

AVIATION AND CHEMISTRY AND TRANSPORT PROCESSES IN THE UPPER TROPOSPHERE AND LOWER STRATOSPHERE

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Uncertainties in transport of nitrogen oxides, measurements of water vapor, coupled NO_x – HO_x reactions, and heterogeneous chemistry of halogens limit our understanding of the climate impacts of aircraft emissions.

Exhaust emissions from aircraft modify the chemical balance in major flight corridors, with significant direct and indirect impacts on global climate. It is estimated that the number of flights will double from present-day rates by about 2025 (ICAO 2007). Unless major changes to combustion systems can be implemented, aircraft emissions can also be expected to double by 2025, along with their attendant consequences on the atmosphere. To determine the effects of current aviation operations on the upper troposphere and lower stratosphere (UTLS) and reliably predict future impacts, we must first understand the fundamental chemical and dynamical processes that occur in this region of the atmosphere. This contribution summarizes the main conclusions that emerged out of a group discussion of two white paper reviews of chemistry and transport (Toohey et al. 2008; McConnell et al. 2008) that were presented at the Aviation Climate Change Research Initiative (ACCRI) Science Meeting (held

in Virginia Beach, Virginia, on 25–27 February 2008).

The most important products of combustion of aircraft fuel (e.g., kerosene) are carbon dioxide (CO_2), water vapor (H_2O), NO_x , soot, and oxides of sulfur (SO_x). Through their interac-

tion with infrared and visible light, CO_2 , H_2O , and soot serve to warm or cool the planet. SO_x , NO_x , and soot alter the nature and radiative properties of particulate matter (aerosols and clouds) or promote formation of new particles by changing the extent of supersaturation through their influence on temperature and water vapor abundances. These three minor products of combustion can also affect the natural abundances of the radiatively important gases ozone (O_3) and methane (CH_4) or cause the vertical redistribution of H_2O and nitric acid (HNO_3) via sedimentation of large cirrus cloud particles. Through such alteration of the radiation balance, aircraft emissions influence atmospheric transport, especially between the troposphere and stratosphere. Water is also important for formation of contrails and cirrus, which influence atmospheric composition by providing surfaces for heterogeneous reactions that enhance ozone-depleting forms of the halogens chlorine and bromine.

These different and, in some cases, offsetting effects have been studied previously. The Intergovernmental Panel on Climate Change (Fahey and Schumann 1999) identified the following aircraft-influenced chemical processes as being most likely to have significant impacts on climate. Enhanced carbon dioxide from direct emissions, as well as ozone enhancements due to subsequent chemistry of NO_x emissions, are expected to warm the climate. Methane decreases, as a result of enhancements of OH resulting from NO_x emissions, are expected to cool the climate. Of these effects, only warming by CO_2 is well understood; the relative scientific understanding of the other processes was rated as fair to poor (Fahey and Schumann 1999). Of particular interest are the indirect influences that aircraft emissions have on the chemistries of ozone and methane through changes to the oxidative capacity of the atmosphere. Such influences could represent more than half of the total impact of aircraft emissions on climate (Fahey and Schumann 1999).

To estimate the range of potential impacts of aircraft emissions of NO_x and HO_x on the chemistry of the UTLS, one must be able to place some bounds on the spatial and temporal variations of the other major sources of these compounds (e.g., convection from the surface or in situ production by lightning). This is because compounds emitted by aircraft represent a relatively small perturbation to the composition of the background atmosphere. Furthermore, processes that affect water vapor in the UTLS (see Fahey and Schumann 1999), such as convection and cirrus formation, are still not well understood. Water vapor is important not only because it is a greenhouse gas that is directly emitted by aircraft, but also because it is a significant source of odd hydrogen (HO_x) in the UTLS. Species in the HO_x family produce and destroy ozone and largely determine the lifetimes of CH_4 and CO ; they also influence NO_x chemistry under the conditions that prevail in the UTLS. Short-

lived organic species and water vapor are important sources of HO_x in the UT. Water vapor is also the source of ice particles in cirrus and polar stratospheric clouds in the UTLS. Relative humidity with respect to ice (RH_i) is a diagnostic quantity that is critical to understanding the role of physical chemistry and dynamics on the formation, growth, and evaporation of ice-containing particles in the UTLS (Heymsfield et al. 2010).

Factors that limit our ability to predict the presence of ice and the extent of uptake of nitric acid are of particular interest to UTLS chemistry. Uptake of HNO_3 into ice crystals and particles is strongly nonlinear with respect to temperature and relative humidity. The rates of heterogeneous reactions that repartition NO_x into NO_y^1 and that release ozone-destroying forms of chlorine vary by several orders of magnitude in the UTLS and are strongly dependent on abundances of condensed HNO_3 (see WMO 2006, and references therein). In addition, a significant confounding factor is that heterogeneous reactions between halogens and temporary NO_x reservoirs can release photolytic sources of HO_x , which in turn destroy methane and accelerate the gas-phase formation of HNO_3 . Enhancements of reactive chlorine also alter methane abundances.

CURRENT UNDERSTANDING AND ISSUES. Since Fahey and Schumann (1999) there has been significant progress in understanding and modeling of atmospheric chemistry in the UTLS. Quantitative understanding of coupled NO_x and HO_x chemistry is essential for quantifying the ozone budget. Recent measurements of HO_x and NO_x in the UTLS (Ren et al. 2008) have greatly improved our understanding of this issue, but serious discrepancies remain, particularly at high levels of NO_x , where the measured concentrations of HO_2 are much larger than those calculated by constrained photochemical models. Another important component of the NO_x – HO_x puzzle is the quantitative understanding of the NO_x budget in the UT. Major sources are delivery of NO_x from the planetary boundary layer (PBL) by large-scale convection and from lightning. Boundary layer sources of NO_x include combustion of fossil fuel, biomass burning in the tropics, and burning of boreal forests, currently believed to contribute over 40 MT yr^{-1} (Houghton et al. 2001). Once lofted to the UTLS, these sources can exceed emissions from air-

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¹ $\text{NO}_y = \text{NO}_x + \text{other nitrogen-containing compounds such as } \text{NO}_3, \text{N}_2\text{O}_5, \text{HNO}_3, \text{HNO}_4, \text{HONO}, \text{ClNO}_2, \text{BrNO}_2, \text{ and peroxyacetylnitrate.}$

craft there—currently $\sim 0.6\text{--}0.7$ MT yr⁻¹ (Houghton et al. 2001) and projected to double by 2020 (Sutkus et al. 2001). The fraction of PBL-NO_x that is transported to the UT by large-scale convection is not well characterized and likely depends on season and continent (Schumann et al. 2000; Singh et al. 2007). The contribution from lightning (Martin et al. 2007; Schumann and Huntrieser 2007) to the UT-NO_x budget is probably of a comparable magnitude to that transported from the PBL.

Removal of NO_y from the UT occurs through transport by the resolved circulation, wet removal in convective clouds, and sedimentation of HNO₃-laden crystals. Our knowledge of the resolved circulation is continually improving, but the other removal processes remain difficult to quantify.

Abundances of OH are important for determining distributions of methane. Increases in tropospheric ozone resulting from aviation emissions would increase OH, thereby decreasing CH₄. These radiative forcings, positive from ozone increases and negative from methane decreases, are offsetting. However, because of their differing lifetimes, the ozone effect will be regional, whereas the methane has an impact globally. The compensating effects are model dependent, perhaps because of underlying uncertainties relating to the differing spatial distributions of NO_x in models and resulting complex feedbacks on O₃ generation and OH production.

The NO_x-NO_y ratio in the UT is important because, together with HO_x, it determines ozone production. Gas-phase chemistry will cycle between NO_x and NO_y, with a tendency to establish a quasi-steady state for this ratio, whereas heterogeneous chemistry that can occur on background aerosols, contrails, and in cirrus cloud tends to favor production of HNO₃, therefore, decreasing the ratio. Also, uptake of HNO₃ by particles, followed by sedimentation, can remove NO_y. Consequently, the issues of chemistry and particle microphysics are inextricably linked, and assessments of the chemical impacts of aircraft emissions must be considered in conjunction with the impacts on aerosols, clouds, and radiation that are discussed in companion papers in this issue.

As an illustration of the importance of aerosol/cloud and chemistry couplings to assessments of the impacts of aircraft, a recent modeling study by Søvde et al. (2007) showed that if the aircraft perturbations to aerosols and clouds (including persistent contrails) were considered in addition to the NO_x perturbations, ozone production was significantly reduced. This is because heterogeneous reactions that activate the background halogen reservoir species

into ozone-destroying forms also convert water to HO_x, while deactivating the ozone-producing NO_x species to HNO₃. The resulting decrease in NO_x-NO_y further reduces the efficiency of ozone production by coupled NO_x-HO_x reactions, with a net result of ozone destruction resulting from aircraft emissions in some regions. The implications of this study have yet to be explored in detail.

In light of the growing importance of coupled aerosols/clouds and chemistry near the tropopause, where specific humidities are very low and heterogeneous reactions could impact the sign of ozone tendencies, it is particularly disconcerting that there are continuing discrepancies of $\sim 30\%$ among in situ measurements of water vapor in this region. At low temperatures, uncertainties of a degree or two become very important for defining the extent of supersaturation often observed in the UT. This knowledge is critical for prescribing the background state of the atmosphere into which aircraft exhaust supplies a significant amount of contrail-forming water vapor and condensation nuclei. Thus, it is important that uncertainties in H₂O and temperature be considered together in any treatment of aircraft-related issues in the UTLS.

The chemical and climate impacts of aircraft are assessed through models. However, aircraft create emissions in plumes of sizes much smaller than are resolvable by current global models. Furthermore, dispersion and heterogeneous processes that are important on these scales may not be well represented in the models. For example, the NO_x conversion to HNO₃ reduces the efficiency of O₃ production. Current plume studies suggest this relation depends quite critically on the background atmosphere (Meilinger et al. 2005).

It is now recognized that exhaust-influenced aerosols and heterogeneous chemistry have more important roles in UTLS chemistry. In addition, NO_x sources from the PBL by convective transport are significantly larger than previously believed, suggesting that aircraft emissions could have a smaller net impact on ozone. In combination, these two new observations could act to reverse the local state of the atmosphere from a predominantly ozone-producing one (e.g., high NO_x) to one that destroys ozone (low NO_x, high active chlorine). Evidence is also mounting that abundances of inorganic bromine in the UT are significantly larger than previously believed, presumably resulting from efficient transport of short-lived bromine sources to the UT. Conversely, high abundances of NO_x transported from the PBL can deactivate the inorganic halogen species.

THE WAY FORWARD. Specific research needs that address important uncertainties in atmospheric chemistry as they relate to the impacts of aviation on climate are given in Brasseur and Gupta (2010). In some cases, observations that can reduce these uncertainties are already available from existing satellites and surface-based monitoring programs and from prior in situ sampling programs. Further analyses of these and other observations will continue to refine our knowledge of the background atmospheric composition and help to quantify the oxidation state of the atmosphere. New projects planned for the coming years [such as the study of the tropical tropopause layer formerly called TC-4 Guam and the Deep Convective Clouds and Chemistry Experiment (DC3)] could be augmented with specific capabilities that could help resolve some of the uncertainties that cannot be addressed readily with existing datasets because of a lack of observations (such as heterogeneous halogen chemistry).

Resolving more long-standing issues, such as the discrepancies in water vapor measurements and associated implications for ice supersaturation and cirrus cloud formation and evolution, may require more creative solutions, because the usual approach of in-flight and laboratory intercomparisons of measurement pairs has not been as successful as hoped or needed. We encourage more frequent measurements directly in aircraft exhaust plumes of different ages and in contrails and cirrus. Such activities could complement upcoming field campaigns, or could be carried out in those dedicated to contrail issues (e.g., Heymsfield et al. 2010). Constrained by observations of a conserved tracer of combustion such as CO₂, systematic errors in measurements of vapor and condensed phases of water can be more readily assessed.

Also of concern are changes that might occur in a future atmosphere under a different climate regime. Many of the important issues in UTLS chemistry are tied directly to atmospheric dynamics in the stratosphere and troposphere and the strength of the overturning circulation. For example, changes in the stratospheric–tropospheric exchange are likely to alter the delivery of ozone from the stratosphere to the troposphere. In a future climate, the strength of large-scale convection may change the balance and amount of NO_x production and PBL sources in the UT. Furthermore, in addition to the increase of aviation emissions by a factor of 2 to 2.5 in the next 20 to 30 years (Sutkus et al. 2003), estimates of surface anthropogenic and “natural” emissions (e.g., Stevenson et al. 2006 and references therein) suggest a similar increase but with a possibly different spatial distribution from contemporary emission patterns.

In the tropics, convection, along with transport into the stratosphere through the tropical tropopause layer, may change. These few examples suggest that it will be important to assess future aviation impact using chemical transport models with meteorological fields derived from future climate simulations and including adequate representation of both the troposphere and the stratosphere. We need to improve the physical treatment of naturally occurring cirrus and contrail cirrus in global climate models (Burkhardt et al. 2010) and the coupled chemistry–climate models indispensable for future assessments.

Finally, it is important to point out that solutions to the unresolved questions in UTLS chemistry will require a concerted effort of the measurements, modeling, and laboratory communities. Therefore, it is recommended that the way forward begin with the formation of a team of investigators that includes members from each of these communities. This team should prioritize the important questions, define strategies for including aircraft emissions issues into existing and future research programs, and continue to refine the list of priorities for studies that reduce the key uncertainties highlighted above.

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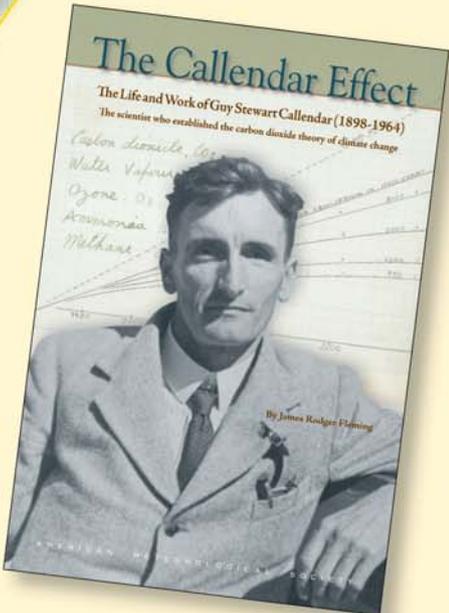
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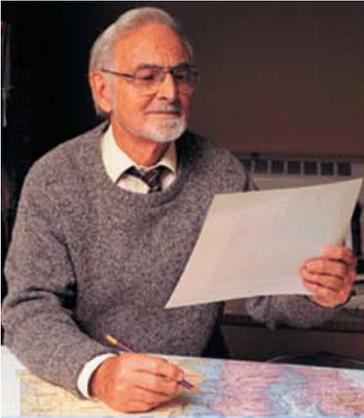
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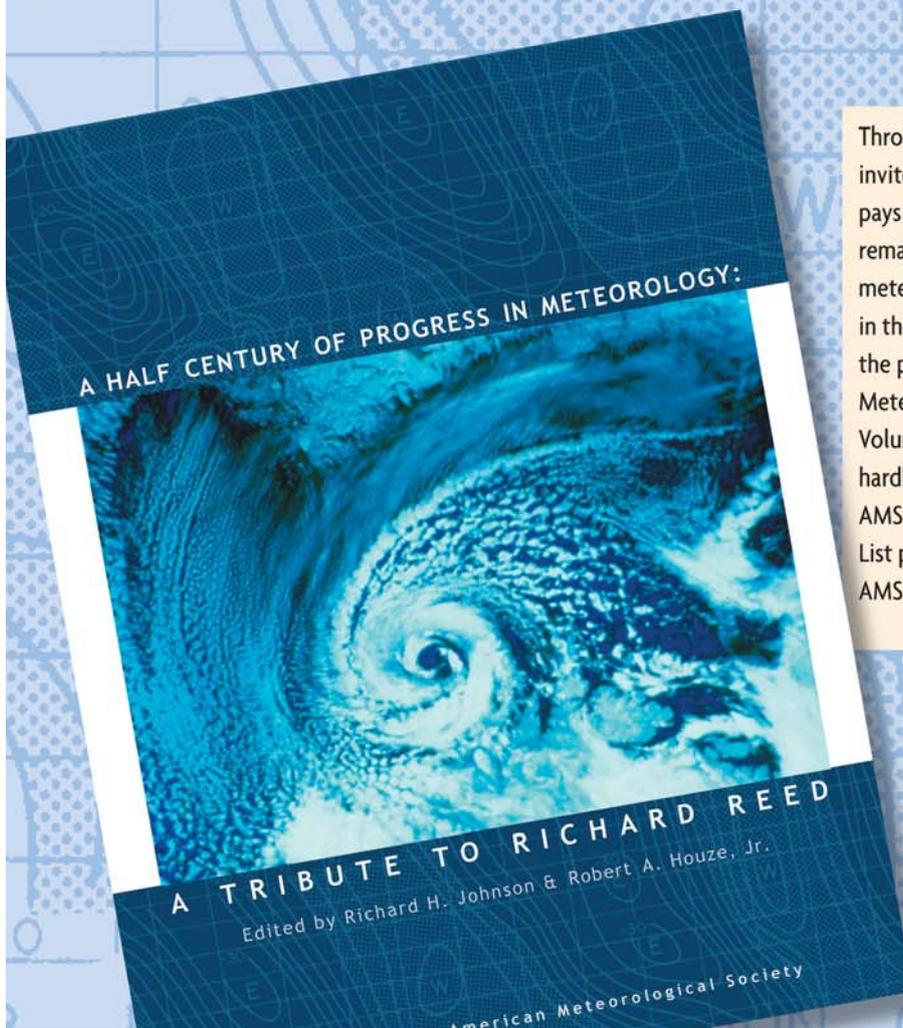
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