

Reactive Chemistry in Aircraft Exhaust

Implications for Air Quality

Ben H. Lee, Ezra C. Wood, Richard C. Miake-Lye, Scott C. Herndon, J. William Munger, and Steven C. Wofsy

Exhaust emitted from jet engines contains high concentrations of combustion by-products, some of which are damaging to human and ecosystem health. As these pollutants mix with the surrounding air, they undergo chemical reactions that eventually break them down to their water-soluble or inert forms. To date, the reactivity of aircraft exhaust has been largely unexplored, and it is not known whether state-of-the-art models account for chemistry at the plume level, which directly relates to air quality downwind of airports. To a large extent, the concentrations of hydroxyl (OH) and hydroperoxyl (HO₂) radicals—collectively called HO_x—present in emitted plumes determine the rate at which components of the exhaust are oxidized. In January 2009, the authors quantified emissions of all HO_x precursors including nitrous acid (HONO), formaldehyde (HCHO), acetaldehyde (CH₃CHO), and ozone (O₃) at the Alternative Aviation Fuels Experiment in Palmdale, California. The results indicate that (a) HO_x production rate due to direct emission of these precursors is orders of magnitude faster in the exhaust plume than in “normal” urban air; (b) the concentration of pollutants in plumes does not reach typical ambient levels until it has been diluted by a factor of about 6,000; and (c) photolysis of HONO in these plumes is by far the biggest source of HO_x during daytime. Analyses of the reactions involving HO_x demonstrate that propagation of these radicals is favored over termination, which indicates that chemical reactivity will continue to be enhanced in these plumes even after being diluted to ambient levels.

There is growing concern regarding aviation emission and its effect on air quality, particularly given the projected increase in global air travel over the coming decades (1–3). The impact of airports on local air quality and public health is not well understood (4). Knowledge of emissions of trace gases and particulate matter has improved in the past decade from measurements close behind aircraft engines in operation (5–8). These measurements of emission indices can be used to generate emission inventories of airports to be utilized as input variables in air quality models. The relationship, however, between emissions and resulting pollutant concentrations is complex and dependent on many variables, including transport and mixing, strength and duration of emission source, proximity to the source, and chemical processing within the atmosphere. Air quality models that do not account for all of these parameters are unlikely to make accurate forecasts.

B. H. Lee, J. W. Munger, and S. C. Wofsy, Harvard University, 20 Oxford Street, Cambridge, MA 02138. E. C. Wood, R. C. Miake-Lye, and S. C. Herndon, Aerodyne Research, Inc., 45 Manning Road, Billerica, MA 01821. Corresponding author: B. H. Lee, hwanlee@fas.harvard.edu.

Transportation Research Record: Journal of the Transportation Research Board, No. 2206, Transportation Research Board of the National Academies, Washington, D.C., 2011, pp. 19–23.
DOI: 10.3141/2206-03

Recent studies have shown that the chemistry in the evolving, diluting exhaust plume is drastically enhanced compared to that of the ambient atmosphere (9). Reaction rates are magnified relative to normal conditions due to concentrated levels of directly emitted reactive species such as volatile organic compounds (VOCs), carbon monoxide (CO), sulfur dioxide (SO₂), and nitrogen oxides (NO_x), all of which are categorized as either a criteria air pollutant or a precursor by the Environmental Protection Agency (10).

The species central to the chemical breakdown of these primarily emitted pollutants in the atmosphere are the hydroxyl (OH) and hydroperoxyl (HO₂) radicals, collectively known, due to the fast interconversion between themselves, as HO_x radicals. HO_x species play a key role in the nonlinear, highly coupled dynamics of atmospheric chemistry (see Figure 1). For instance, oxidation of VOCs by HO_x lowers the concentration of the parent VOC, but leads to the formation of potentially more harmful secondary organic aerosols and oxygenated VOCs. Increased chemical activity also leads to the formation of tropospheric ozone (O₃), another criteria air pollutant and greenhouse gas, as well as a major OH precursor.

At the Alternative Aviation Fuels Experiment (AAFEX) conducted in January 2009, mixing ratios were observed of all of the dominant HO_x precursors emitted in aircraft exhaust, including nitrous acid (HONO), formaldehyde (HCHO), acetaldehyde (CH₃CHO), and O₃. Measurements show that photolysis of these HO_x precursors during daytime results in plumes that are drastically more reactive than air unperturbed by emissions. Analyses suggest that the enhanced reactivity persists even after plumes have diluted down to ambient levels several kilometers downwind. These results call for the need to account for these species that are driving the chemistry, in order to properly assess impact of airports on downwind air quality.

METHODS

Measurements of a whole suite of gaseous species and particulate matter were made during AAFEX at various distances (between 3 m and approximately 150 m) behind a DC-8 jet, which was choked on the runway at the NASA Dryden Flight Research Center in Palmdale, California. A total of 12 experiments, each lasting several hours, were conducted over a span of a week at various times of the day to test the wide range of ambient conditions as variables on emissions. Different fuel types (traditional and synthetic) were fed into the engine, which during each experiment was varied from idle to take-off conditions. A detailed report on the experimental setup, mission goals, and summary results is presented by Bulzan et al. (11).

In this study, the focus is on HO_x radical precursors such as HCHO and ethene (measured by a dual pulsed-mode infrared laser absorption spectrometer), CH₃CHO and propene (proton-transfer reaction

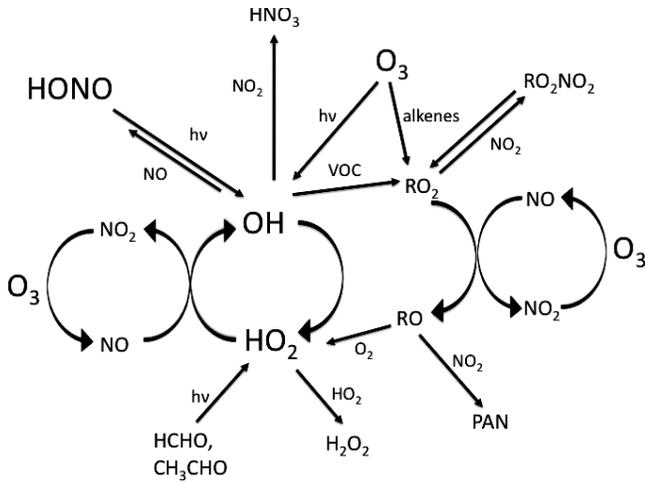


FIGURE 1 Simplified schematic of chemical reactions occurring in the troposphere. OH and HO₂, collectively known as HO_x, are responsible for the breakdown of VOCs and other reactive species. Note the cyclic nature of both HO_x (= OH + HO₂) and NO_x (= NO + NO₂), interconverting between one another while generating O₃ with each cycle. This cycling is ultimately terminated by the reaction between NO₂ and OH forming nitric acid (HNO₃), which is eventually deposited and lost from the atmosphere (hν = energy from sunlight; RO₂ = alkylperoxy radicals; PAN = peroxyacyl nitrate).

mass spectrometer), and HONO (continuous-wave-mode infrared laser absorption spectrometer). In addition, measurements of carbon dioxide (CO₂) were made using a nondispersive infrared gas analyzer. The various instrumentations, though they differ in technique, essentially operate by drawing ambient air through an inlet composed of a particle filter or inertial separator (to keep the

instruments free of interfering particles) through tubing (to keep the instruments out of the path of jet exhaust) and into the instrument where concentrations are quantified. All of the instruments were set up to allow sampling response times of less than 1 s to be able to resolve the rapid fluctuations in the level of pollutants in the exhaust.

RESULTS

Figure 2 shows a brief time-series of HONO and CO₂ mixing ratios observed during AAFEX. In Figure 2a and b, note how the levels of both gases co-vary together in time because of their common emission source and due to atmospheric mixing similarly processing both gases from engine exit to the sampling point. The slope of the correlation plot between HONO and CO₂ (Figure 2c) is commonly called the emission ratio (ER) and is significant because it quantifies the emission signature of the species of interest (in this case, HONO) relative to CO₂, which is a main by-product of fossil-fuel combustion and readily traceable to the amount of fuel consumed. To adhere to International Civil Aviation Organization standards, the emission index (EI) is reported here in units of mass (g) of x per mass (kg) of fuel consumed,

$$EI_x = \left(\frac{\text{moles of } x}{\text{moles of CO}_2} \right) \times \left(\frac{\text{molecular mass of } x}{\text{molecular mass of CO}_2} \right) \times EI_{CO_2}$$

where EI CO₂ is the emission index of CO₂, which for jet fuel is 3,160 g of CO₂ emitted per kg of fuel consumed.

Figure 3 shows the EI of HONO plotted as a function of rated engine thrust. Each data point at a given engine setting in Figure 3 is the AAFEX campaign averaged value, which is composed of hundreds of emission indices calculated from individual plumes lasting anywhere

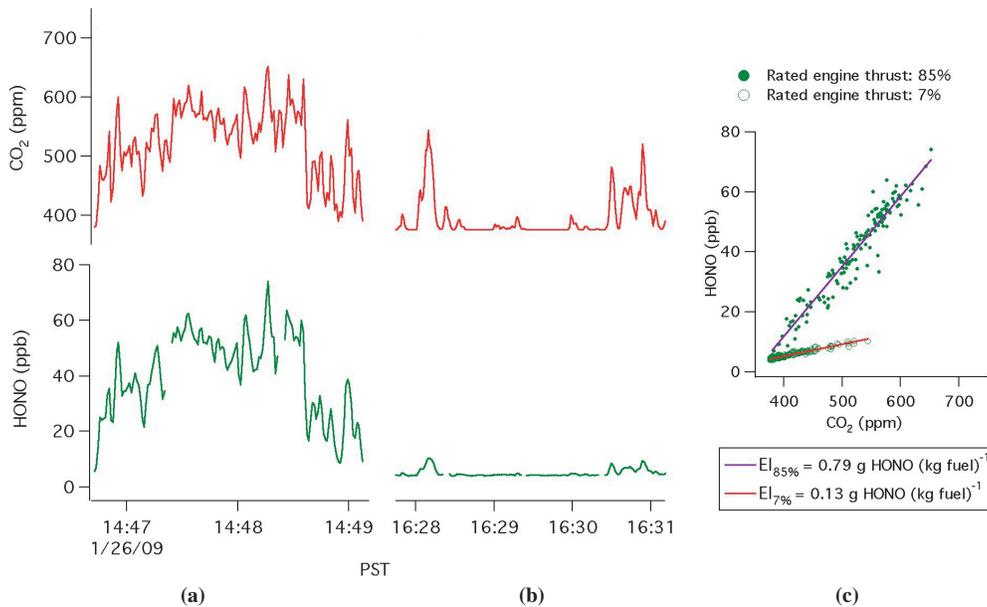


FIGURE 2 Mixing ratios of HONO (parts per billion, ppb) and CO₂ (parts per million, ppm) observed in aircraft exhaust. Twelve experiments were conducted over a period of 1 week under widely varying ambient conditions and engine settings, which ranged from idle to full thrust. Above is a brief excerpt of 1-s time resolution data. Note how the levels of HONO and CO₂ covary together in time at (a) high engine power (85% thrust), as well as at (b) low engine power (7% thrust). (c) HONO plotted against CO₂ clearly shows the dependence of their relationship on engine setting.

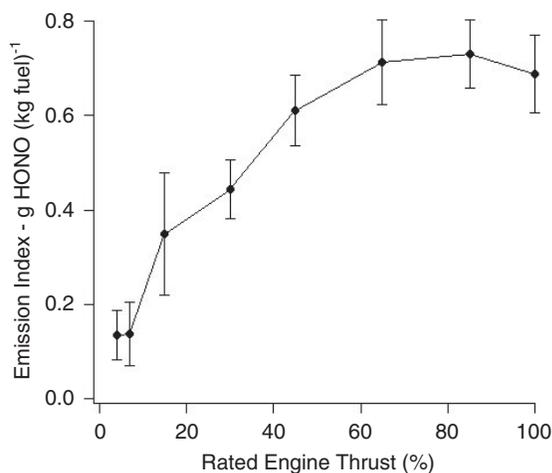
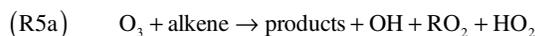
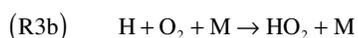
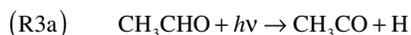
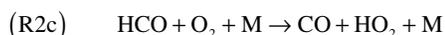
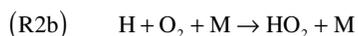
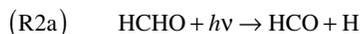
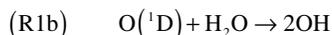
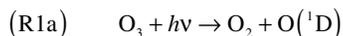


FIGURE 3 HONO emission index from a single CFM-56 jet engine plotted as a function of rated engine thrust. Each EI value represents the campaign average of all observed individual plumes, each lasting from a few seconds to approximately 30 s. The error bars represent the 1- σ of the average.

from a few to 30 s. Approximately 0.1 g of HONO is emitted on average for every kilogram of fuel consumed at engine idle (~7% rated engine thrust) and increases nearly 7-fold at 60% rated engine thrust, beyond which EI for HONO remains fairly constant. HONO is formed within the engine primarily by the gas-phase reaction between nitric oxide (NO) and OH. As the engine power is increased from idle thrust, the concentrations of both NO and OH in the engine increase, resulting in greater HONO EI values. HONO EI is not significantly affected by ambient temperature (which ranged from slightly below 0°C to 23°C); relative humidity (20% to 70%); presence of sunlight; wind speed or direction; or fuel type (traditional jet fuel, coal-derived or natural-gas derived synthetic fuels). The dominant variable influencing HONO EI is the engine power setting (Figure 3).

DISCUSSION OF RESULTS

In typical unperturbed ambient atmosphere, HO_x is predominantly generated by sunlight-induced photolysis of O₃ and HCHO with some contributions from the photolysis of HONO and the ozonolysis reaction between O₃ and various alkenes (mainly ethene and propene), as illustrated by the reactions listed below.



where $h\nu$ represents the energy from sunlight absorbed by the reactants, and RO₂ represents alkylperoxy radicals.

The rates at which these reactions proceed are dependent on the reactant concentrations and the rate constants, which for the photolysis reactions (R1–R4) are a function of the intensity and wavelength of the incident radiation. Consequently, since each of the five chemical reactions (R1–R5) listed above yield at least one HO_x radical (either OH or HO₂), the total HO_x production rate is given by the sum of the reaction rates of R1 through R5.

$$(R6) \quad P(HO_x) = R1 + R2 + R3 + R4 + R5 \\ = 2 \times j_{1b} \times [O(^1D)][H_2O] + 2 \times j_2 \times [HCHO] + 2 \\ \times j_3 \times [CH_3CHO] + j_4 \times [HONO] + k_4 \times [O_3] \\ \times [\text{alkene}](HO_x \text{ yield})$$

where the j values are photolysis rate constants and k values are the reaction rate constants. Table 1 lists the photolysis rates for O₃, HCHO, CH₃CHO, and HONO under typical cloudless sky conditions at 30° solar zenith angle obtained using the TUV model developed by the National Center for Atmospheric Research (12). The concentration of the reactant species at engine exit is calculated from the ERs with respect to CO₂ observed at AAFEX. Since the concentration of CO₂ at the engine exit is well known (2.1% at engine idle and 4% at high power), the corresponding concentration of the species of interest at engine exit is simply the product of the ER and the CO₂ concentration at engine exit.

Figure 4a shows the production rate of HO_x in exhaust plumes due to the photolysis of emitted precursors relative to what is typically observed in the ambient atmosphere, plotted as a function of plume dilution. A dilution factor of 1 represents conditions at engine exit before any mixing or dilution has taken place. The emission rates of precursors used in the calculation here are representative of those observed at engine idle and the photolysis rates are from conditions listed in Table 1. This figure shows that the HO_x production rate is several orders of magnitude faster inside the exhaust plume at the engine exit and only reaches those observed in normal air after being diluted by a factor of about 6,000. A breakdown of the relative strengths of the precursors shows that HONO is the biggest contributor to HO_x production due in part to its fast photolysis rate (Table 1), followed by HCHO, then the ozonolysis reactions of ethene and propene, and lastly CH₃CHO (Figure 4b).

Relating dilution factor to actual distance from emission source is problematic, since the rate at which dilution occurs in the ambient atmosphere is governed by numerous factors including wind speed,

TABLE 1 Photolysis Rates of HO_x Precursors Emitted from Jet Exhaust

Reaction	Precursor	Photolysis Rates
R1a	O ₃	3.4 × 10 ⁻⁵
R2a	HCHO	3.2 × 10 ⁻⁵
R3a	CH ₃ CHO	5.4 × 10 ⁻⁶
R4	HONO	2.1 × 10 ⁻³

NOTE: Rates are calculated for typical cloudless winter midday condition at 30° solar zenith angle.

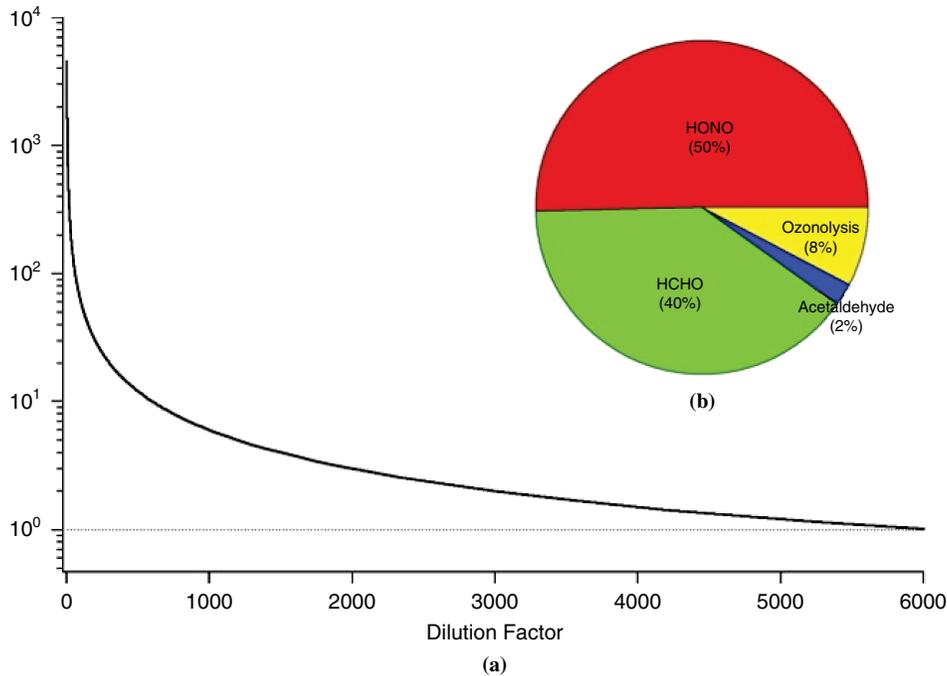


FIGURE 4 (a) Ratio of HO_x radical production rate in jet exhaust relative to those under typical urban conditions (~0.5 parts per trillion per second), plotted versus plume dilution factor. HO_x is produced from the photolysis of precursors, including HONO, HCHO, CH₃CHO, and the ozonolysis reactions between O₃ and alkenes. (b) Relative strengths of HO_x sources in jet exhaust.

wind shear, and geographic conditions. Figure 5 shows dilution factors estimated from measured CO₂ levels (relatively inert at these time scales) observed in diluting, evolving plumes sampled at various distances from airports in numerous field campaigns including AAFEX. Observations from these campaigns with varying ambient conditions and geographic layouts indicate that dilution due to mixing occurs at a relatively predictable rate at these distances and that concentration of an emitted species reaches background levels of normal air between approximately 1 and 4 km (0.6 and 2.4 mi) downwind of airports.

It is, however, important to stress here that based on previous measured EIs of reactive gases and the rates at which they are oxidized by HO_x radicals, the authors calculate that more than 95%

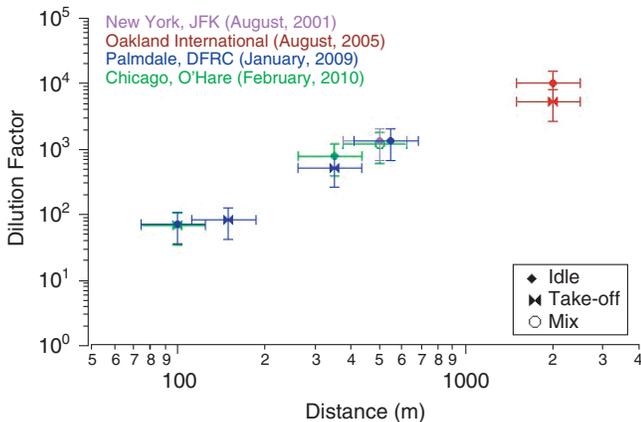


FIGURE 5 Plume dilution factor calculated from CO₂ measurements made at varying distances from the emission source, plotted versus distance.

of the OH radical produced in these plumes react with VOCs and CO because they are emitted in large quantities from idling engines due to inefficient fuel combustion. These reactions tend to favor cycling between OH and HO₂ while generating noxious gases such as O₃ and alkyl peroxy radicals. This branching of chemistry (Figure 1) thus represents propagation of HO_x. The reaction between OH and NO₂ forming HNO₃—which is readily lost from the atmosphere through deposition, thus terminating the cycling between OH and HO₂—occurs less frequently. In short, the regeneration of HO_x species due to the rapid cycling between OH and HO₂ is favored in these plumes over termination. The decrease in HO_x production rate diagrammed in Figure 4 only takes into account dilution and not the propagation due to cycling. Consequently, enhanced reactivity (faster HO_x production than in normal air) is sure to persist farther downwind than the 1 to 4 km calculated above.

Last, it should be noted that HO_x production in these plumes occurs only during daytime through sunlight-induced photolysis of emitted precursors. During nighttime, emissions from airports would lead to the buildup of these HO_x precursors as well as the other emitted pollutants such as VOCs, NO_x, and SO₂ in the nighttime air. This nighttime buildup is enhanced because of the so-called nocturnal boundary layer as it traps emissions at the surface due to an inversion in the vertical temperature profile. Therefore, nighttime emissions can serve as a significant pulse of reactivity in the morning immediately following sunrise when photolysis commences.

CONCLUSION

This paper presents measurements of HO_x precursors in aircraft exhaust made during the AAFEX field campaign in January 2009 at the NASA Dryden Flight Research Center. Analyses show that

photolysis of HONO (50%) is the dominant source of HO_x in exhaust plumes, followed by photolysis of HCHO (40%), the ozonolysis reactions between O₃ and light alkenes (8%), then photolysis of CH₃CHO (2%). Due to the enhanced levels of precursors, the reactivity of emitted plumes reaches HO_x production rates usually observed in ambient air after it is diluted by three to four orders of magnitude, or approximately between 1 and 4 km downwind of emission sources. However, due to the cyclic nature—reaction followed by regeneration—of the HO_x radicals, enhanced chemistry likely persists much farther downwind.

Analyses presented here provide strong evidence for the need to account for HO_x precursors in engine exhaust because of its role in driving chemistry. This is required in order to realistically translate airport emission inventories to enhancements in the pollutant levels downwind and ultimately to assess the effects on the health of nearby communities. Species such as tropospheric ozone and secondary organic aerosols are not directly emitted from engines but are harmful by-products of the transformations driven by chemistry. The measurements made during AAFEX will help bridge that gap in understanding between emissions and impact and allow future modeling efforts to improve assessments.

All of the HO_x precursors discussed above are in some form already monitored by the International Civil Aviation Organization, which sets certification guidelines for aviation-related emissions of CO, NO_x, and total VOCs. HONO is indirectly included in the NO_x inventory, as are HCHO, CH₃CHO, ethane, and propene in the total VOC inventory. Therefore, explicit regulation of these gases is likely not necessary; however, determining the scaling of these particular species to their respective inventories would greatly aid future modeling programs.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Transportation Research Board for the Airport Cooperative Research Program Award.

The contributions of the coauthors are as follows:

- Ezra C. Wood was the point person on the field during AAFEX. He contributed a great deal during the instrument setup as this was the first field deployment for the lead author. Wood also helped refine the direction of the analyses presented here.
- Richard C. Miake-Lye was in charge of organizing the logistics of AAFEX for both research teams from Harvard University and Aerodyne Research. His expertise in the field of aeronautics and combustion chemistry also was of great help in the writing of this report.
- Scott C. Herndon was responsible for the collection of all data sets excluding that of nitrous acid during AAFEX as well as other field campaigns, used in the analyses presented in this report.

- J. William Munger is the coadvisor to the lead author. He aided in the construction of the instrument and its peripherals utilized during the AAFEX field campaign.

- Steven C. Wofsy is the main thesis adviser to the lead author. He helped revise and refine the report.

REFERENCES

1. Lee, D. S., D. W. Fahey, P. M. Forster, P. J. Newton, R. C. N. Wit, L. L. Lim, B. Owen, and R. Sausen. Aviation and Global Climate Change in the 21st Century. *Atmospheric Environment*, Vol. 43, No. 22–23, 2009, pp. 3520–3537.
2. Mohn, T. At German Airports, Bees Help Monitor Air Quality. *Itineraries*, June 28, 2010 (Sept. 4, 2010). Available from: http://www.nytimes.com/2010/06/29/business/29airports.html?ref=air_pollution.
3. Penner, J. E. *Aviation and the Global Atmosphere*. Cambridge University Press, Cambridge, United Kingdom, 1999.
4. Klemm, R., R. Wyzga, and E. Thomas. Daily Mortality and Air Pollution in Atlanta: August 1998–December 2006. *Epidemiology*, Vol. 20, No. 6, 2009, p. S223.
5. Anderson, B. E., G. Chen, and D. R. Blake. Hydrocarbon Emissions from a Modern Commercial Airliner. *Atmospheric Environment*, Vol. 40, No. 19, 2006, pp. 3601–3612.
6. Miake-Lye, R. C., B. E. Anderson, W. R. Cofer, H. A. Wallio, G. D. Nowicki, J. O. Ballenthin, D. E. Hunton, W. B. Knighton, T. M. Miller, J. V. Seeley, and A. A. Viggiano. SO_x Oxidation and Volatile Aerosol in Aircraft Exhaust Plumes Depend on Fuel Sulfur Content. *Geophysical Research Letters*, Vol. 25, No. 10, 1998, pp. 1677–1680.
7. Spicer, C. W., M. W. Holdren, D. L. Smith, D. P. Hughes, and M. D. Smith. Chemical Composition of Exhaust from Aircraft Turbine Engines. *Journal of Engineering for Gas Turbines and Power*, Vol. 114, No. 1, 1992, pp. 111–117.
8. Yelvington, P. E., S. C. Herndon, J. C. Wormhoudt, J. T. Jayne, R. C. Miake-Lye, W. B. Knighton, and C. Wey. Chemical Speciation of Hydrocarbon Emissions from a Commercial Aircraft Engine. *Journal of Propulsion and Power*, Vol. 23, No. 5, 2007, pp. 912–918.
9. Wood, E. C., S. C. Herndon, M. T. Timko, P. E. Yelvington, and R. C. Miake-Lye. Speciation and Chemical Evolution of Nitrogen Oxides in Aircraft Exhaust Near Airports. *Environmental Science and Technology*, Vol. 42, No. 6, 2008, pp. 1884–1891.
10. U.S. National Air Pollution Control Administration. *Air Quality Criteria for Photochemical Oxidants*. Washington, D.C., 1970.
11. Bulzan, D., B. Anderson, C. Wey, R. Howard, E. H. Winstead, A. Beyersdorf, E. Corporan, M. J. DeWitt, C. D. Klingshirm, S. C. Herndon, R. Miake-Lye, E. C. Wood, K. Tacina, D. S. Liscinsky, D. Hagen, P. Lobo, and P. Whitefield. *Gaseous and Particulate Emissions Results of the NASA Alternative Aviation Fuel Experiment (AAFEX)*. ASME Turbo Expo 2010: Power for Land, Sea, and Air (GT2010), Glasgow, United Kingdom, June 14–18, 2010, pp. 1195–1207.
12. Hutzinger, O. *The Handbook of Environmental Chemistry*. Springer-Verlag, New York, 1980, p. v.

The ACRP Selection Panel for the Graduate Research Award Program on Public-Sector Aviation Issues peer-reviewed this paper.