

Hydrocarbon emissions from a modern commercial airliner

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Abstract

We report selected carbon species emission indices (EIs) for a Rolls Royce RB211-535-E4 turbofan engine that were acquired during the NASA EXperiment to Characterize Aircraft Volatile Aerosol and Trace-species Emissions (EXCAVATE). Conducted during winter 2002, the mission focused upon characterizing the exhaust constituents of the NASA Boeing 757 aircraft during ground-based operation. Carbon species concentrations were determined by chromatographic analyses of whole air samples collected 10 m behind the engine exit plane as engine power was varied from ground idle to about 60% of maximum rated thrust. Ambient air samples were also collected and analyzed to facilitate correction of calculated EIs for background concentrations. Results are consistent with previous observations and indicate that, on a relative basis, turbine engines emit considerable amounts of light hydrocarbon species at idle, but significantly lesser amounts at higher engine powers.

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1. Background

Aircraft consume about 3% of the fossil fuels burned in the atmosphere each year, about 10% of this during landing and takeoff cycles (i.e., Friedl, 1997). Though the combustion of this fuel primarily produces carbon dioxide and water, a small fraction is emitted as non-methane hydrocarbons (NMHCs). These compounds are ozone precursors, can condense to form particles that impact visibility and inhibit respiratory function, and may be toxic or carcinogenic to exposed animal life. Though minis-

cule in comparison to the levels produced by automobiles and other surface-based transportation systems and judged to have only a minor impact upon ozone budgets at cruise altitudes (Friedl, 1997), aircraft NMHC emissions can potentially impact air quality and present a health hazard to workers, residents, and travelers within and around airport terminal areas.

To understand, better predict, and mitigate the impact of aircraft operations upon local air quality, detailed information on NMHC emissions, e.g. speciation of NMHC emissions, by aircraft is required (e.g., Pison and Menut, 2004). At present, such data is exceedingly sparse. The International Civil Aviation Organization (ICAO) does require that all commercial aircraft engines be emission certified, meaning that their emissions of CO, NO_x,

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total hydrocarbons (HC) and smoke must be measured at idle, approach, climb out, and take-off powers to ensure that they meet certain standards. However, HC measurements made in these studies are the lump sum of all hydrocarbons, including contributions from methane and other species. In addition, no corrections are made for background HC levels within the engine intake air.

In response to this measurement need, several recent studies have determined NMHC speciation within turbine engine exhaust plumes. Spicer and coworkers investigated the gas-phase emissions of both military (GE F101 and F110; Spicer et al., 1992) and commercial engines (TF-39 and CFM-56-3; Spicer et al., 1994). At engine idle, they found that emissions were dominated by cracking products, unburned fuel, and products of incomplete combustion, with ethene, propene, acetylene and formaldehyde comprising 30–40% of the total HC budget. At higher engine powers, relative NMHC emissions dropped by a factor of 20–50 and unburned fuel components disappeared. Slemr et al. (2001) report similar findings for an older technology engine (Rolls Royce M45H Mk501) and a more modern commercial high bypass turbofan (CFM 56-2C1). Further, they note that the emission indices for these engines are highly power dependent and dominated by alkenes and alkynes related to fuel cracking and aromatic compounds arising from unburned fuel. Both Slemr et al. (1999, 2001) and Spicer et al. (1992, 1994) note that NMHC emissions are likely dependent upon engine type, use, and maintenance history as well as fuel composition.

Although the Spicer et al. (1994) and Slemr et al. (2001) studies provide significant insight into NMHC emissions from aircraft, their conclusions are drawn from limited sampling of just a few of the more than 300 types of commercial engines that are presently in use within the commercial aviation fleet and listed within the ICAO emissions data base (www.qinetiq.com/aircraft/aviation.html). Clearly, data from a broader range of gas turbine engines are needed to provide a better statistical base for parameterizing aircraft NMHC emissions in regional and global modeling assessments. For this reason, NMHC determinations were included as part of the measurement priorities for the NASA EXperiment to Characterize Aircraft Volatile Aerosol and Trace-species Emissions (EXCAVATE).

EXCAVATE was conducted during January 2002 with the primary objectives of characterizing

the aerosol and aerosol precursor emissions from a modern commercial turbofan engine (Anderson et al., 2005). The NMHC emission study was focused on the Rolls Royce RB211-535E4 turbofan engines mounted on the NASA Langley Boeing 757 (B757). These high bypass ratio engines were designed for low NO_x and hydrocarbon emissions and are capable of generating 40,000 lbs thrust. About 80% of the B757 aircraft in service use Rolls Royce RB211-535E4 engines. Whole air samples were collected from the exhaust plume of the right engine as it was operated at a variety of power settings and from the background air being drawn into the engine intake. The samples were shipped to the University of California at Irvine where gas chromatographic techniques were used to assay their hydrocarbon species content. We subsequently used this concentration data in concert with simultaneous engine CO₂ emission measurements to calculate emission indices for each of the measured species. The paragraphs below describe our sample collection and analysis procedures, present the RB211-535E4 NMHC emission observations, and compare our results to those from previous studies.

2. Experiment

The EXCAVATE experiment was carried out at NASA Langley Research Center's aircraft "run-up" facility during January 2002. Basically a large concrete pad with a sturdy blast-fence installed across the rear to deflect exhaust plumes up and away from surrounding vegetation, this facility is located next to a heavily wooded area on the west side of Langley Air Force Base Field in Hampton, VA and is several hundred meters from other stationary or mobile pollution sources. NMHC samples were collected over a short period of time (~3 h) on a Sunday afternoon when local traffic was very light and airport operations were at a minimum. Air samples were drawn from the exhaust plume through a forward facing inlet, diluted at the inlet tip with dry N₂, then collected in evacuated stainless steel canisters. The stainless-steel sampling probe was positioned 10 m downstream and on the centerline of the B757 right engine (RB211-535E4) exit plane. At the 10 m probe position, the plume velocity varied from 60 m s⁻¹ (idle) to over 200 m s⁻¹ (high cruise), implying that sample air aged <0.2 s before reaching the sampling inlet. A total of 11 samples were collected, 8 of

engine emissions and 3 of background air in the vicinity of the B757. The 8 engine exhaust samples corresponded to 4 different engine power settings (i.e., idle, approach, low cruise, and high cruise) and two batches of JP-5 fuel that contained distinctly different sulfur contents (810 and 1820 ppm by weight). We will refer these two batches as low sulfur and high sulfur fuels in our later discussion. Different power settings were obtained by adjusting the fuel flow rate while monitoring the engine pressure ratio. Fuel flow rates, pressure ratios, turbine speeds, and exhaust gas temperatures were recorded from cockpit instrumentation. From simultaneous aerosol measurements we noted that the emissions varied significantly just after engine start and when power was reduced from higher settings to idle. We thus collected the whole air samples after the engine had been running at a given power setting for several minutes to ensure that the combustor temperatures and pressures had attained equilibrium.

Details of the analytical procedures employed by the UCI laboratory are given by Sive (1998), Colman et al. (2001), and Blake et al. (2003), so only a brief description will be given here. Aliquots of air from each canister were preconcentrated in a liquid nitrogen-cooled loop. This sample was directed to five different gas chromatographic column/detector combinations. Electron capture detectors (ECD, sensitive to halocarbons and alkyl nitrates), flame ionization detectors (FID, sensitive to hydrocarbons), and quadrupole mass spectrometers (MSD, for unambiguous compound identification and selected ion monitoring) were employed. The first column–detector combination (abbreviated as “DB5ms/MSD”) was a DB5ms column (J&W; 60 m, 0.25 mm I.D., 0.5 μm film thickness) output to a MSD (HP-5973). The second combination (“DB1/FID”) was a DB-1 column (J&W; 60 m, 0.32 mm I.D., 1 μm film thickness) output to a FID (HP-6890). The third combination (“PLOT-DB1/FID”) was a PLOT column (J&W GS-Alumina; 30 m, 0.53 mm I.D.) connected in series to a DB-1 column (J&W; 5 m, 0.53 mm I.D., 1.5 μm film thickness) and output to an FID. The fourth combination (“Restek1701/ECD”) was a RESTEK 1701 column (60 m, 0.25 mm I.D., 0.50 μm film thickness), which was output to an ECD. The fifth combination (“DB5-Restek1701/ECD”) was a DB5 (J&W; 30 m, 0.25 mm I.D., 1 μm film thickness) column connected in series to a RESTEK 1701 column (5 m, 0.25 mm I.D., 0.5 μm

film thickness) and output to an ECD. The DB5ms/MS, DB1/FID, PLOT-DB1/FID, Restek1701/ECD, and DB5-Restek1701/ECD combinations received 10.1%, 15.1%, 60.8%, 7.2%, and 6.8% of the sample flow, respectively. The canister air was also analyzed for CO using GC with FID, as described by Hurst (1990) and Lopez (2002) using a packed column GC separation of CO followed by reduction to methane on a nickel catalyst and detection by FID. As summarized in Table 1, the analytical accuracy for the species reported here ranges from 2% to 20% and the precision

Table 1
Summary of measurement precision and accuracy

Species	Detection limit	Precision (%)	Accuracy (%)
CO ₂	5 ppmv	1	1.5
CO	5 ppbv	5	5
CH ₄	10 ppbv	0.1	1
OCS	25 pptv	3	5
DMS	1 pptv	3	5
CS ₂	1 pptv	3	10
CH ₃ Cl	50 pptv	5	5
Methyl nitrate	0.05 pptv	5	10
Ethyl nitrate	0.05 pptv	5	10
<i>iso</i> -Propanyl nitrate	0.05 pptv	5	10
<i>n</i> -PrONO ₂	0.05 pptv	5	10
2-BuONO ₂	0.05 pptv	5	10
Ethane	5 pptv	2	5
Ethene	5 pptv	2	5
Ethyne	5 pptv	2	5
Propane	5 pptv	2	5
Propene	5 pptv	2	5
<i>i</i> -Butane	5 pptv	2	5
<i>n</i> -Butane	5 pptv	2	5
1-Butene	5 pptv	3	5
<i>i</i> -Butene	5 pptv	3	5
<i>trans</i> -2-butene	5 pptv	3	5
<i>cis</i> -2-butene	5 pptv	3	5
<i>i</i> -Pentane	5 pptv	3	5
<i>n</i> -Pentane	5 pptv	3	5
1,3-Butadiene	5 pptv	3	5
Isoprene	5 pptv	5	5
2-Methylpentane	5 pptv	3	5
3-Methylpentane	5 pptv	3	5
<i>n</i> -Hexane	5 pptv	3	5
<i>n</i> -Heptane	5 pptv	3	5
Benzene	5 pptv	3	5
Toluene	5 pptv	3	5
Ethylbenzene	5 pptv	3	5
<i>m</i> -Xylene	5 pptv	3	5
<i>p</i> -Xylene	5 pptv	3	5
<i>o</i> -Xylene	5 pptv	3	5
1,3,5-Trimethylbenzene	5 pptv	3	10
1,2,4-Trimethylbenzene	5 pptv	3	10

of these measurements varies by compound from 0.1% to 5%. The measurement of CO₂ was carried out using a modified LI-COR model 6252 non-dispersive infrared (NDIR) spectrometers previously described by Anderson et al. (2005). The instrument precision and accuracy are 1% (1 σ) and 1.5%, respectively.

3. Results and discussions

Along with run specific information, Table 2 lists the dilution-corrected mixing ratios of 38 carbon species that were measured in each of the eleven samples collected during EXCAVATE. As noted earlier, eight of the samples were obtained from the

Table 2
Summary of observations

Species or parameters	Sulfur content = 810 ppmw				Sulfur content = 1820 ppmw				Background samples		
	Engine power setting ^a				Engine power setting ^a				#1	#2	#3
	4–7%	26%	47%	61%	4–7%	26%	47%	61%			
Exhaust CO ₂ (ppmv)	2761	3206	5006	6346	2058	3111	4900	6509	—	—	—
Sample CO ₂ (ppmv)	1235	1404	1384	1305	1222	865	1088	1102	—	—	—
dilution ratio	2.24	2.28	3.62	4.86	1.68	3.60	4.50	5.91	—	—	—
CO (ppmv)	16.7	1.36	1.76	2.22	23.4	2.15	2.03	2.68	0.17	0.18	0.28
CH ₄ (ppmv)	1950	2600	1800	2410	2159	2320	1400	1390	1707	1854	1769
OCS (pptv)	999	985	503	1040	895	1454	518	721	516	504	478
DMS (pptv)	67	5	LOD	LOD	52	LOD	9	59	59	37	31
CS ₂ (pptv)	92	46	25	39	52	212	14	71	13	6	13
CH ₃ Cl (pptv)	1133	980	594	826	692	1001	1035	1761	634	644	626
Methyl nitrate (pptv)	130	14	18	65	169	17	31	147	33.9	14.8	8.2
Ethyl nitrate (pptv)	19	8	8	14	23	10	8	20	4.5	3.7	4.8
<i>iso</i> -Propyl nitrate (pptv)	26	21	21	22	19	19	16	27	14.5	14	14.9
<i>n</i> -Propyl nitrate (pptv)	4	3	4	4	4	3	3	5	1.1	1	1.2
2-Butyl nitrate (pptv)	31	25	21	19	22	23	16	18	18.3	18.6	18.9
Ethane (ppbv)	17.2	3.14	2.24	1.92	23.4	3.42	1.78	1.80	2.45	2.14	2.47
Ethene (ppbv)	368	0.88	0.49	0.76	577	1.78	0.56	1.11	0.41	0.30	0.59
Ethyne (ppbv)	129	1.18	0.75	0.77	198	1.25	0.63	0.60	0.78	0.66	1.06
Propane (ppbv)	4.97	1.70	1.18	1.05	2.72	1.58	0.91	0.96	1.48	1.19	1.53
Propene (ppbv)	68.0	0.22	0.14	0.24	110	0.34	0.24	0.39	0.08	0.04	0.12
<i>i</i> -Butane (ppbv)	0.75	0.32	0.36	0.27	0.29	0.42	0.27	0.25	0.29	0.20	1.21
<i>n</i> -Butane (ppbv)	2.31	0.92	0.81	0.72	1.77	0.91	0.59	0.56	0.82	0.61	1.80
1-Butene (ppbv)	13.3	0.05	0.07	0.07	21.6	0.09	0.05	0.09	0.03	0.01	0.05
<i>i</i> -Butene (ppbv)	4.81	1.10	0.39	0.70	7.07	0.60	1.00	1.54	0.05	0.05	0.16
<i>trans</i> -2-butene (ppbv)	1.34	0.05	0.03	0.02	2.10	0.03	0.03	0.04	0.01	0.01	0.04
<i>cis</i> -2-butene (ppbv)	1.06	0.02	0.01	LOD	1.72	0.03	0.04	0.03	0.01	0.01	0.04
<i>i</i> -Pentane (ppbv)	1.15	0.44	0.32	0.27	0.48	0.46	0.24	0.19	0.31	0.22	0.92
<i>n</i> -Pentane (ppbv)	0.35	0.15	0.13	0.10	0.34	0.18	0.09	0.10	0.13	0.10	0.66
1,3-Butadiene (ppbv)	15.2	LOD	LOD	LOD	23.8	LOD	LOD	LOD	0.01	—	0.06
Isoprene (ppbv)	2.47	0.04	LOD	LOD	2.76	0.27	LOD	LOD	0.01	0.01	0.02
2-Methylpentane (ppbv)	0.08	0.08	0.07	0.06	0.15	0.09	0.06	0.06	0.09	0.05	0.16
3-Methylpentane (ppbv)	0.14	0.06	0.04	LOD	0.10	0.09	LOD	LOD	0.07	0.06	0.13
<i>n</i> -Hexane (ppbv)	0.22	0.10	0.04	0.10	0.24	0.11	0.04	0.23	0.06	0.03	0.30
<i>n</i> -Heptane (ppbv)	1.85	0.61	1.76	2.05	1.26	0.98	1.17	5.05*	0.47	0.75	28.2
Benzene (ppbv)	11.3	0.36	0.27	0.50	17.6	0.51	0.29	0.30	0.18	0.14	0.23
Toluene (ppbv)	4.06	0.94	0.76	0.82	5.13	1.27	0.79	1.38	0.34	0.25	3.57
Ethylbenzene (ppbv)	0.65	0.13	0.07	0.10	0.71	0.26	0.19	0.14	0.08	0.04	0.12
<i>m</i> -Xylene (ppbv)	0.83	0.22	0.16	0.30	0.95	0.54	0.41	0.38	0.12	0.05	0.22
<i>p</i> -Xylene (ppbv)	0.62	0.18	0.14	0.21	0.65	0.39	0.36	0.31	0.08	0.04	0.16
<i>o</i> -Xylene (ppbv)	1.13	0.29	0.23	0.33	1.21	0.67	0.52	0.48	0.08	0.05	0.17
1,3,5-Trimethylbenzene (ppbv)	0.29	0.12	0.08	0.17	0.42	0.45	0.29	0.18	0.10	0.03	0.11
1,2,4-Trimethylbenzene (ppbv)	0.71	0.37	0.34	0.41	0.95	1.04	0.73	0.58	0.05	0.02	0.08

^aEngine power setting is given in percent of maximum rated thrust.

*Sample reading abnormally high due to potential influence of contamination and/or background fluctuation.

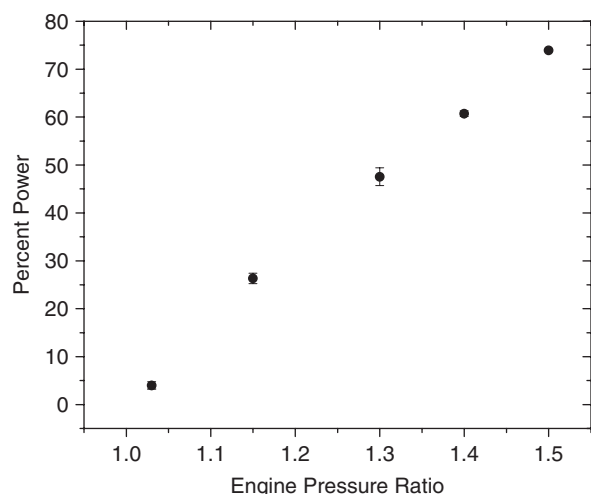


Fig. 1. Plot showing relationship between engine pressure ratio (EPR) and percent of maximum thrust as calculated using fuel flow rates specified on ICAO data sheets for the RB211-535-E4 engine.

engine exhaust plume as it ran at engine pressure ratios (EPR) of 1.03, 1.15, 1.3 and 1.4 and burned low sulfur and high sulfur JP-5 fuels. Based on fuel burn statistics obtained from the ICAO data base, we calculate that the selected EPRs correspond to power settings of approximately 7% (idle), 26% (~approach), 47% (~low cruise), and 61% (~high cruise) of maximum rated thrust (see Fig. 1), respectively. Because of safety considerations, we were unable to operate the engine at higher thrust settings. Three background air samples were collected at the beginning, in middle and near the end of the experiment to determine the ambient concentrations of each measured species. The CO_2 values shown in the list were determined using two different non-dispersive infrared instruments, one monitoring concentrations in the dry N_2 -diluted sample air that was aspirated into the whole-air canisters (as diluted by dry N_2) and the other measuring mixing ratios in undiluted air collected from the engine exhaust with a separate inlet probe. The ratio of the CO_2 concentrations yield the sample dilution ratios (see Table 2) that were used for correcting the carbon species concentrations to those that would have been observed in undiluted exhaust flow 10 m behind the engine exhaust plane. We estimate that the overall uncertainty associated with the dilution factor derived in this manner is about $\pm 20\%$, which can mainly be attributed to variations in sample line flows and pressures during the time of sample collection. This is the dominant

source of the overall uncertainty associated with the canister sampling.

As indicated earlier, three background samples were collected in the immediate vicinity of the B757 to determine the ambient conditions, e.g., levels of NMHC's and CO. It should be noted that the third background sample contained highly elevated levels of a wide range of species, including CO and several reactive NMHC species (e.g., *i*-Butane, *n*-butane, and *n*-heptane). Although the canister could have been contaminated, it is possible that the sample itself was affected by local emissions. Because of this uncertainty, we have treated this sample as an outlier.

Although the high sulfur JP-5 fuel contains 2.2 times more sulfur than the low sulfur fuel, the total observed organic sulfur species (mostly OCS) show no systematic difference between the low sulfur and high sulfur fuels. There are also no consistent trends for OCS and CS_2 with varying engine power although their mixing ratios are factors of 1.8 and 4.5 (excluding one outlier), respectively, higher than background concentrations. This suggests that the sources of the OCS and CS_2 are insensitive to the fuel sulfur content, at least for the levels tested in this study. In light of reports that CS_2 reacts with O to form OCS, it is conceivable that the OCS enhancements were produced during high temperature combustion processes (Azatyan, 2003). For the more reduced compound CS_2 , it is unclear whether its enhancement is due to high temperature synthesis within the combustor or to the presence of trace amounts of unburned fuel. In contrast, the DMS levels were dramatically reduced from approximately ambient levels at idle to near the instrument detection limit as engine power was increased. We speculate that ambient DMS is essentially burned (oxidized) out of the exhaust stream at combustor temperatures associated with high engine powers.

As expected, CO_2 was the most abundant carbon-based effluent from the RB211-535E4 engines (Table 2). Observed exhaust concentrations of this species were about 2 orders of magnitude higher than CO and CH_4 , the next most prevalent compounds. CO_2 concentrations within the core-flow of the exhaust (non by-pass flow) are governed by the fuel air ratio (FAR) within the combustor; FAR settings accessed during EXCAVATE produced exhaust plume CO_2 mixing ratios ranging from 16000 ppmv at idle to 36000 ppmv at high cruise thrust. Levels within the plume at 10 m were lower and significantly more variable, as they

depended not only upon the engine power setting, but also upon mixing with ambient air. For the high sulfur fuel case shown in Table 2, CO₂ values measured at 7 and 61% power were 2058 and 6509 ppmv at the 10 m sampling location compared to 17500 and 32000 ppmv at 1 m, respectively (data not shown). These observations suggest that, over the 10 m distance, the plume dilutes by factors of 8.5 and 4.9 at the low and high power settings, respectively. Moreover, plume dilution and CO₂ concentrations were significantly more variable at idle than the other power settings. This is because even a slight cross-wind could shift the plume center line away from the 10 m sampling inlet. As evidence, we note that CO₂ was about 35% higher for the low sulfur case than for the high sulfur case at 10 m (Table 2), even though measurements recorded from the 1 m probe showed no difference in exhaust-plane CO₂ concentrations between the two runs.

In contrast to CO₂, we observed large decreases in CO, alkane, alkene, and aromatic compounds (e.g., CO, ethane, ethene, and benzene) with increasing engine power for both fuels. For example, the observed CO levels decreased by a factor of ~8 for both low and high sulfur fuels as engine power was increased from idle to 61%. Over the same power range, the relative reduction in alkene species is even more dramatic. Propene mixing ratios decreased by a factor ~280 and isoprene dropped from ~2.5 ppbv to less than <5 pptv (i.e., detection limit) in going from 7 to 61% of maximum thrust. It is noted that the isoprene levels observed at idle were far higher than the background values. However, this is not a total surprise as isoprene is observed in automobile exhaust (e.g., McLaren et al., 1996; Borbon et al., 2001). The changes in alkane and aromatic compounds are much more modest, typically under a factor of 10. As a result, the alkene species constitute over 90% of the observed total NMHC at idle but less than 20% at higher engine power settings. However, note that exhaust mixing ratios of the NMHC species are significantly larger than background concentrations even for the highest engine power setting. For the high and low sulfur fuel cases, alkene and aromatic species mixing ratios were slightly enhanced in the high sulfur samples at idle, but exhibited no systematic differences at higher engine powers. It is unlikely that the NMHC emission differences observed at idle can be attributed to fuel composition—they are more likely caused by slight differences in engine power setting. CO mixing ratios were also quite

different between the two cases as were levels of soot and non-volatile particle emissions (Anderson et al., 2005). A subsequent study conducted on a CFM-56 engine revealed that its NMHC emissions are highly sensitive to combustor temperature and that factor of two or more changes in pollutant emission indices could be obtained by reducing the engine power from 7% to 4% (Changley Wey, NASA Glen Research Center, private communication, 2004). Finally, note that *n*-heptane mixing ratio for the high sulfur fuel case at 61% power was abnormally elevated; its value is 4–5 times higher than the other high sulfur fuel samples obtained at lower power settings. By contrast, *n*-heptane mixing ratios for the low sulfur fuel remain to be fairly constant for all samples. No similar trends were found in previous studies. Since the cause for this abnormal reading cannot be identified with available data, we have marked this reading with an “*” to indicate its abnormality.

Turbine engines primarily emit CO and NMHC species as a result of incomplete combustion of fossil fuels. The relative amount of trace-gas emissions depends upon combustor temperature and pressure, fuel to air ratio, and the extent to which fuel is atomized and mixed with inlet air. According to certification data archived by ICAO, all engines produce less CO and NMHC emission per kg of fuel burned as their power levels are increased above idle. In comparison to our observations, Spicer et al. (1994) found that TF-39 and CFM-56 engines exhibited larger decreases in NMHC and CO emissions with increasing engine power. These differences can be mostly accounted for by fact that the TF-39 and CFM-56 engines produce much higher levels of emissions at idle than do the RB211-535E4. We also note that the RB-211-535E4 was specifically designed to produce lower levels of NO_x and trace-carbon emissions.

With regard to CH₄, Table 2 shows some modest difference between the low and high sulfur fuels. Overall, exhaust CH₄ readings are typically within 20% of background levels. Two of the samples recorded for the high sulfur fuel showed values lower than background at low and high cruise engine power levels, which suggest that under some conditions the engine actually burns methane out of the background air. This observation is not surprising, since negative methane emission indices were observed for this same aircraft in flight during the SUCCESS mission (Vay et al., 1998) and Spicer et al. (1992) note that most high efficiency engines

tend to produce minor amounts of CH₄ at idle and consume it at higher engine powers. The difference among the observations cannot be readily explained, but the data suggests that the CH₄ emissions from RB211-E535E4 engine are quite minor.

For CH₃Cl, mixing ratios within the plume were typically comparable to background levels, but two samples exhibited enhancements >2σ above the highest ambient reading. It may seem implausible that halo-carbon species would be emitted as a by-product of fossil fuel combustion, but there are several possible sources of chlorine associated with aviation. Refineries often use salt driers to remove water from fuel, making it possible to have small amounts of carry-over into the distillates. Also, if the fuel was transported by barge, there could be contamination from the salt water used to ballast the barge—our fuel was obtained from the military's Craney Island fuel depot near Norfolk, Virginia. Another possibility is that the chlorine was derived from volatilization of sea-salt particles randomly aspirated into the engine's in-take air stream. This is plausible, considering the short distance from the test site to Chesapeake Bay and the windy conditions that prevailed on the day of the experiment. Additional tests are needed to further verify and better understand these findings.

Table 2 shows that plume concentrations of alkylnitrate species were well above background, with methyl nitrate, *iso*-propyl nitrate, and 2-butyl nitrate accounting for 80–90% of the total enhancement. The presence of these species is not surprising, considering the availability of alkanes and NO_x within the exhaust plume. Methyl nitrate, the most abundant species, was three-fold higher than ambient at high engine power (61%), five times higher at idle (7%), but tended to be somewhat depleted at medium powers (26% and 47%). Interestingly, medium thrust levels are also where the product of alkane and NO_x concentrations within the plume reach a minimum.

Table 3 lists mass emission indices (EIs) in units of g kg⁻¹ fuel burned for CO and CH₄ and mg kg⁻¹ fuel burned for the remainder of the measured species. EIs were calculated using the following formula:

$$EI_x = EI_{CO_2} \times \Delta[X]/\Delta[CO_2] \times [AMU_x]/[AMU_{CO_2}], \quad (1)$$

where EI_{CO₂} is calculated from the fuel carbon content assuming combustion to be 100% efficient,

Δ[X] and Δ[CO₂] are the enhancements of compound X and CO₂ within the plume, respectively, and AMU_x and AMU_{CO₂} are the molecular weights of X and CO₂, respectively. A nominal value of 3160 g kg⁻¹ fuel burned was used for EI_{CO₂} and an average background CO₂ level of 370 ppmv was subtracted from the canister concentrations to obtain Δ[CO₂]. The assumed EI_{CO₂} value is consistent with previous studies that show engine combustion efficiency variation is within a few percent for the engine power setting from idle to 80% of the maximum (e.g., Spicer et al., 1994, 1992). Δ[X] values were determined by subtracting average background mixing ratios of X from the dilution corrected values measured in the plume. Cases where X was consumed within the combustor yielded negative EI values. In this study, we have evaluated the emission index of a species if its plume enhancement, Δ[X], is twice the combined uncertainties from both the engine exhaust and background values, otherwise only the upper limits are reported. The uncertainty associated with the engine exhaust sample is dominated by the dilution factor while the uncertainties in background are mostly due to ambient variation as well as the other emission sources not known to this study.

Examining the tables we note that, other than CO₂, CO and CH₄ are by far the most abundant trace carbon species in engine exhaust, the former arising from incomplete combustion of jet fuel and the latter derived primarily from background air. At engine idle, CO comprises ~1% of the total carbon emissions, but contributes <0.1% at cruise (61%), indicating that the engine runs much more efficiently at the higher temperatures and pressures associated with high power settings. The emission index, EI_{CO}, is 14 and ~28 g kg⁻¹ for the two samples (for low sulfur and high sulfur fuels) taken at idle and between 0.7 and 0.8 g kg⁻¹ in samples acquired at power settings more typical of cruise and climb (47–61% of maximum thrust). These compare well to the RB211-535E4 values archived in the ICAO Engine Emissions Data Bank (<http://www.qinetiq.com/aircraft/aviation.html>) of 13–20 g kg⁻¹ for idle; 1.1–2.7 g kg⁻¹ for approach; 0.3–1.2 g kg⁻¹ for climb out; and 0.3–1.0 g kg⁻¹ for take off. The modest difference between our results and the ICAO values may arise from a number of factors, including slight differences in power settings, our possible collection of samples when the engine was not operating at thermal equilibrium, differences between individual engines or between

Table 3
Summary of emission indices

Species	Low sulfur JP-5 fuel (sulfur content = 810 ppmw) ^a			High sulfur JP-5 fuel (sulfur content = 1820 ppmw)			
	Engine pressure setting			Engine pressure setting			
	4–7%	26%	47%	61%	26%	47%	61%
CO (g kg ⁻¹)	14 ± 3	0.8 ± 0.2	0.7 ± 0.2	0.7 ± 0.2	28 ± 6	1.5 ± 0.3	0.8 ± 0.2
CH ₄ (mg kg ⁻¹)	<50	<42	<26	<20	<71	<44	<19
OCS (mg kg ⁻¹)	0.9 ± 0.4	0.7 ± 0.3	<0.01	0.4 ± 0.2	1.0 ± 0.5	1.5 ± 0.5	<0.008
DMS (mg kg ⁻¹)	<0.03	-0.07 ± 0.02	<0.05	<0.04	<0.04	<0.08	<0.01
CS ₂ (mg kg ⁻¹)	0.19 ± 0.04	0.07 ± 0.02	0.02 ± 0.01	0.03 ± 0.01	0.14 ± 0.04	0.40 ± 0.09	0.05 ± 0.01
CH ₃ Cl (mg kg ⁻¹)	0.8 ± 0.4	<0.03	<0.02	<0.01	<0.05	<0.03	0.7 ± 0.2
MeONO ₂ (mg kg ⁻¹)	0.24 ± 0.07	<0.03	<0.02	0.04 ± 0.02	0.5 ± 0.1	<0.03	0.11 ± 0.03
EiONO ₂ (mg kg ⁻¹)	0.04 ± 0.01	0.010 ± 0.004	0.006 ± 0.002	0.011 ± 0.003	0.07 ± 0.02	0.013 ± 0.005	0.017 ± 0.004
<i>i</i> -PrONO ₂ (mg kg ⁻¹)	0.04 ± 0.03	<0.001	<0.001	<0.001	<0.002	<0.001	0.015 ± 0.007
<i>n</i> -PrONO ₂ (mg kg ⁻¹)	0.009 ± 0.003	0.004 ± 0.001	0.005 ± 0.001	0.004 ± 0.001	0.014 ± 0.004	0.004 ± 0.001	0.005 ± 0.001
2-BuONO ₂ (mg kg ⁻¹)	0.05 ± 0.02	<0.002	<0.001	<0.001	<0.003	<0.002	<0.001
Ethane (mg kg ⁻¹)	14 ± 3	<0.2	<0.1	<0.08	27 ± 6	<0.2	<0.08
Ethene (mg kg ⁻¹)	310 ± 62	0.38 ± 0.14	<0.03	0.14 ± 0.06	689 ± 138	1.1 ± 0.3	0.25 ± 0.08
Ethyne (mg kg ⁻¹)	100 ± 20	<0.06	<0.03	<0.03	219 ± 44	0.4 ± 0.2	<0.03
Propane (mg kg ⁻¹)	4.8 ± 1.3	<0.23	<0.14	<0.11	2.6 ± 1.1	<0.23	<0.10
Propene (mg kg ⁻¹)	86 ± 17	0.2 ± 0.1	<0.02	0.09 ± 0.04	196 ± 39	0.3 ± 0.1	0.16 ± 0.04
<i>i</i> -Butane (mg kg ⁻¹)	0.9 ± 0.3	<0.09	<0.05	<0.04	<0.15	<0.09	<0.04
<i>n</i> -Butane (mg kg ⁻¹)	2.8 ± 0.8	<0.2	<0.1	<0.1	2.6 ± 0.9	<0.23	<0.1
1-Butene (mg kg ⁻¹)	22 ± 4	0.05 ± 0.02	0.04 ± 0.01	0.03 ± 0.01	52 ± 10	0.11 ± 0.03	0.05 ± 0.01
<i>i</i> -Butene (mg kg ⁻¹)	8.0 ± 2	1.5 ± 0.3	0.3 ± 0.1	0.4 ± 0.1	17 ± 3	0.8 ± 0.2	1.0 ± 0.2
<i>trans</i> -2-Butene (mg kg ⁻¹)	2.2 ± 0.5	0.05 ± 0.01	0.014 ± 0.005	0.007 ± 0.003	5 ± 1	0.024 ± 0.008	0.021 ± 0.006
<i>cis</i> -2-Butene (mg kg ⁻¹)	1.8 ± 0.4	0.015 ± 0.007	<0.002	-0.005 ± 0.002	4.1 ± 0.8	0.031 ± 0.009	0.014 ± 0.004
<i>i</i> -Pentane (mg kg ⁻¹)	1.9 ± 0.5	<0.1	<0.07	<0.05	<0.2	<0.1	<0.05
<i>n</i> -Pentane (mg kg ⁻¹)	0.5 ± 0.2	<0.04	<0.03	<0.02	0.7 ± 0.2	<0.04	<0.02
1,3-Butadiene (mg kg ⁻¹)	25 ± 5	<0.01	<0.007	<0.005	55 ± 11	<0.01	<0.005
Isoprene (mg kg ⁻¹)	5 ± 1	0.05 ± 0.02	<0.01	<0.01	8 ± 2	0.5 ± 0.1	<0.008
2-Methylpentane (mg kg ⁻¹)	<0.06	<0.05	<0.03	<0.02	0.3 ± 0.1	<0.05	<0.02
3-Methylpentane (mg kg ⁻¹)	0.20 ± 0.08	<0.02	-0.03 ± 0.01	<0.07	<0.03	<0.02	<0.06
<i>n</i> -Hexane (mg kg ⁻¹)	0.4 ± 0.1	<0.046	<0.028	<0.02	0.8 ± 0.2	0.15 ± 0.07	0.18 ± 0.05
<i>n</i> -Heptane (mg kg ⁻¹)	4 ± 1	<0.5	1.8 ± 0.6	1.7 ± 0.6	3 ± 1	<0.5	5 ± 1*
Benzene (mg kg ⁻¹)	26 ± 5	0.4 ± 0.2	<0.04	0.3 ± 0.1	58 ± 12	0.7 ± 0.2	0.16 ± 0.08
Toluene (mg kg ⁻¹)	10 ± 2	1.5 ± 0.5	0.7 ± 0.2	0.6 ± 0.2	19 ± 4	2.4 ± 0.6	1.2 ± 0.3
Ethylbenzene (mg kg ⁻¹)	1.9 ± 0.4	<0.07	<0.04	<0.03	2.9 ± 0.7	0.6 ± 0.2	0.10 ± 0.05
<i>m</i> -Xylene (mg kg ⁻¹)	2.4 ± 0.6	0.4 ± 0.2	<0.08	0.3 ± 0.1	3.9 ± 0.9	1.3 ± 0.3	0.4 ± 0.1
<i>p</i> -Xylene (mg kg ⁻¹)	1.8 ± 0.4	0.34 ± 0.13	0.14 ± 0.07	0.20 ± 0.07	2.7 ± 0.6	0.9 ± 0.2	0.5 ± 0.1
<i>o</i> -Xylene (mg kg ⁻¹)	3.4 ± 0.7	0.6 ± 0.2	0.27 ± 0.09	0.33 ± 0.09	5 ± 1	1.7 ± 0.4	0.8 ± 0.2
1,3,5-Trimethylbenzene (mg kg ⁻¹)	0.8 ± 0.3	<0.2	<0.10	<0.08	1.8 ± 0.5	1.2 ± 0.3	<0.07
1,2,4-Trimethylbenzene (mg kg ⁻¹)	2.4 ± 0.5	1.0 ± 0.2	0.6 ± 0.1	0.5 ± 0.1	5 ± 1	3.2 ± 0.7	0.76 ± 0.17

^aEngine power setting is given in percent of maximum rated thrust.

* Estimate influenced by abnormally high *n*-heptane reading due to potential contamination and/or background fluctuation.

old and new engines, or differences in analytical techniques.

As for CH_4 , the difference between the exhaust readings and background was less than the 2σ uncertainty for all samples. Thus, only the estimated upper limits of EI_{CH_4} values are reported in Table 3. Although the ICAO data-base does not report EIs for this species, our results are consistent with those of others (Spicer et al., 1992, 1994; Vay et al., 1998; Slemr et al., 2001), which suggest that turbine engines are not a significant source of CH_4 .

Sulfur species EIs are listed Table 3 and show that OCS values are less than 1.5 mg kg^{-1} and CS_2 has an upper limit of 0.4 mg kg^{-1} . These values, although being significant, are extremely small in comparison with the fuel sulfur content. Previous studies have indicated the major sulfur emissions from jet engines are primarily in the form of SO_2 , H_2SO_4 , and particulate sulfate. It is not clear whether these reduced sulfur compounds are formed from combustion processes or simply a component of unburned fuel. In the case of DMS, the exhaust levels systematically decrease from the background levels to the detection limit as engine power increases. We believe that DMS was depleted in most samples collected at high engine powers suggesting that the engine consumes this species from background air at high combustor temperatures. This is reflected in the negative EI values shown in Table 3.

As noted above, alkylnitrate species were slightly enhanced within the plume. As for EIs, the sum for all five species is $<0.5 \text{ mg kg}^{-1}$ at idle and $<0.1 \text{ mg kg}^{-1}$ at high cruise. Comparing this to the RB211-535E4 ICAO values of 4 and $\sim 18 \text{ g kg}^{-1}$ NO_x at idle and climb out power, respectively, we conclude that an insignificant amount of aircraft emissions are sequestered as RNO_x species.

The remaining species listed in the tables are hydrocarbons and showed a great range of enhancement ratios within the engine exhaust plume relative to background air. Data are presented for 27 NMHC species with 2–9 carbon atoms. Fig. 2 shows that at idle, the engine primarily emits species containing 2–4 carbon atoms (contributing over 80% of the total), but when engine power is increased to high cruise power setting, light HC emissions are greatly reduced and nearly all NMHC emissions consist of species with 4 and more carbon atoms. Spicer et al. (1994) notes that jet fuel is primarily composed of species with five or more carbons and, by weight, 70% of the compounds it

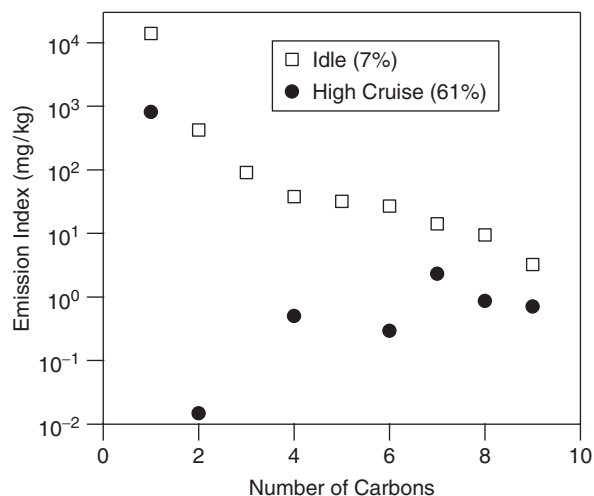


Fig. 2. Carbon species emissions at idle and high cruise power (i.e., 7% and 61% of the maximum rate thrust, respectively) plotted as a function of the number of carbons in each compound for low sulfur fuel. CO and CH_4 compose the single carbon group which accounts for the majority of mass emissions at both power settings.

contains have 11–14 carbons. Thus, the low molecular weight species found in the exhaust are derived from reactions occurring within the combustor rather than being residual, unburned fuel. Aromatic compounds are present in the fuel, but are also byproducts of incomplete hydrocarbon oxidation, thus the enhancements in benzene and toluene mixing ratios can be either “combustion” or “fuel” derived. As discussed earlier, the high sulfur fuel *n*-heptane observation is abnormally elevated, the high estimates of EI is clearly influenced and marked. Finally, it should be noted that EI estimates, especially when power level above idle, would have significant high biases if the background were not taken out of the exhaust sample readings. We estimate the magnitude of the high bias would be commonly in the range of a factor of two or higher.

Table 4 provides a summary of the NMHC emissions from the RB211-535E4 engine for each of the exhaust samples, broken down into the functional groupings of alkanes (all single bonded hydrocarbons), alkenes (at least one double bond), alkynes (at least one triple bond), and aromatic compounds (benzene ring compounds). Fig. 3 shows a plot of the fraction of the NMHCs emitted in each functional group over the range of engine power settings. At idle, over 90% of the emissions are double or triple-bonded, straight chain

Table 4
Summary of NMHC mass emission indices

Species or parameters	Low sulfur JP-5 fuel (sulfur content = 810 ppmw)				High sulfur JP-5 fuel (sulfur content = 1820 ppmw)			
	Engine pressure setting ^a				Engine pressure setting ^a			
	4–7% (idle)	26% (approach)	47% (L. cruise)	61% (H. cruise)	4–7% (idle)	26% (approach)	47% (L. cruise)	61% (H. cruise)
CO (g kg ⁻¹)	14±3	0.8±0.2	0.7±0.2	0.7±0.2	28±6	1.5±0.3	0.8±0.2	0.8±0.2
Total NMHC EI (mg kg ⁻¹)	638±68	9±1	4.3±0.8	4.6±0.7	1379±152	19±2	5.9±0.8	10±1
Alkanes (mg kg ⁻¹)	29±4	2.0±1.0	1.9±0.7	1.4±0.6	38±6	3.5±1.1	<0.6	4.8±1.2*
Total alkenes (mg kg ⁻¹)	460±65	2.2±0.3	0.5±0.1	0.7±0.1	1025±144	2.8±0.3	1.1±0.2	1.5±0.2
Total alkynes (mg kg ⁻¹)	100±20	<0.2	<0.07	<0.05	219±44	0.4±0.2	<0.06	<0.04
Total aromatics (mg kg ⁻¹)	49±6	4.6±0.6	2.0±0.3	2.5±0.3	98±13	12±1	4.7±0.5	3.5±0.4
Alkane fraction (%)	4±1	22±11	44±19	31±14	3±1	19±6	<1	49±14
Alkene fraction (%)	72±13	24±5	11±3	15±3	74±13	15±2	19±4	15±3
Alkyne fraction (%)	16±4	<3	<2	<1	16±4	2±1	<1	<1
Aromatic fraction (%)	8±1	50±10	45±12	54±11	7±1	64±8	80±14	36±7

^aEngine power setting is given in percent of maximum rated thrust.

* Estimate influenced by abnormally high *n*-heptane reading due to potential contamination and/or background fluctuation.

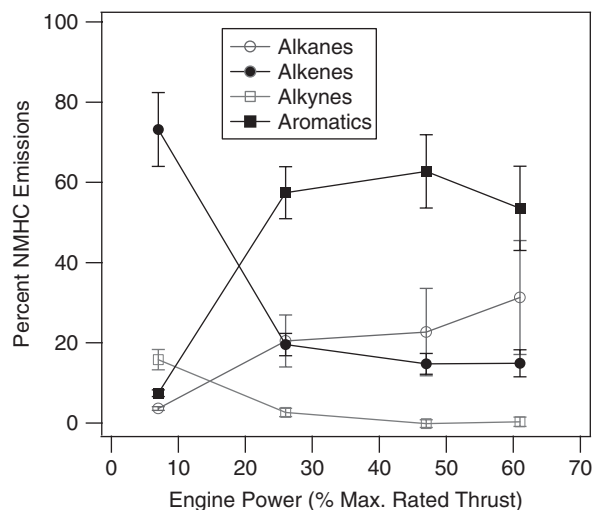


Fig. 3. Averaged hydrocarbon emissions from the RB211-535E4 engine using high and low sulfur fuels as a function of power setting, broken down into the fractional contribution from different functional groups. Note that CH₄ has been excluded from the alkane group and only low sulfur fuel point included in the plot for the highest power level (see discussion in the test).

hydrocarbons, whereas at high power, these compounds account for <20% of the total. The fractional contribution of aromatic compounds grow from <10% to >50% as power is increased from idle to climb-out settings, respectively. Alkanes are the least abundant species at low power, but generally comprise 20–40% of the total NMHC mass emissions at high powers.

In terms of individual species, at idle, the most abundant were ethene, ethyne, and propene. Their mixing ratios were enhanced by factors of 200–1000 above those measured in ambient air, and, taken together, accounted for 88% of the measured NMHC emissions on a mixing ratio basis. Ethene alone contributed nearly 50% to the total emissions, which is, excluding contributions from oxygenated HC species that we did not measure, consistent with observations from military engines acquired by Spicer et al. (1992) and the CFM-56-2 engines of the NASA DC-8 by Slemr et al. (2001). At higher engine powers, these species all but disappear, and *n*-heptane and toluene become more dominant. As noted above, these could be either fuel or combustion derived.

As shown in Table 4 and illustrated in Fig. 4, total NMHC emissions drop off precipitously as power is increased. At idle, the engine emits ~1 g kg⁻¹ of 2–9 carbon HC compounds, whereas at 61% of the maximum, which is slightly less than

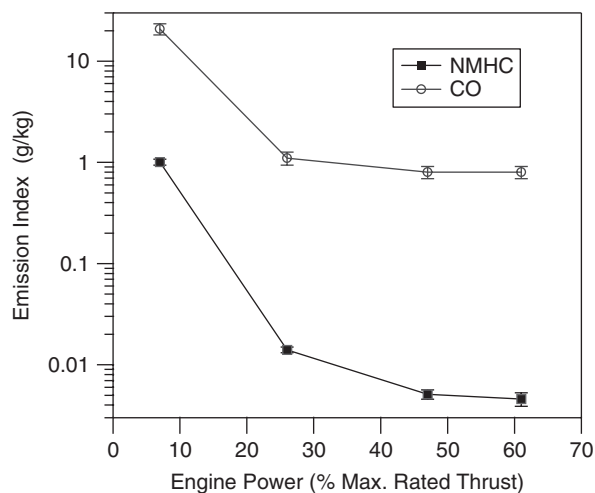


Fig. 4. Average CO and total NMHC emission indices over both high and low sulfur fuels as a function of engine power setting from idle to high cruise. Note that only low sulfur fuel point included in the plot for the highest power level (see discussion in the text).

climb-out power, it produces $\sim 5 \text{ mg kg}^{-1}$, or about factor of 200 less. Similar power-related reductions were apparent in the CO emissions (Table 3 and Fig. 4). Variations in CO and NMHC EIs were highly correlated (Fig. 5) which one might expect since the C–O bond is of comparable strength to the double carbon bonds found in alkenes that are so abundant within the plume at low engine temperatures. The lower emissions at high engine powers in general supports the results of Simpson et al. (2000), who observed no significant carbon-species enhancements in highly diluted aircraft plumes sampled in the North Atlantic Flight Corridor during the NASA SONEX airborne campaign.

Comparing our total NMHC EIs with ICAO data, we find relatively good agreement at idle, but that EXCAVATE values tend to be somewhat lower at higher engine powers. The ICAO archive reports values of 0.4–1, 0.04, and 0.01 g kg^{-1} at idle, approach, and climb-out, respectively. These compare to our observations of 0.6–1.4, 0.01–0.02, and $\sim 0.005 \text{ g kg}^{-1}$ for roughly the same power settings, respectively. ICAO engine emission qualification tests are performed with either multi-gas analyzers or bare flame ionization detectors that give an integrated signal proportional to the total hydrocarbons present in the sample. Thus, differences between the EXCAVATE and ICAO values can probably be attributed to contributions from species such as the oxygenated HC compounds that we did

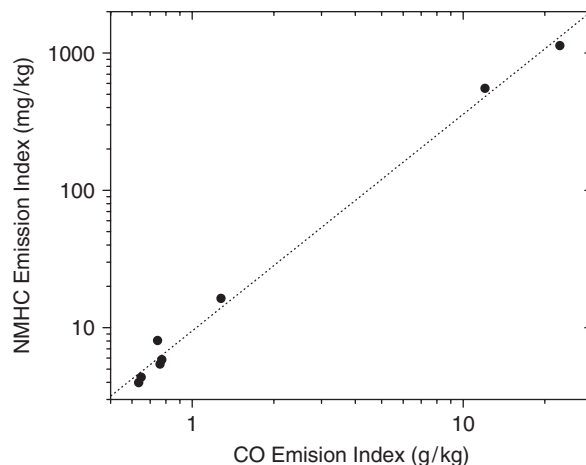


Fig. 5. Total NMHC EI plotted as a function of CO EI.

not measure as well as to the fact that ICAO data are not corrected for ambient NMHC contributions. We note that Spicer et al. (1994) resolved 182 chromatographic peaks on samples collected in the exhaust of a CFM-56 engine and found significant amounts of formaldehyde, acetaldehyde, and acetone that, at high power settings, accounted for > 50% of the total NMHC emissions.

Two separate batches of JP-5 fuel were burned in the tests, thus one might expect to see some systematic differences in the NMHC emissions based on the differences in the fuel hydrocarbon matrices. Examining Table 4, we see that total NMHC emissions were slightly higher for 1820 ppmw Sulfur fuel than the 810 ppmw sulfur fuel. These differences are particularly notable at idle where the total NMHC EI for the high S fuel is ~ 2 times (1.4 vs. 0.64 g kg^{-1}) that of the low sulfur fuel. Though these differences are significant, they may be more apparent than real. As discussed earlier, we have attributed the differences between high and low sulfur fuel to the sampling sequence as related to difference in the engine running status.

4. Summary and conclusions

As a part of the NASA-sponsored EXCAVATE study, tests were conducted to determine the relative emissions of NMHC compounds by Rolls Royce RB211-535-E4 turbofan engine mounted on the NASA B757 aircraft as a function of engine power and fuel composition. Similar to the previous studies, NMHC emission indices were observed to be strong functions of power, with idle values being dramatically larger than those seen at the highest power

settings. The speciation of NMHC emissions also shifted with power: at idle, alkenes (mainly ethene) constituted more than 70% of the observed total NMHC emissions, whereas at 61% of maximum rated thrust, aromatic species typically (mostly toluene) accounted for over 50% of the total. In addition to NMHCs, enhanced concentrations of alkynitrate species were observed in the engine exhaust. However, EIs for these species were several orders of magnitude lower than typical NO_x EIs for gas-turbine engines so that their emission by aircraft would have little impact on local reactive nitrogen budgets. Exhaust concentrations of reduced organic sulfur species (i.e., OCS and CS_2) were also enhanced slightly above ambient levels, but the EIs for these species showed no particular trend with engine power or fuel sulfur content. At higher powers, several species, including CH_4 and DMS, exhibited negative EIs suggesting that they were actually burned out of background air as it passed through the engine. Finally, corrections for ambient concentrations are shown to be critical for accurately evaluating the emission indices, especially at high engine powers and for relatively dilute exhaust plumes.

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