
 635

636 A modeling study by Kraabol et al. [2002] found that reactions that form odd-nitrogen
 637 reservoirs in aircraft plumes and persistent contrails reduce the magnitude of changes in
 638 ozone as a result of the conversion of ~25-35% of the aircraft NO_x to NO_y. A subsequent
 639 study by Meilinger et al. [2005] found that NO_y formation depends very strongly on
 640 heterogeneous reactions, especially in the lowermost stratosphere. Figure 4 shows the
 641 shift in NO_y partitioning due to heterogeneous chemistry in a persistent contrail. In the
 642 lowermost stratosphere, NO_x is completely converted to HNO₃ in a matter of hours,
 643 whereas without a contrail, even after a few days, conversion of NO_x to NO_y is only
 644 50%. According to Meilinger et al. [2005], in the lower stratosphere, ozone destruction
 645 by chlorine and bromine enhances that due to NO+O₃ in the early plume and dominates
 646 over NO_x-induced ozone production in the aged plume. This is the result of combined
 647 effects of halogen activation and denoxification by heterogeneous reactions on contrail
 648 ice particles. The situation in the upper troposphere is less clear, and the tendency of
 649 ozone depends strongly on temperatures in the initial plume and persistent contrail.
 650 However, reductions in net ozone production or shifts from ozone production to loss
 651 result from the more complete treatment of heterogeneous chemistry. The recent
 652 modeling study of Sovde et al. [2007] examines the global implications of heterogeneous
 653 reactions on the ozone changes induced by aircraft exhaust products. Although they focus
 654 on the impacts of a mixed fleet for the year 2050, there are some important new
 655 conclusions that extend the results of Meilinger et al. [2005] to hemispheric scales. (It is
 656 also important to note that even in a mixed fleet, operations of subsonic aircraft dominate
 657 the overall emissions budget). As shown in Figure 5, the most significant implication of
 658 more rapid conversion of NO_x to NO_y is the complete reversal in the sign of the response
 659



660

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

665 of ozone to nitrogen emissions (e.g., see Figure 2) from net production to net loss below
666 18 km (i.e., in the upper troposphere) and from net loss to net production above 24 km.
667 Although the two ozone change curves shown in the right panel of Figure 2 and Figure 5
668 have similar shapes, they are nearly mirror images of one another, as Figure 2 deals with
669 the quantity ozone loss, whereas Figure 5 shows ozone gain, with altitude. Using
670 reasonable estimates for an average vertical profile of ozone, the percent change in ozone
671 near 25 km in Figure 5 is about +2 to +4%, whereas near the mid-latitude tropopause (12-
672 16 km) the change is of comparable magnitude, but opposite in sign. In essence, one
673 could achieve similar changes to those modeled in Figure 2 by *decreasing* NO_x by ~10%.

674

675 It is worthwhile to consider how it is possible for the sign of the impacts of NO_x
676 emissions to completely reverse since the last major reviews of aviation (and even the
677 2006 Workshop). Hints can be found in the study by Meilinger et al. [2005] discussed
678 above and one by Hendricks et al. [2000] who investigate the influence of naturally
679 occurring bromine on the chemistry of aircraft emissions in the UT/LS. First, the
680 partitioning of NO_x emissions is shifted far more toward HNO₃ in the more recent studies
681 than in the model used to generate Figure 2 (and presumably the state-of-the-art models
682 used at the time of the 1999 IPCC Assessment). Second, (and largely a consequence of
683 this shift from NO_x to HNO₃) the relative contributions of the NO_x, HO_x, and halogen
684 families to ozone loss in the UT/LS differ in the more recent model simulations from
685 those used for previous assessments.

686

687 Hendricks et al. [2000] found the somewhat surprising result that bromine radicals, even
688 at the minor abundances that are thought to be present in the UT/LS, efficiently convert
689 NO_x to NO_y by heterogeneous hydrolysis of BrONO₂ on background and aircraft-
690 produced aerosols. They showed that this process can even be an important pathway for
691 denoxification in the lowermost stratosphere. As noted by Meilinger et al. [2005], such
692 halogen chemistry becomes significantly more important in exhaust-influenced air in the
693 plumes of aircraft, in cirrus, and in persistent contrails. This issue will be addressed in
694 more detail in Section 3, since the role of halogens in aviation impacts has received little
695 attention and remains one of the major uncertainties in UT/LS chemistry.

696

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

709 and heterogeneous reaction rates with respect to relative humidity, temperature, and
710 abundances of H₂O and HNO₃, the details of plume formation and dispersion, particle
711 growth, composition, and sedimentation, and the ability to predict the presence of ice
712 crystals in the UT/LS all become essential factors in assessing the chemistry of aircraft
713 exhaust. In light of the clearly dominant role played by water vapor in all of these issues,
714 the next section will examine progress in understanding water vapor in the UT/LS.

715

716 **2.c.IV. Water Vapor and Supersaturation**

717 H₂O abundances in the UT/LS are controlled by a combination of transport processes.
718 Both large- (e.g., Brewer-Dobson circulation) and small-scale (e.g., waves, convection)
719 processes are important [IPCC 1999; SPARC 2000]. Temperature, chemistry (e.g., CH₄
720 oxidation) and microphysics also play roles. Transport phenomena are key elements in
721 UT water distribution; these include such occurrences as horizontal transport from the
722 tropics to sub-tropics and midlatitudes and vertical motions associated with mesoscale
723 convection, midlatitude cyclones and downward transport from the stratosphere.

724

725 SPARC [2000] noted that there has been a 2 ppm increase of H₂O (~1%/yr) in the
726 stratosphere since the mid-1950s, about 0.55 ppm of which can be attributed to increases
727 in CH₄, while the source of the remaining ~1.5 ppm (75% of the total) remains unknown.
728 Trends in relative humidity in the upper troposphere have been found in some latitude
729 bands, but there is no apparent global trend; variability from ENSO, large-scale
730 circulation modes and temperature all contribute to the complexity of attributing trends.

731

732 Agreement amongst measurements of H₂O in the lower stratosphere (60-100 mb) has
733 always been problematic. Although typically clustering within 10% of each other, some
734 individual instruments have systematically differed from the mode of the measurements
735 by 25-30%. The source of this disagreement is under investigation.

736

737 Water measurements in the upper troposphere are less numerous than those in the
738 stratosphere, and they are less reliable overall. Radiosonde data are not sufficiently
739 accurate for determining trends at the level of importance for understanding perturbations
740 by aircraft. Measurements from TOVS are reasonable, on average, but very difficult to
741 validate because of the high temporal and spatial variability of H₂O vapor in the UT. The
742 measurement of tropospheric water vapor amounts via radio occultation of Global
743 Positioning Satellite (GPS) signals has become a fairly mature technique, and methods
744 for determining vertical profiles of water with high vertical resolution (a few hundred
745 meters) are under development [e.g., Troller et al., 2006].

746

747 Since the last water vapor assessment [SPARC 2000], a number of uncertainties relevant
748 to aircraft impacts have been addressed in some detail, as described below:
749 Intercomparison experiments and laboratory work for stratospheric water vapor
750 instruments have been ongoing; validation of satellite H₂O retrievals and numerous
751 correlative measurements have been conducted; improvements in radiosonde H₂O
752 measurements have been made; a number of process studies have been conducted to
753 investigate the role of convection and cloud microphysical properties in UT/LS H₂O
754 distributions and studies of stratosphere-troposphere exchange mechanisms.

755

756 *Intercomparison and Validation*

757 Detailed intercomparisons of lidar, radiosondes, and frost-point sensors (AFWEX)
758 revealed that the frost-point/chilled mirror measurements are “drier” (i.e., lower water
759 vapor) than the others by 10-25% in the UTLS [Ferrare et al., 2004]. During the 2003
760 AWEX-G campaign, (designed to validate the AIRS measurements from the A-train
761 satellites), six radiosonde-type sensors were flown against the University of Colorado
762 Cryogenic Frostpoint Hygrometer (CFH). With appropriate corrections for solar heating,
763 data from the Vaisala RS-90 sensor was found to be suitably accurate for use in
764 validation studies [Miloshevich et al., 2006].

765

766 Intercomparisons between the satellite-based POAM measurement (solar occultation) and
767 the in situ MOZAIC data set showed that POAM water vapor values are about 10%
768 higher than those determined with capacitive humidity sensors flown on several in-
769 service aircraft [Nedoluha et al., 2002]. Finally, based on comparisons made during the
770 SONEX and POLINAT campaigns in 1997, Tunable Diode Laser (TDL) and cryogenic
771 hygrometers were found to agree to within their stated instrumental accuracies of 10%
772 [Vay et al., 2000], whereas a similar intercomparison conducted between the POLINAT
773 and MOZAIC datasets found water vapor measurements to agree within 5% [Helten et
774 al., 1999]. However the agreement between measured values of relative humidity was
775 worse, potentially pointing to temperature measurement problems.

776

777 Perhaps of most significance for this White Paper will be the upcoming results from the
778 AquaVIT blind intercomparison that was carried out at the AIDA chamber in Karlsruhe
779 in Fall 2007 (<http://imk-aida.fzk.de/campaigns/RH01/Water-Intercomparison-www.htm>).
780 This formal program brought together more than twenty instruments that measure water
781 vapor and/or condensed water for a two-week measurement campaign. The results of a
782 formal blind intercomparison among a subset of the instruments are due out Spring 2008,
783 and should elucidate some of the reasons why water vapor measurements in the cold, dry
784 UTLS have disagreed to a level that is greater than their reported uncertainties.

785

786 *Observations in UT*

787 Observations of relative humidity over ice (RHi) and supersaturation in the upper
788 troposphere have been analyzed in detail, and both radiosonde measurements and those
789 derived from the chilled-mirror “SnowWhite” frost point hygrometer show frequent
790 supersaturation with respect to ice during wintertime (24% of time) [Vaughan et al.,
791 2005]. Data from MLS show occurrences of high supersaturations in only about 0.5% of
792 observations overall, with considerably larger frequencies of occurrence found over
793 Antarctica [Spichtinger et al., 2002]. Only one direct observation of RHi relevant for
794 assessing supersaturation in an aircraft-related contrail has been reported. Gao et al.
795 [2005] argued that the high supersaturations they observed might be due to co-
796 condensation of other species (e.g., HNO₃) in cloud particles.

797

798 *Climatology/Mechanistic Studies*

799 Ten years of MOZAIC data have been compiled to relate UT water to deep convection
800 and moisture transport [Luo et al., 2007]. Interannual variability is observed to correlate

801 in some cases with average temperature and/or ENSO, but is not fully explained by
802 either. Regional differences are well-explained by convective frequency. However, no
803 trend in H₂O abundances has been found in the MOZAIC data over the period Aug 1994
804 to Dec 2003 [Bortz et al., 2006].

805

806 Comparison of global or mechanistic model results with observations can also provide
807 insight into the significance of various transport processes for determining the water
808 vapor distribution. For example, MOZART model results and HALOE water vapor data
809 are in good agreement with respect to the seasonal cycle of vertical transport (the so-
810 called “tape recorder”), but some significant differences exist in distributions around the
811 tropopause [Park et al., 2004]. Much of this difference is attributed to the model’s
812 treatment of moisture transport in the monsoon regions, as well as stratosphere-
813 troposphere exchange in those areas. Similar results were obtained when comparing
814 simulations from the NCAR Community Atmosphere Model (CAM 3.0) to HALOE
815 observations and reanalyses by ECMWF. Deficiencies in the calculation of stratospheric
816 water vapor are attributed to weaknesses in the model’s core stratospheric dynamics, in
817 particular, the lack of a QBO and crude representation of planetary waves [Gulstad and
818 Isaksen, 2007]. The authors also note the importance of the model’s temperature fields,
819 which continue to show a polar cold bias; this particularly affects water vapor
820 distributions in the southern hemisphere.

821

822 To date, mechanistic model simulations have focused on the representation of water
823 vapor in the tropics. For example, tropical climatologies of H₂O, CO, HNO₃ and O₃ are
824 compared to calculations of vertical profiles of the same species obtained from four
825 models with differing parameterizations of convection [Folkins et al., 2006]. No single
826 model/parameterization emerged as “best”, with each having some failings in its ability
827 to reproduce observations. Comparisons of balloon-borne water vapor observations over
828 Brazil with profiles calculated by the Brazilian Regional Atmospheric Modeling System
829 (BRAMS) and ECMWF global analyses illustrate the importance of both model vertical
830 resolution and the treatment of microphysics in the ability to calculate realistic water
831 vapor profiles [Marécal et al., 2007].

832

833 **2.c.V. UT/LS Temperatures**

834 Atmospheric temperature is a fundamental quantity in all areas that this SSWP considers
835 – gas-phase and heterogeneous chemistry, the formation and persistence of condensed
836 matter (e.g., cirrus, contrails, polar stratospheric clouds), and transport processes. Thus
837 uncertainties in our knowledge of the mean temperature in the UT/LS, as well as its
838 natural variability, impact a wide range of processes important for understanding the
839 impacts of aircraft emissions on climate. Furthermore, the inability of models to
840 adequately simulate the temperatures in the atmospheric regions of interest may have
841 significant impacts on their treatment of heterogeneous processes and parameterizations
842 of microphysics (in addition to the role of temperature in model dynamics, such as the
843 classic GCM “cold pole” problem). A review of the temperature trends associated with
844 the broader climate change issue is beyond the scope of this document and controversies
845 surrounding the temperature record for the surface and mid-troposphere will not be
846 discussed.

847
848 A comprehensive review of temperature trends in the stratosphere was published in 2001
849 [Ramaswamy et al., 2001]. This work indicated that temperature trends in the lower
850 stratosphere were negative (-0.5 ± 0.25 °C/decade) and consistent with known trends in
851 stratospheric ozone as well as other greenhouse gases. These authors noted, however, that
852 better knowledge of the vertical profiles of ozone and water vapor, and their changes,
853 throughout the upper troposphere and lower stratosphere were critical for proper
854 attribution of the observed temperature changes. Stratospheric temperature trends updated
855 through 2005 are presented in Chapter 5 of WMO [2006] and are consistent with those
856 reported earlier.

857
858 Similar exhaustive trend studies for the UT/LS have not been carried out, although data
859 for this region do exist (from radiosondes, satellites and even in-service aircraft). One
860 regional study [Bencherif et al., 2006] uses radiosonde data gathered over South Africa to
861 show that temperatures are decreasing throughout the UT/LS (200 hPa and altitudes
862 above) between 1980 and 2001. In that region, upper tropospheric temperatures have
863 decreased at a rate of -0.10 ± 0.18 °C/decade, a value similar to that reported by Parker et
864 al. [1997] for an analysis based on globally gridded radiosonde observations.

865
866 Sensitivity of the rates of chemical processes to temperature can be significant. In general
867 an error of a degree or two makes little difference in the rate of a gas-phase process;
868 however, the same cannot be said for heterogeneous chemical transformations. The
869 composition of condensed phases is often a strong function of temperature, as is the
870 threshold for condensation. For example, at 200 K, a 1-K change in temperature changes
871 the saturation vapor pressure of water over ice by approximately 15%. When coupled to
872 uncertainties in water vapor measurements, errors in temperature observations or
873 calculations can have dramatic impacts on the determination of conditions such as
874 supersaturation or the presence of polar stratospheric clouds, and hence, chlorine
875 activation.

876

877 **2.d. Present State of Measurements and Data Analysis**

878 To understand the photochemistry of ozone in the UT/LS, it is important to know the
879 distributions of the major species that produce ozone (HO_x, NO_x, and hydrocarbons) and
880 those that destroy it (HO_x, ClO_x, BrO_x, and NO_x). Due to the strong coupling between
881 species within the radical families and between species from different families, it is not
882 necessary to measure all of the important species simultaneously. However, it is
883 important to have a good understanding of interrelationships between the major ozone-
884 forming/destroying radicals under the wide range of conditions that prevail where aircraft
885 emissions can be found. This includes temperatures that can range from ~190-240 K,
886 solar zenith angles from 0 degrees to greater than 90 degrees, and ozone abundances that
887 range from tens to thousands of ppb.

888

889 Not only is it a primary emission product of combustion, NO_x has a controlling influence
890 on partitioning within the HO_x and halogen families. Therefore, measurements of NO_x in
891 the UT/LS are important for defining the range of variation of the other ozone-controlling
892 radicals. Results from a number of major aircraft campaigns, some designed to validate

893 new orbiting platforms, as well as routine measurements from commercial airliners
894 equipped with instrumentation, have provided a wealth of information relevant for
895 understanding oxidation, as well as ozone formation and loss, in the UT/LS. The results
896 summarized in section 2.c for UT NO_x and HO_x chemistries have provided a strong
897 foundation for new modeling studies to address the impacts of NO_x emissions on ozone
898 and methane in the broader upper troposphere and lower stratosphere. However, new
899 results pointing to a reversal in the impacts on ozone in aircraft contrails and cirrus
900 clouds raises important questions about the completeness of the measurements.
901 Unfortunately, observations in regions of low NO_x have not been a major priority of
902 recent aircraft campaigns, and key satellite instruments do not have sufficient vertical or
903 horizontal resolution to examine these kinds of issues in narrow regions where
904 heterogeneous chemistry could play a dominant role.

905

906 Our understanding of the distribution of water vapor and the processes that control it
907 remains problematic. In the regions where heterogeneous chemistry would be most
908 important (i.e., at or near the tropopause), long-standing discrepancies between
909 measurements makes it extremely difficult to predict the chemical response to any
910 perturbation, let alone one that includes potential ice nuclei, water vapor and important
911 co-condensable species such as nitric acid, plus species that can inhibit ice formation
912 (such as volatile organic compounds). Although this issue is addressed in detail in
913 another SSWP in the context of cirrus and persistent contrail formation, the critical role
914 that these observations play in allowing for the prediction of the reactivities of particles
915 and, hence, their importance to this SSWP, cannot be understated. Resolution of this
916 problem is critical for assessing the impacts of aircraft emissions on particle formation,
917 heterogeneous chemistry, redistribution of condensable species, transport of emissions to
918 the stratosphere, and production of HO_x. Currently, the reported differences of up to 30%
919 between widely respected measurements is unacceptable, especially when they imply
920 strange behavior for particles that could change our fundamental view of the nature of
921 aerosols and clouds [e.g., cubic ice, nitric acid antifreeze, and very large
922 supersaturations].

923

924 Important results on water vapor measurements are expected in 2008 from the recent
925 AquaVIT intercomparison discussed in Section 2.c.IV.; however, it is important to note
926 that laboratory intercomparisons of the same or similar instruments have been carried out
927 before, and while they have answered some questions, they have largely been
928 unsuccessful at resolving the major discrepancies in the atmospheric measurements
929 themselves. Consequently, the state of *agreement* among water vapor measurements
930 remains inadequate for assessing the key remaining aviation impacts issues, even though
931 the instruments themselves may be in a mature state.

932

933 A new approach to water vapor intercomparisons would be welcome. One approach that
934 could be promising - dedicated flights into the combustion plumes of rockets and aircraft
935 - is described in more detail below. In 2008, potentially important results will be
936 forthcoming from a small pilot program called "PUMA" (Plume Ultrafast Measurements
937 Acquisition) that explore the nature of the discrepancy between water vapor
938 measurements in the UT/LS and the implications of heterogeneity on interpretations of

939 non-linear processes (such as threshold behaviors for condensation and evaporation of
940 ice, HOx and halogen photochemistry, and redistribution of major species, such as H₂O
941 and NO_x). Preliminary analyses of H₂O and particulate water data in evaporating plumes
942 are quite promising, and indicate that future measurements in these environments could
943 play a critical role in validating the accuracies of water vapor measurements. An
944 interesting question raised by these studies is whether the highly perturbed plumes
945 represent a realistic environment for investigating fundamental photochemical and
946 dynamical issues important in the UT/LS. From the point of view of the assessment of
947 aircraft emissions, it would seem that such environments, especially the plumes and
948 persistent contrails produced by aircraft themselves, would be ideal natural ‘laboratories’
949 for studying important processes identified in these SSWPs. In addition, there are some
950 who argue that pushing measurements outside their normal dynamic range is one sure
951 way to find problems that might help in identifying those issues that are important under
952 more normal conditions.

953

954 Finally, it is important to note here that satellite observations, with a few noteworthy
955 exceptions, have not yet been a major driving force in refining our understanding of
956 aircraft impacts. However, following completion of validation activities, new results from
957 the AURA platform, as well as those from SCIAMACHY, ACE, etc., will be analyzed in
958 light of the issues raised here and in previous assessments. It is very likely that significant
959 new insights into convective sources of NO_x and NO_y, HO_x, and aerosols will be
960 forthcoming from analyses of observations made from numerous satellite platforms. Such
961 results will be especially important in defining the basic state of the UT/LS into which
962 aircraft emissions represent a small, but important, perturbation.

963

964 **2.e. Current estimates of climate impacts and uncertainties**

965 Since the IPCC [1999] Assessment and the Sausen [2005] of the Brasseur et al. [1998]
966 European Report, there are no direct comparative model studies that address current
967 estimates of climate impacts and uncertainties. However, on the basis of the new results
968 presented above, some general conclusions can be drawn. First, on the basis of improved
969 understanding of upper tropospheric sources of NO_x, in particular, due to lightning and
970 convection from the PBL, it can be interred that the climate impact of aircraft emissions
971 on regional and global scales will be reduced. Second, on the basis of studies showing an
972 increased sensitivity of NO_x and NO_y to heterogeneous chemistry, it is likely that for
973 subsonic emissions there will be regions of the atmosphere where aircraft NO_x and
974 particles may, in fact, result in ozone losses, especially in the tropopause and LS regions.
975 On the basis of this result, one would expect the climate impacts of subsonic aircraft
976 emissions to be smaller than previously believed, and possibly reversed in sign relative to
977 previous evaluations (e.g., negative instead of positive), whereas the impacts of
978 supersonic emissions would be greater than previously believed, and positive instead of
979 negative. Third, the observation of nitric acid-containing particles in the UT/LS, along
980 with measurements indicating more vigorous transport of NO_x from the surface, raises
981 the possibility that NO_x and NO_y are processed more rapidly in the UT/LS than
982 previously believed. Finally, the presence of reactive halogens in the UT/LS, species that,
983 at the abundances that have been observed, can only coexist with NO_x if there is rapid
984 heterogeneous processing, raises the possibility for highly non-linear photochemistry that

985 can result in a net positive or net negative change in ozone with aircraft emissions of
986 NO_x and particles.

987

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

998

999 The growing body of HO_x observations in the UT indicates that OH abundances are at
1000 the high end of most model predictions, resulting in a lower lifetime for methane in the
1001 UT. This implies that, at least in these regions, methane will have a greater sensitivity to
1002 perturbations on NO_x and aerosols due to aircraft emissions. In addition, the potential for
1003 an increased role in halogen chemistry in cirrus and persistent contrails raises the
1004 possibility that aircraft perturbations to methane may currently be underestimated, as the
1005 reaction of methane with chlorine atoms is likely to be more important in the UT/LS than
1006 is currently believed.

1007

1008 **2.f. Interconnectivity with other SSWP theme areas**

1009 As has been discussed earlier, the chemistry of aircraft emissions is highly non-linear and
1010 strongly coupled with important processes dealt with in other SSWPs, including
1011 formation of persistent contrails and cirrus. Furthermore, and potentially more
1012 problematic for assessing impacts, emissions of NO_x could alter redistribution of NO_y
1013 and water, not only from aircraft exhaust, but from the background atmosphere as well if
1014 the addition of NO_x results in enhanced large-particle stability and sedimentation. It is
1015 also possible for NO_x influences to impact transport of NO_y and H₂O (although the latter
1016 may be too small to matter) from the UT into the LS. As noted in Section 2.d., the
1017 greatest uncertainty for this SSWP is due to the implications of continuing discrepancies
1018 in water vapor measurements in the cold and dry regions of the UT/LS. Thus, there is a
1019 strong interconnection between this SSWP and those on particle microphysics and
1020 contrail and cirrus cloud formation.

1021

1022 **3. Outstanding issues**

1023 Progress made in areas highlighted in Section 2.c., especially that relating to the
1024 importance of heterogeneous chemistry, raise new questions about the fundamental
1025 chemistries of NO_x, HO_x, and halogens, and the interactions of ice and nitric acid in the
1026 UT/LS, all which can have important consequences in future assessments of aviation
1027 impacts. Key new findings in these areas are summarized in Section 3.a. Although their
1028 impacts have not yet been adequately assessed, their tendency to push the effects of
1029 aviation emissions in the same general direction that has been found in model studies

1030 summarized in Section 2.c.III. is somewhat troublesome, in that they have the ability to
1031 offset some of the advances that have occurred over the past decade.

1032

1033 **3.a. Science**

1034 The key developments in UT chemistry summarized in Section 2.c. place considerably
1035 more emphasis on the role of heterogeneous chemistry of non-aircraft species, such as the
1036 halogens, on understanding the distributions of background H₂O and nitrogen oxides, and
1037 on the need for new studies that address chemical heterogeneities of the UT/LS. One of
1038 the interesting consequences of the increased importance of heterogeneous processes is
1039 the change in sign of ozone response with NO_x perturbation described earlier. This
1040 section will highlight important issues listed in the 2006 Workshop [Wuebbles et al.,
1041 2006] that remain unresolved, and new findings that raise new questions about chemistry
1042 in the UT that must be understood before uncertainties in the impacts of aircraft
1043 emissions on chemistry in the UT/LS can be reduced further.

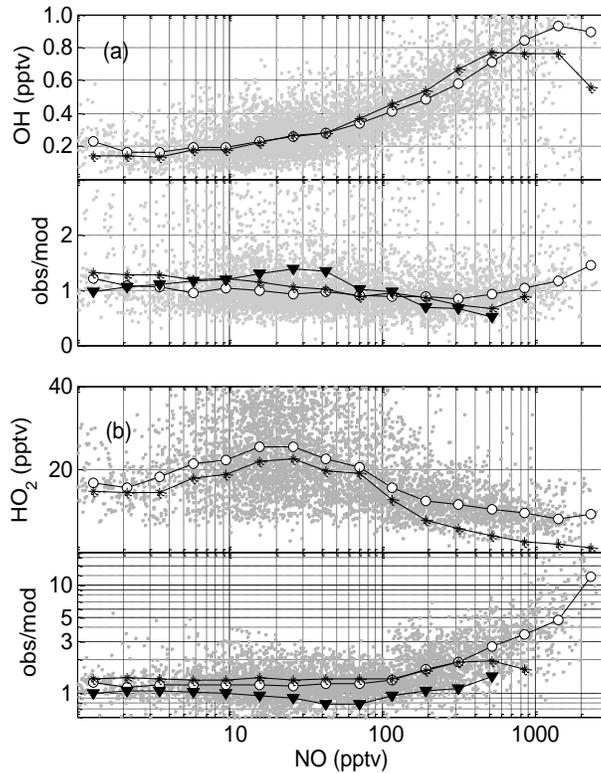
1044

1045 **3.a.I. Discrepancies in Coupled HO_x and NO_x Chemistry**

1046 The ability to realistically simulate ozone production and loss and the coupling between
1047 CH₄, CO, OH, and O₃ relies upon an accurate model representation of the response of
1048 HO_x (and, to a lesser extent, halogen radicals) to variations in NO_x. There have been a
1049 significant number of campaigns where NO, NO₂, OH, HO₂, and ozone have been
1050 measured simultaneously, and the first-order linkages between the NO_x and HO_x
1051 families have been demonstrated. However, model comparisons with HO_x observations
1052 have been somewhat problematic [Faloona et al., 2000]. Olson et al. [2006] show that
1053 most of the previous model-measurements discrepancies at high NO_x (e.g. during
1054 SONEX) can be explained by non-linearities of HO_x chemistry under highly variable
1055 conditions for NO_x (i.e., the model timescales are too long, relative to the measurements,
1056 such that averages of derived quantities do not represent quantities derived from averages
1057 of the individual measurements – see also Wild and Prather [2006]).

1058

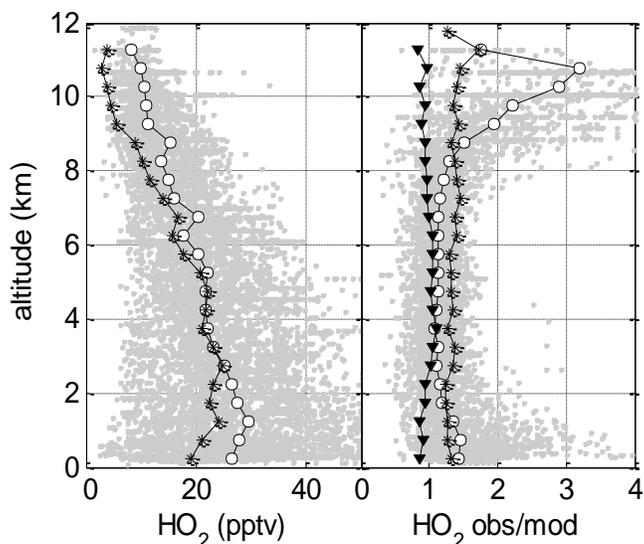
1059 Despite considerable progress that has been made in the area of tropospheric HO_x
1060 chemistry, as noted in two very recent papers [Hudman et al., 2007; Ren et al., 2008],
1061 observations continue to highlight important discrepancies between models and
1062 measurements. Figure 6 taken from Ren et al. [2008] shows how well models agree with
1063 measurements of HO_x during three recent major field campaigns for which there were
1064 comprehensive suites of measurements of sources of HO_x. The agreement between
1065 modeled and measured OH is quite good over most of the range, except, perhaps, at the
1066 very highest NO where a slight underprediction develops for INTEX-A (where the
1067 highest NO values were observed). However, at high NO, measured HO_x exceeds that
1068 from the model by as much as an order of magnitude at highest NO. Further insight into
1069 this issue is gained by examining the altitude dependence of the discrepancy, as shown in
1070 Figure 7. Clearly these results are problematic for assessments of the impacts of aviation,



1071
 1072
 1073
 1074
 1075
 1076
 1077
 1078
 1079
 1080
 1081
 1082
 1083
 1084
 1085
 1086
 1087
 1088
 1089
 1090
 1091

Figure 6. (a) Comparison of NO dependence for observations of OH (upper panel) and the ratio of measured-to-modeled OH (lower panel). (b) Comparison of NO dependence for observations of HO₂ (upper panel) values and the ratio of measured-to-modeled HO₂ 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 NO_x 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 (HO₂NO₂), whose abundance is determined by the coupled photochemistry of HO_x and NO_x, may help provide some answers [Murphy et al., 2002; Kim et al., 2007]. In a new report of simultaneous in situ observations of HO₂NO₂, NO₂, and HO₂, at aircraft cruise altitudes, Kim et al. [2007] found that abundances of HO₂NO₂ were about a factor-of-two low than those calculated with assumed photochemistry and observed abundances of HO₂ and NO₂. This discrepancy can be reconciled if one of the measurements (most likely HO₂NO₂ or HO₂) were in error (too small or too large,



1092
1093

1094 **Figure 7.** Similar to Figure 3, but for HO₂. (left panel) Comparison of the median
1095 vertical profiles of measured (circles) and modeled (stars) of OH for INTEX-A. (right
1096 panel) Measured-to-modeled OH in INTEX-A (circles), TRACE-P (stars) and PEM
1097 Tropics B (triangles). Individual 1-minute measurements from INTEX-A are shown (gray
1098 dots) [from Ren et al., 2008].
1099

1100

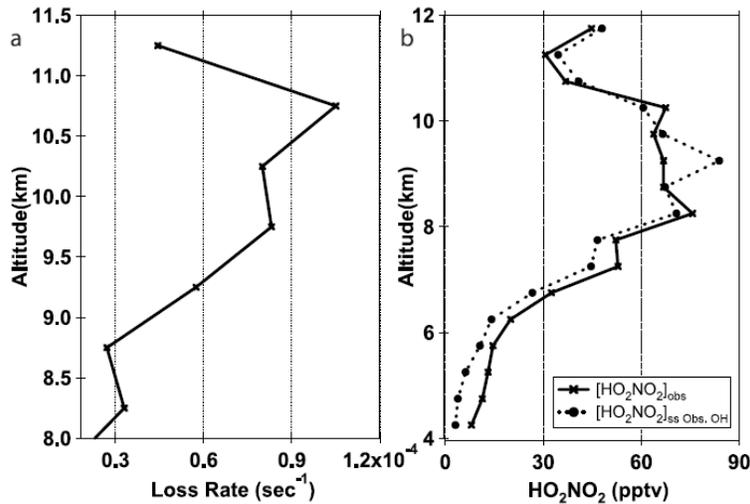
1101 respectively). However, it is interesting to note that the trend in this discrepancy with
1102 altitude is similar to that of Figure 7, raising the possibility of missing or poorly
1103 understood chemistry coupling HO_x to NO_x in the relatively cold and dry upper
1104 troposphere. It is particularly problematic for assessments of aircraft emissions that the
1105 discrepancy is largest at cruising altitudes for most large subsonic aircraft.

1106

1106 3.a.II. Halogen Chemistry

1107 In any modeling study of the impacts of a perturbation, it is important to start with a
1108 correct description of the composition of the background atmosphere. In previous aircraft
1109 assessments [Brasseur et al., 1998; IPCC 1999] it has been assumed that reactive
1110 halogens are not present in sufficient abundances to significantly impact ozone chemistry.
1111 Such a view was not based on observations, as there were few reliable observations of
1112 ClO and BrO in the UT/LS. Following the first observations of enhanced ClO in the
1113 lowermost stratosphere in 1991 [e.g., Avallone et al., 1993], ozone loss due to
1114 heterogeneous chemistry on cirrus clouds was proposed as a way to explain a gap
1115 between modeled and measured ozone trends in the midlatitude LS [e.g., Borrmann et al.,
1116 1996; Solomon et al., 1997]. A detailed examination of water vapor and ClO
1117 measurements in the UT/LS found no evidence for heterogeneous activation of chlorine
1118 [Smith et al., 2001]. However, subsequent measurements of ClO in the Arctic and
1119 examination of measurements over the continental US, both near the tropopause, found
1120

1120



1121

1122 Figure 8. Implications of new observations reported by Kim et al. [2007] revealed an
 1123 imbalance of production minus loss representing 50% of the magnitude of the production
 1124 rate calculated from observed abundances of HO_2 and NO_2 (left panel). HO_2NO_2
 1125 abundances were in good agreement with steady-state calculations based on observed
 1126 abundances of OH (right panel), suggesting a problem with coupled HO_2/NO_2 chemistry
 1127 or one of the observations.

1128

1129 evidence for widespread chlorine activation in regions of high particulate loading
 1130 [Thornton et al., 2003, Thornton et al., 2007]. The diurnal behavior of reactive chlorine
 1131 was very suggestive of rapid in situ processing by aerosols [Thornton, 2005].

1132

1133 As noted in Section 2.c.III., modeling studies that included heterogeneous processing of
 1134 NO_x found significant changes in the response of ozone to aircraft emissions. In one case
 1135 [Meilinger et al., 2005], it was the consideration of heterogeneous reactions on ice in
 1136 persistent contrails that led to important changes in ozone response. In the case of the
 1137 study by Hendricks et al. [2000], simply including heterogeneous reactions of bromine
 1138 nitrate, significant denoxification occurred in some regions with important consequences
 1139 on ozone. Finally, in the very recent study by Sovde et al. [2007], properly accounting for
 1140 known heterogeneous reactions on aircraft-perturbed aerosol particles resulted in a
 1141 complete reversal in sign of the ozone response to increased emissions in the UT. Based
 1142 on these results alone, a reexamination of the role of heterogeneous reactions on
 1143 background aerosols and in persistent contrails and cirrus using updated photochemical
 1144 parameters is warranted.

1145

1146 Adding to the complexity of this issue, over the past decade there have been a number of
 1147 reports (more than will be referred to here – see Salawitch et al. [2005]) of larger-than-
 1148 expected abundances of BrO in the upper troposphere. Salawitch et al. [2005] make a
 1149 strong case for the need to add upwards of 2-4 ppt of bromine to the stratospheric budget,
 1150 either by transport of inorganic species (such as BrO, BrONO_3 , and HOBr) or short-lived
 1151 organic sources. In light of the increased number of surface sources required to explain
 1152 recent NO_x and HOx measurements in the UT, it seems reasonable that both types of
 1153 species could contribute to this ~10-20% enhancement in the total bromine budget by

1154 short-lived species [e.g., Sinnhuber and Folkins, 2006]. However, there are some
1155 important caveats. First, it is only the remotely sensed observations of BrO that point to a
1156 need to increase the bromine budget beyond what measurements of organic source gases
1157 seem to suggest – in other words, beyond about 4 ppt of bromine from short-lived
1158 compounds [e.g., Dorf et al. 2006a]. Second, even the remote sensing observations of
1159 BrO do not agree; they split roughly 50/50 in number between those that agree [Schofield
1160 et al., 2004]; Sinnhuber et al., 2005] with a budget based on measurements of source
1161 gases and some short-lived compounds near the tropopause [e.g., Schauffler et al., 1999]
1162 and those that suggest missing nearly double those short-lived sources of bromine [e.g.,
1163 Sioris et al., 2006; Theys et al., 2007].

1164
1165 This issue is treated in great detail in the recent WMO Ozone Report [2006], so will not
1166 be discussed further here, other than to note that due to the importance of bromine in
1167 some regions of the UT/LS (e.g., Hendricks et al., 2000), new observations of BrO with
1168 high spatial resolution, and in conjunction with observations of NO_x and HO_x, may be
1169 required to resolve this issue.

1170

1171 **3.a.III. Potential Surprises**

1172 “Our vision is often more obstructed by what we think we know than by our lack of
1173 knowledge.” These words of Krister Stehdahl, the Harvard Professor of Divinity, apply
1174 well to this problem. It is important to remember the lessons of the 1985 WMO Ozone
1175 Assessment, where the consensus view at the time was that the ClO dimer and
1176 heterogeneous reactions would not play important roles in stratospheric ozone chemistry.
1177 This lesson seems relevant to this White Paper, and the authors view several issues that
1178 fall in this category as the most important in terms of limiting our ability to accurately
1179 assess the current impacts of aviation on UT/LS chemistry and predict future impacts.

1180

1181 *Scavenging of NO_y*

1182 Another important series of new observations are those related to the formation of nitric-
1183 acid containing ice particles in the UT/LS [Voigt et al. 2007, Voigt et al. 2007, and Popp
1184 et al. 2006]. The fact that such particles are larger, and less abundant than other particles
1185 suggests that their sedimentation could impact distributions of reactive nitrogen and
1186 water in the UT/LS. Redistribution and/or removal of NO_y and H₂O from the UT/LS
1187 could result in important non-linearities that are presently not treated adequately in
1188 models. For example, it is possible that addition of aircraft NO_x, followed by enhanced
1189 sedimentation of nitric acid-containing particles, could denitrify a narrow layer centered
1190 about the flight corridor. In the tropics, such a process could even mean that aircraft
1191 emissions ‘seed’ the removal of NO_y and water, thereby decreasing transport of these
1192 species to the stratosphere (i.e. a negative feedback loop). Recent observations of
1193 significant chlorine activation in broad region near the polar tropopause where NO_y-
1194 containing particles were also observed [Thornton et al., 2003] suggest that such a
1195 feedback is possible. Thus, it is important to understand better uptake of NO_y species on
1196 ice particles and the role of temperature and water vapor (i.e. RH_i) on such processes.
1197 Key to such an understanding will be the accuracies of measurements of water vapor and
1198 condensed water in the UT/LS.

1199

1200 *Non-linear Processes – Feedbacks and Plume Dispersion*

1201 The issue of potential surprises due to a lack of understanding of plume dispersion must
1202 be examined in greater detail. One of the ubiquitous features of in situ measurements of
1203 many types is their high degree of heterogeneity to very small scales [Richard et al. 2006,
1204 and Lovejoy et al. 2007]. In fact, for reactive species, this can translate down to sub-
1205 meter scales [unpublished results from the PUMA campaign]. Therefore, it is insufficient
1206 to assume simple gaussian plume dispersion when it is known that constituents exhibit a
1207 high degree of variability, even hours after they are emitted. This is especially the case
1208 when differences between vertical mixing and horizontal shear forces result in
1209 filamentary structures [e.g Fairley et al., 2007] that are difficult to describe with a simple
1210 gaussian parameterization.

1211
1212 We also lack a basic understanding of non-linear processes that can occur in the
1213 heterogeneous environment of an aircraft plume and persistent contrail. With the likely
1214 addition presence of solid or liquid mixtures of HNO₃ and H₂O (e.g. nitric acid
1215 trihydrate), in which the stability is proportional to the density of the plume raised to a
1216 power as large as four, and where heterogeneous reaction rates are strong non-linear
1217 functions of relative humidity and composition, this problem has only become more
1218 difficult to handle following observations of nitric acid-containing particles in the UT/LS.
1219 In a sense, this issue, along with the non-linear coupling between HO_x, ClO_x, BrO_x, and
1220 NO_x, is reminiscent of the ozone hole. While the effects will not be as severe, their role
1221 in the aircraft emissions assessment process is only now being addressed in sufficient
1222 detail.

1223
1224 **3.b. Measurements and analysis**

1225 New and improved measurements and analysis of existing data should help to address
1226 some of the outstanding issues highlighted above. As noted previously, reanalysis of HO_x
1227 measurements may help to resolve some discrepancies between models and
1228 measurements that have been noted previously. It is also possible, perhaps likely, that
1229 such analyses will raise new questions. In addition, ongoing observations of HO_x, along
1230 with NO_x, source gases, and tracers of transport from the PBL and stratosphere, as are
1231 planned for major campaigns such as ARCTAS in 2008 are critical for efforts to map out
1232 seasonal and regional variations of this critical oxidizer. Such observations will provide
1233 important constraints for models used to assess the role of HO_x chemistry, especially that
1234 related to methane oxidation.

1235
1236 New, fast response, in situ measurements in aircraft plumes, including particles, water
1237 vapor, several good tracers of combustion and mixing (e.g. CO₂ and CO), ice water
1238 content, HO_x, NO_x, and at least one halogen radical would go far toward reducing
1239 uncertainties resulting from non-linear processes. The capability exists for such
1240 measurements, although to date, they have not been carried out downstream of an aircraft
1241 or in aircraft flight corridors (the potential to rectify this situation exists during
1242 ARCTAS).

1243
1244 Continued analyses of satellite data, particularly those with sufficient horizontal
1245 resolution to identify regions of interesting chemistry (e.g. in persistent contrails, the

1246 North Atlantic Flight Corridor, or in the tropopause region), may shed light on the
1247 importance of potential non-linearities that may be difficult to examine by in situ
1248 methods. Of particular value would be studies of correlative measurements of clouds and
1249 trace constituents (e.g. TES, MLS, SCIAMACHY, OMI, AIRS, MODIS) that might
1250 reveal linkages between cloud occurrences and constituent abundances.

1251
1252 Efforts should continue to understand bromine and chlorine chemistry in the UT/LS, in
1253 particular the variations of abundances of BrO and ClO. Of particular interest would be
1254 high-resolution correlative measurements of these species with HO₂, OH, and NO_x, along
1255 with their respective source gases. Observations in aircraft plumes and flight corridors
1256 would be especially helpful for constraining plume dispersion models. Finally, it will
1257 likely be necessary to carry out frequent water vapor measurements intercomparisons to
1258 continue to refine our understanding of the factors that influence the discrepancies that
1259 have been observed between various techniques.

1260
1261 **4.a. Prioritization of Issues Based on Impact**
1262 The outstanding issues identified above can be prioritized on the basis of the level of
1263 scientific understanding and the magnitude of the terms each represents in the most
1264 recent IPCC “Radiative Forcing”-like representation of aviation effects on climate.
1265 Referring to Figure 1, this would suggest that improvements in understanding of the
1266 processes that impact the distribution of ozone (28 mW m⁻² and “fair”) and the lifetime of
1267 methane (□20 mW m⁻² and “fair”) will be most significant. Of lesser importance are the
1268 impacts on direct radiative forcings due to emissions of CO₂, H₂O, sulfate and soot.
1269 Finally, of least importance would be investigation of issues that were not considered in
1270 detail in previous impacts assessments.

1271
1272 However, it is also worthwhile to consider prioritization of issues on the basis of the
1273 extent to which they may represent a dramatic shift in our basic understanding of the
1274 impacts of aviation. In this case, those issues deemed of least importance using the
1275 present framework of the IPCC Forcings, as outlined above, could be considered of
1276 highest priority from the point of view of uncertainty or “surprise”. For example, if a
1277 proper treatment of heterogeneous chemistry on aircraft-produced particles or of aircraft
1278 emissions of NO_x and H₂O on background aerosols results in a reversal of the sign of
1279 ozone change in the UT/LS, this would essentially render as moot the prioritization of
1280 issues based on the previous IPCC-like forcings. That is, because the sign for the
1281 radiative impact of aircraft-induced ozone changes could, in fact, be negative, a result
1282 that is outside the present estimate of uncertainty for that particular term in Figure 1.
1283 While the possibility of this type of “surprise” is relatively small, given recent
1284 observations that raise questions about our understanding of heterogeneous chemistry in
1285 the UT/LS, it is prudent to examine the potential consequences of previously unknown
1286 processes before expending much effort toward reducing the uncertainties of processes
1287 that were previously believed to be the most important.

1288
1289 In the section that follows, we approach the prioritization from these different
1290 perspectives, beginning first with the conventional approach of prioritizing the issues on

1291 the basis of reducing the current list of uncertainties. We then follow with a prioritization
1292 of issues based on the potential for a major shift in our understanding of the impacts.

1293

1294 *Priority 1 – Water Vapor Measurements*

1295 Long-standing discrepancies among water vapor measurements (both in situ and remote)
1296 in the coldest and driest regions in the UT/LS continue to limit efforts to accurately
1297 quantify the role of heterogeneous chemistry in conversion of NO_x to NO_y, to model
1298 HO_x production and loss, to predict the frequency and extent of halogen activation, and
1299 to model the distribution of exhaust emissions (in particular, sedimentation of NO_x and
1300 H₂O) in the UT/LS. Of critical importance is the characterization of the role of
1301 supersaturation (i.e., R_{Hi}) in particle formation and growth, both highly non-linear
1302 processes.

1303

1304 One method for assessing the accuracy of water vapor measurements is to examine
1305 observations from different pairs of instruments in a series of informal intercomparisons.
1306 From such opportunities, it is known that particular instruments report data that is
1307 consistently as much as 40% larger than all other techniques under the driest conditions
1308 in the UT/LS. These data have led researchers to conclude that large supersaturations
1309 (well over 150% in some cases) exist. Because all of the in situ instruments have been
1310 characterized separately in the laboratory, it has been argued that carefully designed and
1311 executed laboratory intercomparisons will help to resolve outstanding differences. A
1312 recent formal (double-blind) intercomparison (AquaVIT) has revealed some issues that
1313 may help to reduce the discrepancy among instruments. However, it will still be
1314 necessary to demonstrate consistent agreement amongst instruments under a wide range
1315 of conditions in actual atmospheric observations before this problem can be considered to
1316 be resolved.

1317

1318 Unfortunately, few, if any, dedicated intercomparison campaigns are being planned that
1319 will adequately address this critical issue. In part, this is due to the high costs that would
1320 be associated with a multi-platform, multi-instrument campaign which would be required
1321 to demonstrate good agreement over the wide range of conditions found in the UT/LS.
1322 For example, a month-long dedicated WB57F campaign based in Houston, designed to
1323 sample across a wide range of latitudes in order to encounter a reasonable dynamic range
1324 of water vapor values would involve over \$1 million in aircraft operating costs and
1325 adequate funds for participant travel and post-mission analysis. In addition, it is unclear
1326 how new measurements obtained in this manner would resolve outstanding issues from
1327 previous campaign involving similar flight tactics. From many perspectives, a new
1328 approach aimed at clearly identifying instrument performance issues is required to make
1329 significant progress in this area, and to lend credibility to the results.

1330

1331 A promising new approach that could be taken to identify key areas of disagreement
1332 between instruments is to deploy them into combustion plumes in the UT/LS, both those
1333 laid down by aircraft and those laid down by rockets. The validity of this approach has
1334 been demonstrated recently in a pilot mission called PUMA (Plume Ultrafast
1335 Measurements Acquisition). In 2004, 2005, and 2006, exhaust emissions from three
1336 rockets (Atlas IIAS and two Space Shuttles) were sampled for particle size distributions,

1337 ice water content, water vapor, temperature, and carbon dioxide. The advantage to this
1338 approach is that a significant range of abundances of H₂O (from ambient levels near 4
1339 ppm to over 30 ppm) are encountered at each altitude where the plumes are sampled,
1340 providing for a slope/intercept analysis for each instrument. Such an approach can reveal
1341 whether measurement differences are due to differences in calibration or to offsets, the
1342 latter of which can be significant for water vapor in the dry UT/LS. One of the
1343 interesting results from PUMA is the demonstration that the contrail evaporation point
1344 (when RHi drops below 100%) serves as an important independent validation of the H₂O
1345 vapor pressure measurement – that is, independent of the CO₂/H₂O emission index,
1346 which constrains the slope of a calibration (the “span” or response function), the instant
1347 when RHi drops below 100%, which can be identified unambiguously by an enhanced
1348 total water measurement such as CLH, is a powerful constraint on the accuracy of a total
1349 water measurement to a level that cannot be achieved in any laboratory calibration based
1350 on water vapor alone.

1351

1352 *Priority 2 – Temperature measurements*

1353 As shown above, in the context of defining RHi, measurements of temperature on most
1354 platforms agree to a level that is better than the agreement amongst water vapor
1355 measurements. However, making accurate temperature measurements is a non-trivial
1356 process, especially on a fast-moving platform, such as the WB57F, ER-2, or HIAPER.
1357 For example, near 200 K, a difference of 1 °C translates into an uncertainty of 10% in
1358 RHi. Thus, any program designed to address water vapor accuracies (especially one that
1359 relies on the vapor-ice transition such as that described above) must also address the
1360 accuracy of temperature measurements. It is the correction from observed to static
1361 temperatures using the “recovery temperature” equation that is most uncertain, as the
1362 correction involves quadratic terms for air speed that rely on highly accurate
1363 measurements of static and dynamic pressure. Consequently, accurate knowledge of the
1364 air flow around the aircraft surface where temperature probes are mounted is critical in
1365 order to determine recovery temperature to better than 1 °C.

1366

1367 One issue that has been raised when different temperature measurements from the
1368 WB57F aircraft have been compared is that placement of inlets can have profound effects
1369 on water vapor measurements in clouds (or at RHi near 100%) due to possible inertial
1370 enhancement of particulate water. It is recommended here that to avoid ambiguities (such
1371 as pressure perturbations near blunt surfaces or under wings), it would be quite useful to
1372 install temperature probes in various locations around the aircraft, especially on wing
1373 pods or under the wings near where water vapor instruments are deployed in any
1374 campaign that has a focus on accuracies of water vapor measurements. Good agreement
1375 between such measurements (say one located on a wing pod and one on the nose) serves
1376 to provide increased confidence that differences between measurements of water vapor
1377 are not due to perturbations of the temperature/pressure field around an instrument. This
1378 approach was used successfully during the PUMA campaign. As shown below, such
1379 measurements represent a very small cost compared to the time that could be lost in post-
1380 mission analyses that must account for potential consequences due to placement of
1381 temperature and pressure measurements.

1382

1383 *Priority 3. HOx Measurements*

1384 Critical to the modeling effort that is required to determine the impact of aircraft
1385 emissions on the global methane budget (and hence the radiative forcing term that is
1386 labeled by “CH₄” in Figure 1) is the ability for the models to accurately simulate global
1387 OH distributions. Not only does the abundance of OH determine the tropospheric lifetime
1388 of methane and the rate of conversion of NO_x to NO_y, OH and HO₂ are important ozone
1389 destroying radicals. In addition, the ability to model the sources of HO_x in the UT/LS
1390 improves knowledge of the surface convective sources that also contribute the budget of
1391 NO_x in the UT/LS. Finally, measurements of OH and the OH/HO₂ ratio provide
1392 constraints on NO_x and halogen chemistries.

1393
1394 A substantial heritage of measurements of OH and HO₂ in the UT/LS has been
1395 established as a result of numerous campaigns involving the ER-2 and DC-8 aircraft.
1396 Because HO_x abundances are fundamental to a number of important processes in models
1397 used to assess aircraft impacts, continuing to add to the current database of HO_x
1398 measurements will serve to reduce important uncertainties in those models. Frequent
1399 intercomparisons between measurements of OH and HO₂ using different techniques will
1400 also help investigators reduce their measurement uncertainties, and should be
1401 encouraged.

1402
1403 *Priority 4 – Coupled HOx/NOx Chemistry*

1404 Possible discrepancies between modeled and measured HO₂NO₂, a compound that
1405 provides a critical link between the photochemistries of HO_x and NO_x families, should
1406 be investigated further. The current discrepancy points out a potential problem with the
1407 new measurements of HO₂NO₂ or one or more of the species that produces it, an error in
1408 a critical photochemical parameter, or missing chemistry that could be important in
1409 determining abundances of NO_x or NO_y in the UT/LS. Efforts to reduce uncertainties in
1410 the measurements of HO₂NO₂ and modeling investigations of potential errors in sources
1411 or sinks of HO₂NO₂ should be encouraged.

1412
1413 *Prioritization based on potential impacts that are currently unknown*

1414 Although important uncertainties remain in the processes listed in the section above, for
1415 all of these it is possible to estimate the likely bounds of their impacts with investigations
1416 that are constrained by known uncertainties in existing measurements. For example,
1417 impacts could be assessed with a model that assumes ice particle formation in the UT/LS
1418 at supersaturations consistent with the low end (i.e., driest) of the water vapor
1419 measurements and with those consistent with the high end of the measurements. Based on
1420 the resulting range of impacts, the need to resolve the discrepancies in water vapor
1421 measurements could be quantified (for example, a range of 10%, rather than 30%, is
1422 required for adequate assessment of this term). However, for several processes, the
1423 observations may be too limited to provide a reliable estimate of the impacts of aircraft
1424 emissions. In this section, these processes are given high priority based on the possibility
1425 that they could be significant, but reasonable bounds cannot yet be placed on their
1426 potential impacts due to lacking observational constraints (e.g., the situation, although
1427 probably not as dramatic, can be likened to that of 1985 when it was believed that

1428 heterogeneous reactions were not significant for ozone balance and that CFC-related
1429 ozone loss would occur in the middle stratosphere at mid-latitudes).

1430

1431 *Priority 1 – Investigations of non-linear effects*

1432 Recent observations of nitric acid-containing particles [Popp, et al., 2006] and
1433 enhancements in reactive chlorine [Thornton et al., 2007] in the UT/LS outside the polar
1434 regions have raised the possibility that heterogeneous reactions could lead to conversion
1435 of NO_x to NO_y, and activation of chlorine, in persistent contrails or cirrus occurring in
1436 flight corridors. It is even possible that NO_y could be redistributed by sedimentation of
1437 particles if they grow large enough in these regions. Such processes are strongly non-
1438 linear in plumes or exhaust-influenced regions, due to the threshold nature of particle
1439 formation and strong water dependence of heterogeneous reactions involving halogens
1440 and NO_y. To understand the role of such processes in UT/LS chemistry, details of the
1441 dispersion of exhaust become extremely important.

1442

1443 At the present time, there are few observations of the variability of constituents in and
1444 subsequent dispersion to the background atmosphere of exhaust plumes. In addition, the
1445 chemical composition of particles in exhaust plumes has only recently begun to be
1446 studied, and measurements of reactive halogens in the UT/LS with instruments sensitive
1447 enough to observe their small-scale (e.g., plume scale) variability have been ignored.
1448 Given the recent model results shown in Sections 2.C.II and 2.C.IV above, it is important
1449 to investigate the potential impacts of dispersion processes on the chemistry of plumes.
1450 Significant progress toward setting possible limits on the importance of such processes
1451 would be possible with modeling efforts that consider extreme cases, such as complete
1452 removal of NO_y by sedimentation in persistent contrails, slow dispersion of plumes, and
1453 rapid heterogeneous reactions. Such studies could then serve to guide observations of
1454 species such as HNO₃, particles, ClO, and BrO that would constrain the impacts of these
1455 processes on the chemistry of ozone in the UT/LS.

1456

1457 *Priority 2 – The Role of Halogen Oxides in Background UT/LS Ozone Chemistry*

1458 Although it is believed that the importance of halogen oxides is limited by excess
1459 abundances of NO_x in the UT/LS, recent observations of widespread, low levels (~1-2
1460 ppt) of BrO throughout the UT/LS and narrow regions with significant enhancements of
1461 ClO raise important questions about our understanding of halogen chemistry in the
1462 altitude region where aircraft emissions have the greatest impact on ozone abundances.
1463 Because coupled NO_x/HC/HO_x (i.e. “smog”) chemistry tends to produce ozone in the
1464 upper troposphere, whereas halogens solely (and rapidly) destroy ozone, a better
1465 understanding of the distributions of halogen radicals is necessary to accurately simulate
1466 the impact of aircraft NO_x and H₂O emissions on ozone in the UT/LS. Of particular
1467 concern is the possibility that NO_x serves as a catalyst for production of halogen oxides
1468 via rapid heterogeneous reactions in the presence of sunlight. This situation is somewhat
1469 the reverse of that in the winter polar stratosphere, where NO_x serves to deactivate the
1470 halogen radicals via formation of relatively stable reservoirs. In the UT/LS at lower
1471 latitudes, however, rapid heterogeneous conversion of inorganic halogen acids (e.g.,
1472 HOBr, HBr, HOCl, and HCl) is limited by availability of oxidants such as ClNO₃ and
1473 BrNO₃, such that addition of NO_x serves as a catalyst for halogen activation, so long as

1474 particulate surface areas are sufficient. With recent studies showing a reversal in sign of
1475 the impact of aircraft emissions on ozone abundances due to more rapid heterogeneous
1476 chemistry and halogen activation, it is important that the issue of distributions of halogen
1477 oxides be revisited.

1478
1479 There are several cost-effective ways that this issue could be approached. First, because
1480 abundances of ClO and BrO are quite small in this region, it would be useful for a team
1481 of investigators composed of modelers and measurements experts to model the impact on
1482 ozone of extreme scenarios involving halogen radicals in the UT/LS using the few
1483 existing observations. The calculated ranges of ozone could then be used to reexamine
1484 the radiative impacts of aircraft emissions. In addition, new high-resolution in situ
1485 measurements of halogen oxides in the UT/LS could be obtained in conjunction with
1486 measurements of NO_x and HO_x as part of larger campaigns designed to study the
1487 oxidative state of the UT/LS. Such measurements in the upper troposphere have had a
1488 very low priority on previous missions, except for the 1998 WB-57F Aerosol Mission
1489 (WAM) and the 2000 SOLVE campaign, results of which have shown that active forms
1490 of chlorine are more prevalent than was believed previously, provided that ample aerosol
1491 surface area abundances ($> 3 \mu\text{m cm}^{-3}$) are available. There are cost-effective ways to
1492 pursue this line of investigation, such as redeploying atomic resonance fluorescence (RF)
1493 instruments that have been used for over two decades for stratospheric measurements and
1494 that were previously flown on the WB-57F and DC-8 aircraft, in this case reconfigured
1495 for improved sensitivity under tropospheric conditions, or by adapting instruments that
1496 use an alternative detection technique (e.g., chemical ionization mass spectrometry -
1497 CIMS). In either case, there will be modest costs (see below) associated with the
1498 laboratory efforts required to optimize the existing stratospheric instruments for use in the
1499 UT/LS or those required to develop new calibrations and to develop a heritage of reliable
1500 observations, in the case of a new measurement technique, such as CIMS.

1501
1502 Laboratory measurements of key rate parameters at low temperatures of the UT/LS will
1503 continue to refine our understanding the sensitivities of NO_x and heterogeneous
1504 chemistries to temperature, relative humidity and pressure, variables that can be
1505 important in the UT/LS.

1506 1507 **4.b. Ability to Reduce Uncertainties**

1508 Given the wealth of new information regarding UT/LS chemistry that has become
1509 available in recent years, the ability to reduce uncertainties in estimates of the climate
1510 impacts of aviation is quite good. Significant progress can be made on nearly all of the
1511 topics presented in this SSWP within 3 to 5 years. The most problematic of the issues,
1512 those involving accuracies of water vapor measurements, plume dispersion, and
1513 heterogeneous chemistry, may require a longer timeframe to achieve the level of
1514 confidence that is associated with attribution of cause-and-effect for ozone destruction in
1515 the stratosphere, but given the level of knowledge already attained in the atmospheric
1516 chemistry community, it is not unreasonable to expect that an effort that is more focused
1517 on resolving the key issues outlined above can see significant progress within the time
1518 frame of 2 three-year grant cycles.

1519

1520 First, and most critical, will be detailed studies with models that can treat plume
1521 chemistry and dispersion to scope out the range of possible impacts of non-linear particle
1522 formation processes and heterogeneous chemistry. Coupled with this knowledge, field
1523 and laboratory studies can be carried out to reduce the uncertainties in the most critical
1524 parameters that are revealed in these model studies. Of particular significance will be
1525 those fields studies that can address plume processes directly with the powerful suite of
1526 instruments and platforms that are currently in the atmospheric sciences arsenal. With
1527 few exceptions (such as better instruments for measuring halogens at part-per-trillion
1528 abundances and new or improved instruments to measure oxygenated source gases for
1529 HO_x), the instruments and platforms required to provide critical observations to constrain
1530 these process models already exist, and the investment in the investigations needed to
1531 answer the critical questions will be valuable for issues that reach beyond the impacts of
1532 aircraft (for example, alternative energy production, changing climate, new technologies,
1533 etc.).

1534

1535 **4.c. Practical Use**

1536 Addressing all of the key issues above will have important practical applications,
1537 including improvements in measurements that address a broad range of atmospheric
1538 issues. Additional model development, especially an accurate and validated plume
1539 dispersion model can be quite useful for studying a number of issues related to climate
1540 change, including source apportionment of CO₂, an issue that will be of major importance
1541 in the future if CO₂ trading schemes become prevalent.

1542

1543 **4.d. Achievability**

1544 As noted in Section 4.b., important results are clearly achievable in all areas outlined in
1545 this SSWP. In most cases, cost will be the primary limiting issue, as some instruments or
1546 platforms that may be required for the most definitive studies will require significant
1547 modifications or deployment costs. Improvements in models that will be necessary to
1548 assimilate the results from new observations may require the development of new codes
1549 (for example, a high-resolution plume dispersion model). However, to date technology
1550 does not seem to be what has limited the development of such a model.

1551

1552 **4.e. Cost**

1553 Addressing the water vapor measurements issue will probably be the most productive use
1554 of funds at this point in time in terms of reducing uncertainties in aircraft climate impacts.
1555 However, due to the high level of interest for other programs (e.g., satellite validation and
1556 climate change studies in general), significant leveraging of funds should be possible, and
1557 should immediately be pursued. However, a business-as-usual approach is very likely not
1558 going to foster significant progress in this area, such that a new and creative program will
1559 be required. It would be helpful to develop clear milestones with broad community
1560 support, with implications for failure of PIs to meet stated accuracies. New and
1561 innovative approaches to validating water vapor (and condensed water) measurements in
1562 the cold and dry UT/LS, such as periodic direct flights in exhaust plumes to calibrate
1563 individual instruments, to reveal discrepancies between instruments, and to monitor
1564 instrumental drift, would be particularly useful. Such efforts that could also build on
1565 recent efforts, such as AquaVIT, to maintain a traceable set of intercomparisons, should

1566 be monitored regularly by a group of scientists who are both knowledgeable in the field,
1567 and outsiders who have an expertise in measurement intercomparisons and validations. It
1568 would be particularly helpful to develop a water vapor standard for calibrations and
1569 traceability, just as was done for ozone measurements, thereby reducing the reliance on
1570 costly large-scale laboratory intercomparisons.

1571
1572 It would be very useful to carry out an in-flight intercomparison of water vapor
1573 measurements in the UT/LS from a common platform, such as the DC-8 or WB-57, one
1574 that involves frequent sampling in aircraft plumes (both wet and dry). Not all instruments
1575 would have to participate in such an intercomparison, but it would be essential to have
1576 sufficient variety of existing instruments that span the range of current measurements
1577 (e.g., from those that are on the low side of the intercomparisons, such as frost point
1578 hygrometers, to those that are on the high side, such as the JPL TDL). Results in dry
1579 plumes can be traced to an absolute value using simultaneous measurements of CO₂,
1580 since the stoichiometry of combustion of aviation fuel is well known.

1581
1582 Overall, a ~\$1-2 million program over five years, with funds provided from a variety of
1583 sources, would catalyze significant progress on this issue, and get away from the
1584 business-as-usual approach of providing limited funding for smaller, term efforts that
1585 piggy-back off larger projects, and end up suffering from too little funding without a
1586 guarantee of continued funds to thoroughly investigate the causes for discrepancies. A
1587 Water Vapor Campaign, whose chief focus is on reducing the uncertainties in
1588 measurements and maintaining a long-term, traceable record, should be a top priority for
1589 an aircraft impacts program, as well as a general world-wide program to monitor climate
1590 change.

1591
1592 With a clear focus on water vapor, other issues can be dealt with on an 'add-value' basis.
1593 For example, studies of non-linear processes in plumes would be a natural add-on to
1594 missions that use combustion plumes as a way to investigate instrument differences and,
1595 potentially, as a way to maintain a long-term calibration standard (assuming that
1596 combustion of kerosene will remain the method of choice for aircraft propulsion for
1597 many decades. Issues that require some instrument development (e.g., halogen and
1598 oxygenated organic compound measurements) should be initiated as soon as possible to
1599 reduce the long lead times that are associated with integration and demonstration of new
1600 instruments on research aircraft. Funding for these developments could be leveraged with
1601 funding agencies like NSF and DOE, insofar as other programs will benefit from the use
1602 of such instruments in other environments (e.g., halogens in the polar boundary layer,
1603 oxygenated compounds in urban pollution/source attribution studies, etc.). International
1604 cooperation would also help to reduce development time and cost, especially where there
1605 are common interests for measurement capabilities (i.e., it is cheaper per unit to build
1606 more than one).

1607
1608 Addition of increments of ~\$300-500 K in a few key areas would likely result in
1609 important progress for most of the issues highlighted in this SSWP. A total program of \$5
1610 million, including the water vapor project mentioned above, would probably reduce most
1611 of the remaining climate uncertainties in aviation operations by half, and change the level

1612 of understanding from poor or fair to good for most, if not all, chemical terms in the
1613 climate forcing framework.

1614

1615 **4.f. Timeline**

1616 Significant progress could be made on all of the issues discussed above within 3-5 years
1617 with an adequately resourced project. The expertise exists in the community and there
1618 would be limited need for development of new techniques. In fact, waiting longer could
1619 inadvertently result in significant additional expenses to carry out similar work, as
1620 experts in some areas retire or become involved in other projects. In the worst case, it is
1621 possible for an opportunity to be lost altogether. Because time is a factor, heritage should
1622 be a major factor in consideration of projects to fund. The cost of missed opportunities is
1623 difficult to estimate, but it vastly exceeds the cost of starting from scratch. instrument to
1624 service. (for example, it would be highly desirable to bring the NOAA-lyman alpha water
1625 instrument back into service, and waiting much longer may preclude this, and
1626 resurrecting this capability from scratch would be prohibitively costly, especially given
1627 the extraordinarily long record of measurements for this instrument) .

1628

1629 *Immediate*

1630 A water vapor program should be developed immediately. This issue will be around for a
1631 long time, and waiting longer will only serve to up the overall cost. Development and
1632 integration of new (or modified) instruments designed to address key ‘missing terms’ or
1633 resolve discrepancies between measurements should also begin as soon as possible. Far
1634 too often, such measurements are missing from major campaigns due to lack of planning
1635 and preparation.

1636

1637 **5. Best Way to Assess Uncertainties with Current Knowledge**

1638 In the absence of improvements in our understanding of the outstanding issues presented
1639 in Section 4.a., there are studies that can be undertaken now to assess the impacts of
1640 aviation on chemistry of the UT/LS that will represent a significant advance since the
1641 1999 IPCC Report. Before recommending such studies, it is important to note that such
1642 an advance does not necessarily imply that all of the specific uncertainties reported in
1643 previous assessments will be improved. It is possible that new observations reported
1644 above may reveal gaps in our understanding that were not foreseen a decade ago.

1645

1646 As noted above, resolving the water vapor measurements discrepancy in the cold, dry
1647 UT/LS is crucial in order to improve our understanding of the climate impacts of aviation
1648 that are linked to chemistry. Therefore, it would be extremely useful to use the best
1649 available 3D global chemical transport models to study the sensitivity of climate impacts
1650 to the two extreme possibilities that are represented in the literature. Based on
1651 uncertainties described in SSWPs dealing with clouds and aerosols, it is unclear whether
1652 the models sufficiently capture the complexities of condensation and dehydration, so it
1653 may not be straightforward to study these extreme cases from ‘first principles.’ That is, a
1654 realistic treatment of particle formation, composition, reactivity, and sedimentation, as a
1655 function of supersaturation on the scales of individual plumes and persistent contrails
1656 may not yet be possible. In this case, it would still be very useful to use some statistical
1657 representation of occurrences of cirrus, contrails, and persistent contrails as a basis for

1658 estimating the frequency of heterogeneous chemistry events [e.g., Bregman et al., 2002;
1659 Meilinger et al., 2005] and their contribution to the $d[O_3]$ and $d[CH_3]$ terms in the
1660 radiative forcing framework (e.g., Figure 1).

1661

1662 It is imperative that the recent results of Sovde et al. [2007] be examined in detail over
1663 the possible ranges of critical parameters such as lightning and convective fluxes of NO_x ,
1664 sources of HO_x , microphysics of mixtures of HNO_3 and H_2O , and background
1665 abundances of halogens. Sensitivity tests of regional and global ozone and methane
1666 responses to aircraft emissions would help to narrow down the list of parameters to those
1667 that contribute to the bulk of the uncertainty in the aircraft RF terms. (This approach is
1668 similar to one taken several decades ago to define which rate parameters were most
1669 critical in determining ozone loss due to chlorine buildup, for example.)

1670

1671 New sensitivity studies should be carried out to address the role of processes that are
1672 highly scale-dependent, such as denoxification, sedimentation, and mixing. Processes that
1673 are important in persistent contrails, for example, may have very different impacts if they
1674 are modeled as being severe, but highly localized, versus moderate and more widespread.
1675 Effects such as redistribution of NO_y by sedimentation are likely to be more severe,
1676 whereas those such as ozone loss due to chlorine activation may be less severe, in the
1677 former case (i.e., highly localized assumption).

1678

1679 Due to the large and growing body of HO_x observations, it would be extremely useful to
1680 reevaluate the " CH_4 " radiative forcing term with a CTM that is either constrained by or
1681 validated with observed OH fields.

1682

1683 Finally, it could be useful to carry out a series of focused observational studies to
1684 quantify the uncertainties in temperature and pressure measurements from aircraft. Not
1685 only will such studies improve our understanding of the uncertainties in past
1686 determinations of supersaturation, they will serve as the basis for much improved
1687 measurements of temperature in the UT/LS for future studies. Of particular value will be
1688 the development of ultra-fast (~ 100 Hz or faster) temperature probe for research aircraft
1689 such as HIAPER, the ER-2, the WB57F and Global Hawk, all of which can play
1690 important roles in defining thermodynamic variables in the UT/LS, but also for
1691 commercial aircraft that could be used to carry out long-term measurements in the
1692 UT/LS.

1693

1694 **6. Summary**

1695 Aircraft emit a variety of species that can alter climate and the chemistry of Earth's
1696 atmosphere. In this context, the most important are emissions of NO_x , particles, and
1697 water vapor, all of which interact to determine ozone distributions in the UT/LS, a region
1698 where radiatively active gases have a strong influence on temperature and dynamics.
1699 Previous assessments pointed to increases in ozone columns and reductions in methane
1700 (from the influence of NO on the OH/HO_2) as the two chemical impacts that were likely
1701 to have the largest impact on climate (aircraft radiative forcing, RF). It was found that
1702 these two terms were of roughly equal magnitude, but opposite sign, so that the net
1703 climate impact of aircraft emissions chemistry was approximately neutral. However, the

1704 understanding of the processes that determine these quantities was considered poor to
1705 fair. In the view that UT/LS chemistry is controlled by NO_x, these two terms will always
1706 cancel, because the processes that result in ozone production will lead to methane
1707 destruction.

1708
1709 New observations and modeling efforts undertaken over the past decade have raised
1710 important questions about the basis for earlier assessments. In particular, NO_x in the
1711 UT/LS is found to be partitioned in long-lived reservoirs to a larger extent than
1712 previously believed, presumably by heterogeneous reactions. Convective and lightning
1713 sources of NO_x to the upper troposphere have also been found to be more important than
1714 previously believed. In addition, reactive bromine and chlorine radicals have been
1715 observed in the UT or LS, implying a greater role for these species in partitioning of
1716 HO_x. Finally, large particles containing nitric acid have been observed in the UT/LS.
1717 Models that include more vigorous heterogeneous chemistry in the UT/LS indicate that
1718 emissions of particles from aircraft may actually reduce ozone in the UT and increase
1719 ozone in the lower stratosphere, the opposite of what was reported in the previous
1720 assessments.

1721
1722 Given that the climate impacts from ozone changes are partially offset by those of
1723 methane changes (assuming that the inverse relationship between NO_x and OH is
1724 maintained under these new conditions), the impact to climate overall may not change
1725 dramatically with this sign reversal in ozone changes. However, if these changes are
1726 confirmed, strategies for reducing the impacts of aircraft emissions on atmospheric
1727 chemistry and climate would be very different than those based on work summarized in
1728 previous assessments. Therefore, it is important that these new findings and their
1729 implications be explored in more detail before designing mitigation strategies.

1730
1731 Significant progress toward reducing the uncertainties in UT/LS chemistry identified here
1732 can be made with modest investments in key areas. The observational and modeling tools
1733 are largely available, thanks to the high priority that has been placed on understanding
1734 UT/LS chemistry. Several high priority studies are recommended here. Of greatest
1735 priority would be supporting efforts to resolve long-standing discrepancies among
1736 measurements of water vapor, including establishment of a water vapor standard that is
1737 appropriate for UT/LS conditions, and carrying out high-resolution measurements of
1738 water vapor, particles, and CO₂ in and around aircraft plumes with a platform such as the
1739 DC-8, WB57F, or HIAPER. Augmentations of measurements of key species to address
1740 coupled radical chemistry to the payloads for major campaigns could reduce uncertainties
1741 in basic ozone loss chemistry.

1742
1743 With added importance of aerosols and clouds to ozone chemistry in the UT/LS, it will be
1744 important to assess the importance of heterogeneous chemistry and aerosol formation and
1745 evolution in aircraft plumes, persistent contrails, and cirrus clouds. Models that treat
1746 plume dispersion with some realism may be necessary, although our knowledge of the
1747 potential range of impacts of plume processes can probably be improved by simple
1748 sensitivity tests that assume extreme bounds for processes such as denoxification and
1749 redistribution of species such as NO_y and H₂O. It would be reasonable to expect that

1750 significant new results to improve our understanding of the impacts of aircraft exhaust on
1751 atmospheric chemistry and climate would be forthcoming within three to five years of
1752 formulation of a focused program to address the major uncertainties presented in this
1753 White Paper for a total expenditure of under \$10 million, including funds from all
1754 sources. There are significant opportunities for synergistic studies that are currently in the
1755 planning stages or underway, with strategic placement of new funds to target particular
1756 elements that are critical for specifically assessing the impacts of aircraft.
1757

1758 **7. References**

1759

- 1760 Anderson, B. E., et al. (2006), Hydrocarbon emissions from a modern commercial
1761 airliner, *Atmospheric Environment*, 40(19), 3601-3612.
- 1762 Arnold, F., A. Kiendler, et al. (2000), Chemiion concentration measurements in jet
1763 engine exhaust at the ground: Implications for ion chemistry and aerosol formation in
1764 the wake of a jet aircraft, *Geophysical Research Letters*, 27(12), 1723-1726.
- 1765 Avallone, L. M., D. W. Toohey, et al. (1993), Balloon-Borne In-Situ Measurements of
1766 ClO and Ozone - Implications for Heterogeneous Chemistry and Midlatitude Ozone
1767 Loss, *Geophysical Research Letters*, 20(17), 1795-1798.
- 1768 Bertram, T. H., A. E. Perring, et al. (2007), Direct measurements of the convective
1769 recycling of the upper troposphere, *Science*, 315(5813), 816-820.
- 1770 Bencherif, H., R. D. Diab, T. Portafaix, B. Morel, P. Keckhut, and A. Moorgawa (2006),
1771 Temperature climatology and trend estimates in the UTLS region as observed over a
1772 southern subtropical site, Durban, South Africa, *Atmospheric Chemistry and Physics*,
1773 6, 5121–5128.
- 1774 Borrmann, S., S. Solomon, et al. (1996), The potential of cirrus clouds for heterogeneous
1775 chlorine activation, *Geophysical Research Letters*, 23(16), 2133-2136.
- 1776 Bortz, S. E., et al. (2006), Ozone, water vapor, and temperature in the upper tropical
1777 troposphere: Variations over a decade of MOZAIC measurements, *Journal of*
1778 *Geophysical Research-Atmospheres*, 111(D5), doi:10.1029/2005JD006512
- 1779 Brasseur, G.P., R.A. Cox, et al. (1998), European scientific assessment of the
1780 atmospheric effects of aircraft emissions, *Atmospheric Environment*, 32 (13), 2329-
1781 2418.
- 1782 Bregman, B., Wang, P. H., and Lelieveld, J. (2002), Chemical ozone loss in the
1783 tropopause region on subvisible ice clouds, calculated with a chemistry-transport
1784 model, *Journal of Geophysical Research-Atmospheres*, 107(D3),
1785 doi:10.1029/2001JD000761.
- 1786 Brunner, D., et al. (2001), Nitrogen oxides and ozone in the tropopause region of the
1787 Northern Hemisphere: Measurements from commercial aircraft in 1995/1996 and
1788 1997, *Journal of Geophysical Research-Atmospheres*, 106(D21), 27673-27699.
- 1789 Brunner, D., et al. (2005), An evaluation of the performance of chemistry transport
1790 models - Part 2: Detailed comparison with two selected campaigns, *Atmospheric*
1791 *Chemistry and Physics*, 5, 107-129.
- 1792 Carslaw, D. C., et al. (2006), Detecting and quantifying aircraft and other on-airport
1793 contributions to ambient nitrogen oxides in the vicinity of a large international
1794 airport, *Atmospheric Environment*, 40(28), 5424-5434.
- 1795 Chughtai, A. R., et al. (2003), The effect of temperature and humidity on the reaction of
1796 ozone with combustion soot: Implications for reactivity near the tropopause, *Journal*
1797 *of Atmospheric Chemistry*, 45(3), 231-243.
- 1798 Colette, A., and G. Ancellet (2005), Impact of vertical transport processes on the
1799 tropospheric ozone layering above Europe. Part II: Climatological analysis of the past
1800 30 years, *Atmospheric Environment*, 39(29), 5423-5435.
- 1801 Colette, A., et al. (2005), Impact of vertical transport processes on the tropospheric ozone
1802 layering above Europe. Part I: Study of air mass origin using multivariate analysis,
1803 clustering and trajectories, *Atmospheric Environment*, 39(29), 5409-5422.

1804 Colette, A., and G. Ancellet (2006), Variability of the tropospheric mixing and of
1805 streamer formation and their impact on the lifetime of observed ozone layers,
1806 *Geophysical Research Letters*, 33(9), doi:10.1029/2006GL025793.

1807 Collins, W. J., et al. (1999), Role of convection in determining the budget of odd
1808 hydrogen in the upper troposphere, *Journal of Geophysical Research-Atmospheres*,
1809 104(D21), 26927-26941.

1810 Colomb, A., et al. (2006), Airborne measurements of trace organic species in the upper
1811 troposphere over Europe: the impact of deep convection, *Environmental Chemistry*,
1812 3(4), 244-259.

1813 Considine, D. B., et al. (2000), A polar stratospheric cloud parameterization for the
1814 global modeling initiative three-dimensional model and its response to stratospheric
1815 aircraft, *Journal of Geophysical Research-Atmospheres*, 105(D3), 3955-3973.

1816 Cooper, O. R., et al. (2006), Large upper tropospheric ozone enhancements above
1817 midlatitude North America during summer: In situ evidence from the IONS and
1818 MOZAIC ozone measurement network, *Journal of Geophysical Research-*
1819 *Atmospheres*, 111(D24), doi:10.1029/2006JD007306.

1820 Cox, V. (2007), *NextGen and Its Impact on Performance Worldwide Symposium on*
1821 *Performance of the Air Navigation System*, Presentation to the ICAO, Montreal,
1822 Quebec, Canada, March 26-30, 2007.

1823 Crawford, J., et al. (1999), Assessment of upper tropospheric HOx sources over the
1824 tropical Pacific based on NASA GTE/PEM data: Net effect on HOx and other
1825 photochemical parameters, *Journal of Geophysical Research-Atmospheres*,
1826 104(D13), 16255-16273.

1827 Dakhel, P. M., et al. (2007), Postcombustion evolution of soot properties in an aircraft
1828 engine, *Journal of Propulsion and Power* 23(5), 942-948.

1829 DeCaria, A. J., et al. (2005), Lightning-generated NOx and its impact on tropospheric
1830 ozone production: A three-dimensional modeling study of a Stratosphere-
1831 Troposphere Experiment: Radiation, Aerosols and Ozone (STERAO-A)
1832 thunderstorm, *Journal of Geophysical Research-Atmospheres*, 110(D14),
1833 doi:10.1029/2004JD005556.

1834 Dessens, O. and P. Simon (2002), The importance of dynamics/chemistry coupling in the
1835 evaluation of aircraft emission impact studies, *Meteorologische Zeitschrift* 11(3),
1836 161-175.

1837 Dorf, M., et al. (2006), Balloon-borne stratospheric BrO measurements: comparison with
1838 Envisat/SCIAMACHY BrO limb profiles, *Atmospheric Chemistry and Physics* 6,
1839 2483-2501.

1840 Dorf, M., et al. (2006), Long-term observations of stratospheric bromine reveal slow
1841 down in growth, *Geophysical Research Letters* 33(24), doi:10.1029/2006GL027714.

1842 Eichkorn, S., et al. (2002), Massive positive and negative chemiions in the exhaust of an
1843 aircraft jet engine at ground-level: mass distribution measurements and implications
1844 for aerosol formation, *Atmospheric Environment* 36(11), 1821-1825.

1845 Esler, J. G., Roelofs, G. J., Kohler, M. O., and O'Connor, F. M., (2004), A quantitative
1846 analysis of grid-related systematic errors in oxidising capacity and ozone production
1847 rates in chemistry transport models. *Atmospheric Chemistry and Physics* 4, 1781.

1848 Fairlie, T. D., et al. (2007), Impact of multiscale dynamical processes and mixing on the
1849 chemical composition of the upper troposphere and lower stratosphere during the

1850 Intercontinental Chemical Transport Experiment-North America, *Journal of*
 1851 *Geophysical Research-Atmospheres* 112(D16), doi:10.1029/2006JD007923.
 1852 Faloon, I., et al. (2000), Observations of HO_x and its relationship with NO_x in the upper
 1853 troposphere during SONEX, *Journal of Geophysical Research-Atmospheres* 105(D3):
 1854 3771-3783.
 1855 Farias, F. and H. ApSimon (2006), Relative contributions from traffic and aircraft NO_x
 1856 emissions to exposure in West London, *Environmental Modelling & Software* 21(4):
 1857 477-485.
 1858 Fehr, T., et al. (2004), Model study on production and transport of lightning-produced
 1859 NO_x in a EULINOX supercell storm, *Journal of Geophysical Research-Atmospheres*,
 1860 109(D9), doi:10.1029/2003JD003935.
 1861 Ferrare, R. A., et al. (2004), Characterization of upper-troposphere water vapor
 1862 measurements during AFWEX using LASE, *Journal of Atmospheric and Oceanic*
 1863 *Technology*, 21(12), 1790-1808.
 1864 Folkins, I., et al. (2006), Testing convective parameterizations with tropical
 1865 measurements of HNO₃, CO, H₂O, and O₃: Implications for the water vapor budget,
 1866 *Journal of Geophysical Research-Atmospheres*, 111(D23), 10.1029/2006JD007325
 1867 Forster, C., et al. (2003), The residence times of aircraft emissions in the stratosphere
 1868 using a mean emission inventory and emissions along actual flight tracks, *Journal of*
 1869 *Geophysical Research-Atmospheres* 108(D12), doi:10.1029/2002JD002515.
 1870 Gao, R. S., et al. (2004), Evidence that nitric acid increases relative humidity in low-
 1871 temperature cirrus clouds, *Science* 303(5657): 516-520.
 1872 Gao, R. S., et al. (2006), Measurements of relative humidity in a persistent contrail,
 1873 *Atmospheric Environment*, 40(9), 1590-1600.
 1874 Gauss, M., et al. (2003), Impact of H₂O emissions from cryoplanes and kerosene aircraft
 1875 on the atmosphere, *Journal of Geophysical Research-Atmospheres*, 108(D10),
 1876 doi:10.1029/2002JD002623.
 1877 Gauss, M., et al. (2006), Impact of aircraft NO_x emissions on the atmosphere - tradeoffs
 1878 to reduce the impact, *Atmospheric Chemistry and Physics* 6, 1529-1548.
 1879 Grewe, V., et al. (2002), Impact of aircraft NO_x emissions. Part 1: Interactively coupled
 1880 climate-chemistry simulations and sensitivities to climate-chemistry feedback,
 1881 lightning and model resolution, *Meteorologische Zeitschrift* 11(3): 177-186.
 1882 Giannakopoulos, C., et al. (2003), Modelling the impacts of aircraft traffic on the
 1883 chemical composition of the upper troposphere, *Proceedings of the Institution of*
 1884 *Mechanical Engineers Part G-Journal of Aerospace Engineering* 217(G5): 237-243.
 1885 Gulstad, L. and I. S.A. Isaksen, (2007), Modeling water vapor in the upper troposphere
 1886 and lower stratosphere, *Terrestrial, Atmospheric and Oceanic Science*, 18, 415-436.
 1887 Haag, W., et al. (2003), Freezing thresholds and cirrus cloud formation mechanisms
 1888 inferred from in situ measurements of relative humidity, *Atmospheric Chemistry and*
 1889 *Physics*, 3, 1791-1806.
 1890 Haverkamp, H., et al. (2004), Positive and negative ion measurements in jet aircraft
 1891 engine exhaust: concentrations, sizes and implications for aerosol formation,
 1892 *Atmospheric Environment* 38(18), 2879-2884.
 1893 Hays, M. D. and R. L. Vander Wal (2007), Heterogeneous soot nanostructure in
 1894 atmospheric and combustion source aerosols, *Energy & Fuels* 21(2), 801-811.

1895 Helten, M., et al. (1999), In-flight comparison of MOZAIC and POLINAT water vapor
1896 measurements, *Journal of Geophysical Research-Atmospheres*, 104(D21), 26087-
1897 26096.

1898 Hendricks, J., et al. (2000), Implications of subsonic aircraft NO_x emissions for the
1899 chemistry of the lowermost stratosphere: Model studies on the role of bromine,
1900 *Journal of Geophysical Research-Atmospheres* 105(D5), 6745-6759.

1901 Herndon, S. C., et al. (2004), NO and NO₂ emission ratios measured from in-use
1902 commercial aircraft during taxi and takeoff, *Environmental Science & Technology*
1903 38(22), 6078-6084.

1904 Herndon, S. C., et al. (2006), Hydrocarbon emissions from in-use commercial aircraft
1905 during airport operations, *Environmental Science & Technology* 40(14), 4406-4413.

1906 Hudman, R. C., et al. (2007), Surface and lightning sources of nitrogen oxides over the
1907 United States: Magnitudes, chemical evolution, and outflow, *Journal of Geophysical*
1908 *Research-Atmospheres* 112(D12), doi:10.1029/2006JD007912.

1909 Immler, F., et al. (2007), Cirrus clouds, humidity, and dehydration in the tropical
1910 tropopause layer observed at Paramaribo, Suriname (5.8 °N, 55.2 °W), *Journal of*
1911 *Geophysical Research-Atmospheres* 112(D3), doi:10.1029/2006JD007440.

1912 Intergovernmental Panel on Climate Change (1999). Aviation and the Global
1913 Atmosphere, Special Report of IPCC Working Groups I and III, Cambridge
1914 University Press, Cambridge, UK.

1915 Jaegle, L., et al. (1999), Ozone production in the upper troposphere and the influence of
1916 aircraft during SONEX: Approach of NO_x-saturated conditions, *Geophysical*
1917 *Research Letters*, 26(20), 3081-3084.

1918 Karcher, B., et al. (2007), Insights into the role of soot aerosols in cirrus cloud formation,
1919 *Atmospheric Chemistry and Physics*, 7(16), 4203-4227.

1920 Karcher, B. and C. Voigt (2006), Formation of nitric acid/water ice particles in cirrus
1921 clouds, *Geophysical Research Letters* 33(8), doi:10.1029/2006GL025927.

1922 Kim, S., L. et al., (2007), Measurement of HO₂NO₂ in the free troposphere during the
1923 Intercontinental Chemical Transport Experiment–North America 2004, *Journal of*
1924 *Geophysical Research - Atmospheres*, 112, doi:10.1029/2006JD007676.

1925 Klemm, O., et al. (1998), Measurements of nitrogen oxides from aircraft in the northeast
1926 Atlantic flight corridor, *Journal of Geophysical Research-Atmospheres* 103(D23):
1927 31217-31229.

1928 Kley, D., J. M. Russell III, and C. Phillips, eds., SPARC Assessment of Upper
1929 Tropospheric and Stratospheric Water Vapour, World Climate Research Programme,
1930 WCRP-113, Dec 2000.

1931 Knighton, W. B., et al. (2007), Quantification of aircraft engine hydrocarbon emissions
1932 using proton transfer reaction mass spectrometry, *Journal of Propulsion and Power*
1933 23(5): 949-958.

1934 Koike, M., et al. (2000), Impact of aircraft emissions on reactive nitrogen over the North
1935 Atlantic Flight Corridor region, *Journal of Geophysical Research-Atmospheres*
1936 105(D3): 3665-3677.

1937 Koike, M., et al. (2002), Reactive nitrogen over the tropical western Pacific: Influence
1938 from lightning and biomass burning during BIBLE A, *Journal of Geophysical*
1939 *Research-Atmospheres*, 108(D3), doi:10.1029/2001JD000823.

1940 Kraabob, A. G., et al. (2002), Impacts of NO_x emissions from subsonic aircraft in a global
1941 three-dimensional chemistry transport model including plume processes, *Journal of*
1942 *Geophysical Research-Atmospheres* 107(D22), .

1943 Labrador, L. J., et al. (2004), Strong sensitivity of the global mean OH concentration and
1944 the tropospheric oxidizing efficiency to the source of NO_x from lightning,
1945 *Geophysical Research Letters*, 31(6), doi:10.1029/2003GL019229.

1946 Lange, L., et al. (2001), Detection of lightning-produced NO in the midlatitude upper
1947 troposphere during STREAM 1998, *Journal of Geophysical Research-Atmospheres*,
1948 106(D21), 27777-27785.

1949 Law, K. S., et al. (2000), Comparison between global chemistry transport model results
1950 and Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft
1951 (MOZAIC) data, *Journal of Geophysical Research-Atmospheres*, 105(D1), 1503-
1952 1525.

1953 Lelieveld, J., et al. (1999), Chlorine activation and ozone destruction in the northern
1954 lowermost stratosphere, *Journal of Geophysical Research-Atmospheres*, 104(D7),
1955 8201-8213.

1956 Leue, C., et al. (2001), Quantitative analysis of NO_x emissions from Global Ozone
1957 Monitoring Experiment satellite image sequences, *Journal of Geophysical Research-*
1958 *Atmospheres*, 106(D6), 5493-5505.

1959 Levy, H., et al. (1999), Simulated tropospheric NO_x: Its evaluation, global distribution
1960 and individual source contributions, *Journal of Geophysical Research-Atmospheres*,
1961 104(D21), 26279-26306.

1962 Li, Q. B., et al. (2005), North American pollution outflow and the trapping of
1963 convectively lifted pollution by upper-level anticyclone, *Journal of Geophysical*
1964 *Research-Atmospheres*, 110(D10), doi:10.1029/2004JD005039.

1965 Lobo, P., et al. (2007), Physical characterization of aerosol emissions from a commercial
1966 gas turbine engine, *Journal of Propulsion and Power* 23(5): 919-929.

1967 Longfellow, C. A., et al. (1999), Reactive uptake on hydrocarbon soot: Focus on NO₂,
1968 *Journal of Geophysical Research-Atmospheres*, 104(D11), 13833-13840.

1969 Lopez, J. P., et al. (2006), CO signatures in subtropical convective clouds and anvils
1970 during CRYSTAL-FACE: An analysis of convective transport and entrainment using
1971 observations and a cloud-resolving model, *Journal of Geophysical Research-*
1972 *Atmospheres*, 111(D9), doi:10.1029/2005JD006104.

1973 Lovejoy, S., et al. (2007), Is isotropic turbulence relevant in the atmosphere?,
1974 *Geophysical Research Letters* 34(15), doi:10.1029/2007GL029359.

1975 Luo, Z. Z., et al. (2007), Ten years of measurements of tropical upper-tropospheric water
1976 vapor by MOZAIC. Part I: Climatology, variability, transport, and relation to deep
1977 convection, *Journal of Climate*, 20(3), 418-435.

1978 Ma, J. Z., and X. J. Zhou (2000), Development of a three-dimensional inventory of
1979 aircraft NO_x emissions over China, *Atmospheric Environment*, 34(3), 389-396.

1980 Ma, J. Z., et al. (2002), Summertime tropospheric ozone over China simulated with a
1981 regional chemical transport model. 2. Source contributions and budget, *Journal of*
1982 *Geophysical Research-Atmospheres*, 107(D22), doi:10.1029/2001JD001355.

1983 Marecal, V., et al. (2006), Modelling study of the impact of deep convection on the utls
1984 air composition - Part I: Analysis of ozone precursors, *Atmospheric Chemistry and*
1985 *Physics*, 6, 1567-1584.

1986 Marécal, V., G. Durré, K. Longo, S. Freitas, E. D. Rivière, and M. Pirre (2007),
1987 Mesoscale modelling of water vapour in the tropical UTLS: two case studies from the
1988 HIBISCUS campaign, *Atmospheric Chemistry and Physics* 7, 1471-1489.

1989 Mari, C., et al. (2002), Sources of upper tropospheric HO_x over the South Pacific
1990 Convergence Zone: A case study, *Journal of Geophysical Research-Atmospheres*,
1991 108(D2), doi:10.1029/2000JD000304.

1992 Mari, C., et al. (2002), On the relative role of convection, chemistry, and transport over
1993 the South Pacific Convergence Zone during PEM-Tropics B: A case study, *Journal of*
1994 *Geophysical Research-Atmospheres*, 108(D2), doi:10.1029/2001JD001466.

1995 Martin, R. V., et al. (2006), Evaluation of space-based constraints on global nitrogen
1996 oxide emissions with regional aircraft measurements over and downwind of eastern
1997 North America, *Journal of Geophysical Research-Atmospheres*, 111(D15),
1998 doi:10.1029/2005JD006680.

1999 Martin, R. V., et al. (2007), Space-based constraints on the production of nitric oxide by
2000 lightning, *Journal of Geophysical Research-Atmospheres*, 112(D9),
2001 doi:10.1029/2006JD007831.

2002 Meijer, E. W., et al. (2000), Model calculations of the impact of NO_x from air traffic,
2003 lightning, and surface emissions, compared with measurements, *Journal of*
2004 *Geophysical Research-Atmospheres*, 105(D3), 3833-3850.

2005 Meier, A. and J. Hendricks (2002), Model studies on the sensitivity of upper tropospheric
2006 chemistry to heterogeneous uptake of HNO₃ on cirrus ice particles, *Journal of*
2007 *Geophysical Research-Atmospheres* 107(D23), doi:10.1029/2001JD000735.

2008 Meilinger, S. K., et al. (2001), On the impact of heterogeneous chemistry on ozone in the
2009 tropopause region, *Geophysical Research Letters*, 28(3), 515-518.

2010 Meilinger, S. K., et al. (2005), Microphysics and heterogeneous chemistry in aircraft
2011 plumes - high sensitivity on local meteorology and atmospheric composition,
2012 *Atmospheric Chemistry and Physics* 5: 533-545.

2013 Miller, T. M., et al. (2005), Mass distribution and concentrations of negative chemiions in
2014 the exhaust of a jet engine: Sulfuric acid concentrations and observation of particle
2015 growth, *Atmospheric Environment* 39(17): 3069-3079.

2016 Miloshevich, L. M., et al. (2006), Absolute accuracy of water vapor measurements from
2017 six operational radiosonde types launched during AWEX-G and implications for
2018 AIRS validation, *Journal of Geophysical Research-Atmospheres*, 111(D9),
2019 doi:10.1029/2005JD006083.

2020 Morris, G. A., et al. (2003), Potential impact of subsonic and supersonic aircraft exhaust
2021 on water vapor in the lower stratosphere assessed via a trajectory model, *Journal of*
2022 *Geophysical Research-Atmospheres*, 108(D3), doi:10.1029/2002JD002614.

2023 Muhle, J., et al. (2002), Biomass burning and fossil fuel signatures in the upper
2024 troposphere observed during a CARIBIC flight from Namibia to Germany,
2025 *Geophysical Research Letters*, 29(19).

2026 Muller, J. F., and G. Brasseur (1999), Sources of upper tropospheric HO_x: A three-
2027 dimensional study, *Journal of Geophysical Research-Atmospheres*, 104(D1), 1705-
2028 1715.

2029 Murphy, J. G., et al. (2004), Measurements of the sum of HO₂NO₂ and CH₃O₂NO₂ in the
2030 remote troposphere, *Atmospheric Chemistry and Physics*, 4, 377-384.

2031 Nedoluha, G. E., et al. (2002), Polar Ozone and Aerosol Measurement III measurements
 2032 of water vapor in the upper troposphere and lowermost stratosphere, *Journal of*
 2033 *Geophysical Research-Atmospheres*, 107(D10), doi: 10.1029/2001JD000793.
 2034 Neuman, J. A., et al. (2006), Reactive nitrogen transport and photochemistry in urban
 2035 plumes over the North Atlantic Ocean, *Journal of Geophysical Research-*
 2036 *Atmospheres*, 111(D23), doi:10.1029/2005JD007010.
 2037 Nyeki, S., et al. (2004), Properties of jet engine combustion particles during the PartEmis
 2038 experiment: Particle size spectra ($d > 15$ nm) and volatility, *Geophysical Research*
 2039 *Letters*, 31(18), doi:10.1029/2004GL020569.
 2040 Olson, J. R., et al. (2004), Testing fast photochemical theory during TRACE-P based on
 2041 measurements of OH, HO₂, and CH₂O, *Journal of Geophysical Research-*
 2042 *Atmospheres*, 109(D15), doi:10.1029/2003JD004278.
 2043 Olson, J. R., et al. (2006), A reevaluation of airborne HO_x observations from NASA field
 2044 campaigns, *Journal of Geophysical Research-Atmospheres* 111(D10),
 2045 doi:10.1029/2005JD006617.
 2046 Park, M., et al. (2004), Seasonal variation of methane, water vapor, and nitrogen oxides
 2047 near the tropopause: Satellite observations and model simulations, *Journal of*
 2048 *Geophysical Research-Atmospheres*, 109(D3), doi:10.1029/2003JD003706.
 2049 Parker, D. E., M. Gordon, D. P. N. Cullum, D.M. H. Sexton, C. K. Folland, and N.
 2050 Rayner (1997), A new global gridded radiosonde temperature database and
 2051 recalculated temperature trends, *Geophysical Research Letters* 24, 1499–1502.
 2052 Parrish, D. D., et al. (2004), Fraction and composition of NO_y transported in air masses
 2053 lofted from the North American continental boundary layer, *Journal of Geophysical*
 2054 *Research-Atmospheres*, 109(D9), doi:10.1029/2003JD004226.
 2055 Peace, H., et al. (2006), Identifying the contribution of different airport related sources to
 2056 local urban air quality, *Environmental Modelling & Software* 21(4), 532-538.
 2057 Petzold, A., et al. (2005), Particle emissions from aircraft engines - a survey of the
 2058 European project PartEmis, *Meteorologische Zeitschrift*, 14(4), 465-476.
 2059 Pierce, R. B., et al. (2007), Chemical data assimilation estimates of continental US ozone
 2060 and nitrogen budgets during the Intercontinental Chemical Transport Experiment-
 2061 North America, *Journal of Geophysical Research-Atmospheres*, 112(D12),
 2062 doi:10.1029/2006JD007722.
 2063 Pison, I. and L. Menut (2004), Quantification of the impact of aircraft traffic emissions
 2064 on tropospheric ozone over Paris area, *Atmospheric Environment* 38(7), 971-983.
 2065 Pitari, G., et al. (2002), Deep convective transport in a two-dimensional model: Effects
 2066 on lower stratospheric aerosols and ozone, *Meteorologische Zeitschrift*, 11(3), 187-
 2067 196.
 2068 Popp, P. J., et al. (2006), The observation of nitric acid-containing particles in the tropical
 2069 lower stratosphere, *Atmospheric Chemistry and Physics* 6, 601-611.
 2070 Popovicheva, O. B., et al. (2004), Water adsorption and crystallization on soot particles,
 2071 *Izvestiya Atmospheric and Oceanic Physics*, 40(2), 193-201.
 2072 Popovicheva, O. B., and A. M. Starik (2007), Aircraft-generated soot aerosols:
 2073 Physicochemical properties and effects of emission into the atmosphere, *Izvestiya*
 2074 *Atmospheric and Oceanic Physics*, 43(2), 125-141.
 2075 Popovicheva, O. B., et al. (2003), Microstructure and water adsorbability of aircraft
 2076 combustor soots and kerosene flame soots: Toward an aircraft-generated soot

2077 laboratory surrogate, *Journal of Physical Chemistry A* 107(47),10046-10054.
 2078 Popovitcheva, O. B., et al. (2000), Experimental characterization of aircraft combustor
 2079 soot: Microstructure, surface area, porosity and water adsorption, *Physical Chemistry*
 2080 *Chemical Physics* 2(19), 4421-4426.
 2081 Ravetta, F., et al. (2001), Experimental evidence for the importance of convected
 2082 methylhydroperoxide as a source of hydrogen oxide (HO_x) radicals in the tropical
 2083 upper troposphere, *Journal of Geophysical Research-Atmospheres*, 106(D23), 32709-
 2084 32716.
 2085 Ramaswamy, V., et al., (2001), Stratospheric Temperature Trends: Observations and
 2086 Model Simulations, *Reviews of Geophysics*, 39, 61-122.
 2087 Reiner, T., et al. (1999), Measurements of acetone, acetic acid, and formic acid in the
 2088 northern midlatitude upper troposphere and lower stratosphere, *Journal of*
 2089 *Geophysical Research-Atmospheres*, 104(D11), 13943-13952.
 2090 Ren, X., et al., (2008), HO_x Chemistry during INTEX-A 2004: Observation, Model
 2091 Calculation and Comparison with Previous Studies, *Journal of Geophysical Research*
 2092 *-Atmospheres*, in press.
 2093 Richard, E. C., et al. (2006), High-resolution airborne profiles of CH₄, O₃, and water
 2094 vapor near tropical Central America in late January to early February 2004, *Journal*
 2095 *of Geophysical Research-Atmospheres* 111(D13), doi:10.1029/2005JD006513.
 2096 Ridley, B. A., et al. (2005), Comments on the parameterization of lightning-produced NO
 2097 in global chemistry-transport models, *Atmospheric Environment*, 39(33), 6184-6187.
 2098 Salawitch, R. J., et al. (2005), Sensitivity of ozone to bromine in the lower stratosphere,
 2099 *Geophysical Research Letters*, 32(5), doi:10.1029/2004GL021504.
 2100 Sauvage, B., et al. (2007), Remote sensed and in situ constraints on processes affecting
 2101 tropical tropospheric ozone, *Atmospheric Chemistry and Physics*, 7, 815-838.
 2102 Sausen, R., et al. (2005), Aviation radiative forcing in 2000: An update on IPCC (1999),
 2103 *Meteorologische Zeitschrift* 14 (4), 555-561.
 2104 Schaufli, S. M., et al. (1999), Distributions of brominated organic compounds in the
 2105 troposphere and lower stratosphere, *Journal of Geophysical Research-Atmospheres*,
 2106 104(D17), 21513-21535.
 2107 Schlager, H., et al. (1999), Regional nitric oxide enhancements in the North Atlantic
 2108 flight corridor observed and modeled during POLINAT 2 - a case study, *Geophysical*
 2109 *Research Letters*, 26(20), 3061-3064.
 2110 Schoeberl, M. R. and G. A. Morris (2000), A Lagrangian simulation of supersonic and
 2111 subsonic aircraft exhaust emissions, *Journal of Geophysical Research-Atmospheres*
 2112 105(D9): 11833-11839.
 2113 Schofield, R., et al. (2004), Retrieved tropospheric and stratospheric BrO columns over
 2114 Lauder, New Zealand, *Journal Of Geophysical Research-Atmospheres*, 109 (D14):
 2115 D14304.
 2116 Schroder, F., et al. (2000), In situ studies on volatile jet exhaust particle emissions:
 2117 Impact of fuel sulfur content and environmental conditions on nuclei mode aerosols,
 2118 *Journal of Geophysical Research-Atmospheres*, 105(D15), 19941-19954.
 2119 Schumann, U., et al. (2002), Influence of fuel sulfur on the composition of aircraft
 2120 exhaust plumes: The experiments SULFUR 1-7, *Journal of Geophysical Research-*
 2121 *Atmospheres*, 107(D15), doi:10.1029/2001JD000813.

2122 Schumann, U. and H. Huntrieser (2007), The global lightning-induced nitrogen oxides
2123 source, *Atmospheric Chemistry and Physics* 7(14), 3823-3907.

2124 Shonija, N. K., et al. (2007), Hydration of aircraft engine soot particles under plume
2125 conditions: Effect of sulfuric and nitric acid processing, *Journal of Geophysical*
2126 *Research-Atmospheres* 112(D2), doi:10.1029/2006JD007217.

2127 Simpson, I. J., et al. (2003), Airborne measurements of cirrus-activated C₂Cl₄ depletion in
2128 the upper troposphere with evidence against Cl reactions, *Geophysical Research*
2129 *Letters*, 30(20), doi:10.1029/2003GL017598.

2130 Singh, H., et al. (2000), Distribution and fate of selected oxygenated organic species in
2131 the troposphere and lower stratosphere over the Atlantic, *Journal of Geophysical*
2132 *Research-Atmospheres*, 105(D3), 3795-3805.

2133 Singh, H. B., et al. (2004), Analysis of the atmospheric distribution, sources, and sinks of
2134 oxygenated volatile organic chemicals based on measurements over the Pacific during
2135 TRACE-P, *Journal of Geophysical Research-Atmospheres*, 109(D15),
2136 doi:10.1029/2003JD003883.

2137 Singh, H. B., L. Salas, et al. (2007), Reactive nitrogen distribution and partitioning in the
2138 North American troposphere and lowermost stratosphere, *Journal of Geophysical*
2139 *Research-Atmospheres* 112(D12), doi:10.1029/2006JD007664.

2140 Sinnhuber, B.M., et al. (2005), Global observations of stratospheric bromine monoxide
2141 from SCIAMACHY, *Geophysical Research Letters* 32(20): L20810.

2142 Sinnhuber, B. M., and I. Folkins (2006), Estimating the contribution of bromoform to
2143 stratospheric bromine and its relation to dehydration in the tropical tropopause layer,
2144 *Atmospheric Chemistry and Physics*, 6, 4755-4761.

2145 Sioris, C. E., et al. (2006), Latitudinal and vertical distribution of bromine monoxide in
2146 the lower stratosphere from Scanning Imaging Absorption Spectrometer for
2147 Atmospheric Chartography limb scattering measurements, *Journal of Geophysical*
2148 *Research-Atmospheres* 111(D14), doi:10.1029/2005JD006479.

2149 Sioris, C. E., et al. (2007), Vertical profiles of lightning-produced NO₂ enhancements in
2150 the upper troposphere observed by OSIRIS, *Atmospheric Chemistry and Physics*
2151 7(16), 4281-4294.

2152 Smith, J. B., et al. (2001), Mechanisms for midlatitude ozone loss: Heterogeneous
2153 chemistry in the lowermost stratosphere?, *Journal of Geophysical Research-*
2154 *Atmospheres* 106(D1): 1297-1309.

2155 Smyshlyaev, S. P., et al. (2003), Model study of the impact of convective processes on
2156 the gas composition of the upper troposphere and lower stratosphere, *Izvestiya*
2157 *Atmospheric and Oceanic Physics*, 39(4), 432-443.

2158 Snow, J. A., et al. (2003), Winter-spring evolution and variability of HO_x reservoir
2159 species, hydrogen peroxide, and methyl hydroperoxide, in the northern middle to high
2160 latitudes, *Journal of Geophysical Research-Atmospheres*, 108(D4),
2161 doi:10.1029/2002JD002172.

2162 Snow, J. A., et al. (2007), Hydrogen peroxide, methyl hydroperoxide, and formaldehyde
2163 over North America and the North Atlantic, *Journal of Geophysical Research-*
2164 *Atmospheres*, 112(D12), doi:10.1029/2006JD007746.

2165 Sorokin, A., et al. (2001), On volatile particle formation in aircraft exhaust plumes,
2166 *Physics and Chemistry of the Earth Part C-Solar-Terrestrial and Planetary Science*,
2167 26(8), 557-561.

2168 Solomon, S., et al. (1997), Heterogeneous chlorine chemistry in the tropopause region,
2169 *Journal of Geophysical Research-Atmospheres* 102(D17): 21411-21429.
2170 Sorokin, A., and F. Arnold (2004), Electrically charged small soot particles in the exhaust
2171 of an aircraft gas-turbine engine combustor: comparison of model and experiment,
2172 *Atmospheric Environment*, 38(17), 2611-2618.
2173 Sorokin, A. and F. Arnold (2006), Organic positive ions in aircraft gas-turbine engine
2174 exhaust, *Atmospheric Environment* 40(32): 6077-6087.
2175 Sovde, O. A., et al. (2007), Aircraft pollution - a futuristic view, *Atmospheric Chemistry*
2176 *and Physics* 7(13), 3621-3632.
2177 Spichtinger, P., et al. (2002), The statistical distribution law of relative humidity in the
2178 global tropopause region, *Meteorologische Zeitschrift*, 11(2), 83-88.
2179 Stendahl, K. (1976): Paul Among Jews and Gentiles, and Other Essays, Fortress Press,
2180 p7.
2181 Stevenson, D. S., et al. (2004), Radiative forcing from aircraft NO_x emissions:
2182 Mechanisms and seasonal dependence, *Journal of Geophysical Research-*
2183 *Atmospheres* 109(D17), doi:10.1029/2004JD004759.
2184 Stevenson, D. S., et al. (2006), Multimodel ensemble simulations of present-day and
2185 near-future tropospheric ozone, *Journal of Geophysical Research-Atmospheres*,
2186 111(D8), doi:10.1029/2005JD006338.
2187 Stickler, A., et al. (2006), Influence of summertime deep convection on formaldehyde in
2188 the middle and upper troposphere over Europe, *Journal of Geophysical Research-*
2189 *Atmospheres*, 111(D14), doi:10.1029/2005JD007001.
2190 Stohl, A., et al. (2002), Export of NO_y from the North American boundary layer during
2191 1996 and 1997 North Atlantic Regional Experiments, *Journal of Geophysical*
2192 *Research-Atmospheres*, 107(D11), doi:10.1029/2001JD000519.
2193 Stohl, A., et al. (2003), A new perspective of stratosphere-troposphere exchange, *Bulletin*
2194 *of the American Meteorological Society* 84(11), 1565.
2195 Talukdar, R. K., et al. (2006), Uptake of HNO₃ on hexane and aviation kerosene soots,
2196 *Journal of Physical Chemistry A* 110(31), 9643-9653.
2197 Theys, N., et al. (2007), Retrieval of stratospheric and tropospheric BrO columns from
2198 multi-axis DOAS measurements at Reunion Island (21 degrees S, 56 degrees E),
2199 *Atmospheric Chemistry and Physics* 7(18), 4733-4749.
2200 Thornton, B. F., et al. (2003), In situ observations of ClO near the winter polar
2201 tropopause, *Journal of Geophysical Research-Atmospheres* 108(D8),
2202 doi:10.1029/2002JD002839.
2203 Thornton, B. F., et al. (2005), Variability of active chlorine in the lowermost Arctic
2204 stratosphere, *Journal of Geophysical Research-Atmospheres* 110(D22)
2205 doi:10.1029/2004JD005580.
2206 Thornton, B. F., et al. (2007), Chlorine activation near the midlatitude tropopause,
2207 *Journal of Geophysical Research-Atmospheres* 112(D18),
2208 doi:10.1029/2006JD007640.
2209 Thakur, A. N., et al. (1999), Distribution of reactive nitrogen species in the remote free
2210 troposphere: data and model comparisons, *Atmospheric Environment*, 33(9), 1403-
2211 1422.

2212 Troller, M., A. Geiger, E. Brockmann and H.-G. Kahle, (2006), Determination of the
2213 spatial and temporal variation of tropospheric water vapour using CGPS networks,
2214 *Geophysical Journal International*, 167, 509–520.

2215 Tsague, L., et al. (2006), Prediction of the production of nitrogen oxide (NO_x) in turbojet
2216 engines, *Atmospheric Environment*, 40(29), 5727-5733.

2217 Tsague, L., et al. (2007), Prediction of emissions in turbojet engines exhausts:
2218 relationship between nitrogen oxides emission index (EINO_x) and the operational
2219 parameters, *Aerospace Science and Technology* 11(6), 459-463.

2220 Tsai, F. J., et al. (2001), A composite modeling study of civil aircraft impacts on ozone
2221 and sulfate over the Taiwan area, *Terrestrial Atmospheric and Oceanic Sciences*
2222 12(1), 109-135.

2223 Vaughan, G., et al. (2005), Water vapour and ozone profiles in the midlatitude upper
2224 troposphere, *Atmospheric Chemistry and Physics*, 5, 963-971.

2225 van Noije, T. P. C., et al. (2006), Multi-model ensemble simulations of tropospheric NO₂
2226 compared with GOME retrievals for the year 2000, *Atmospheric Chemistry and*
2227 *Physics*, 6, 2943-2979.

2228 Vay, S. A., et al. (2000), Tropospheric water vapor measurements over the North Atlantic
2229 during the Subsonic Assessment Ozone and Nitrogen Oxide Experiment (SONEX),
2230 *Journal of Geophysical Research-Atmospheres*, 105(D3), 3745-3755.

2231 Voigt, C., et al. (2006), Nitric acid in cirrus clouds, *Geophysical Research Letters* 33(5).

2232 Voigt, C., et al. (2007), In-situ observations and modeling of small nitric acid-containing
2233 ice crystals, *Atmospheric Chemistry and Physics* 7(12), 3373-3383.

2234 von Kuhlmann, R. and M. G. Lawrence (2006), The impact of ice uptake of nitric acid on
2235 atmospheric chemistry, *Atmospheric Chemistry and Physics* 6, 225-235.

2236 Wang, C., and R. G. Prinn (2000), On the roles of deep convective clouds in tropospheric
2237 chemistry, *Journal of Geophysical Research-Atmospheres*, 105(D17), 22269-22297.

2238 Wang, Y., et al. (2000), Evidence of convection as a major source of condensation nuclei
2239 in the northern midlatitude upper troposphere, *Geophysical Research Letters*, 27(3),
2240 369-372.

2241 Wang, Y. H., et al. (2000), Influence of convection and biomass burning outflow on
2242 tropospheric chemistry over the tropical Pacific, *Journal of Geophysical Research-*
2243 *Atmospheres*, 105(D7), 9321-9333.

2244 Wang, C. X., and Z. M. Chen (2006), Effect of CH₃OOH on the atmospheric
2245 concentration of OH radicals, *Progress in Natural Science*, 16(11), 1141-1149.

2246 Wei, C. F., et al. (2001), Modeling of ozone reactions on aircraft-related soot in the upper
2247 troposphere and lower stratosphere, *Atmospheric Environment*, 35(35), 6167-6180.

2248 Weisenstein, D.K., et al. (1993), Effects On Stratospheric Ozone From High-Speed Civil
2249 Transport - Sensitivity To Stratospheric Aerosol Loading, *Journal of Geophysical*
2250 *Research-Atmospheres*, 98(D12), 23133-23140.

2251 Wey, C.C., et al. (2007), Overview on the aircraft particle emissions experiment, *Journal*
2252 *of Propulsion and Power* 23(5), 898-905.

2253 Wey, T. and N. S. Liu (2007), Modeling jet engine aerosols in the postcombustor flow
2254 path and sampling system, *Journal of Propulsion and Power* 23(5), 930-941.

2255 Wild, O. and M. J. Prather (2006), Global tropospheric ozone modeling: Quantifying
2256 errors due to grid resolution, *Journal of Geophysical Research-Atmospheres*
2257 111(D11), doi:10.1029/2005JD006605.

2258 Wilson, C. W., et al. (2004), Measurement and prediction of emissions of aerosols and
2259 gaseous precursors from gas turbine engines (PartEmis): an overview, *Aerospace*
2260 *Science and Technology* 8(2), 131-143.

2261 World Meteorological Organization (2006), Scientific Assessment of Ozone Depletion
2262 2006 (WMO/UNEP), World Meteorological Organization Global Ozone Research
2263 and Monitoring Project—Report No. 50.

2264 Wormhoudt, J., et al., (2007), Nitrogen oxide (NO/NO₂/HONO) emissions measurements
2265 in aircraft exhausts, *Journal of Propulsion and Power* 23(5), 906-911.

2266 Wuebbles, D., et al. (2006): A report of findings and recommendations, Workshop on the
2267 Impacts of Aviation on Climate Change, June 7-9, Boston, MA.

2268 Yang, X., et al. (2005), Tropospheric bromine chemistry and its impacts on ozone: A
2269 model study, *Journal of Geophysical Research-Atmospheres*, 110(D23),
2270 doi:10.1029/2005JD006244.

2271 Yelvington, P. E., et al. (2007), Chemical speciation of hydrocarbon emissions from a
2272 commercial aircraft engine, *Journal of Propulsion and Power* 23(5), 912-918.

2273 Zhang, R. Y., et al. (2000), Enhanced NO_x by lightning in the upper troposphere and
2274 lower stratosphere inferred from the UARS global NO₂ measurements, *Geophysical*
2275 *Research Letters*, 27(5), 685-688.

2276 Ziereis, H., et al. (1999), In situ measurements of the NO_x distribution and variability
2277 over the eastern North Atlantic, *Journal of Geophysical Research-Atmospheres*,
2278 104(D13), 16021-16032.

2279 Ziereis, H., et al. (2000), Distributions of NO, NO_x, and NO_y in the upper troposphere
2280 and lower stratosphere between 28 degrees and 61 degrees N during POLINAT 2,
2281 *Journal of Geophysical Research-Atmospheres*, 105(D3), 3653-3664.