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# Chemical Characterization of the Fine Particle Emissions from Commercial Aircraft Engines during the Aircraft Particle Emissions eXperiment (APEX) 1 to 3

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**S** Supporting Information

**ABSTRACT:** This paper addresses the need for detailed chemical information on the fine particulate matter (PM) generated by commercial aviation engines. The exhaust plumes of seven turbofan engine models were sampled as part of the three test campaigns of the Aircraft Particle Emissions eXperiment (APEX). In these experiments, continuous measurements of black carbon (BC) and particle surface-bound polycyclic aromatic compounds (PAHs) were conducted. In addition, time-integrated sampling was performed for bulk elemental composition, water-soluble ions, organic and elemental carbon (OC and EC), and trace semivolatile organic compounds (SVOCs). The continuous BC and PAH monitoring showed a characteristic U-shaped curve of the emission index (EI or mass of pollutant/mass of fuel burned) vs fuel flow for the turbofan engines tested. The time-integrated EIs for both elemental composition and water-soluble ions were heavily dominated by sulfur and  $\text{SO}_4^{2-}$ , respectively, with a  $\sim 2.4\%$  median conversion of fuel S(IV) to particle S(VI). The corrected OC and EC emission indices obtained in this study ranged from 37 to 83 mg/kg and 21 to 275 mg/kg, respectively, with the EC/OC ratio ranging from  $\sim 0.3$  to 7 depending on engine type and test conditions. Finally, the particle SVOC EIs varied by as much as 2 orders of magnitude with distinct variations in chemical composition observed for different engine types and operating conditions.



## INTRODUCTION

The fine particulate matter (PM) emissions from commercial aviation are of environmental concern both from the standpoint of local air quality and their impact on the global climate. Airports located in large urban areas not only contribute to the lack of compliance with the  $\text{PM}_{2.5}$  (particles  $\leq 2.5 \mu\text{m}$  in aerodynamic diameter) National Ambient Air Quality Standard in the U.S. but can also cause health concerns for residents living in adjacent areas.<sup>1</sup> It is also anticipated that major expansions to many airports will be required to meet the demand for future air travel in the U.S. which is expected to double, or even triple, within the next 20 years.<sup>2</sup> In addition, the black carbon emissions generated by aircraft at altitude have been implicated in the formation of contrails and contrail-induced cirrus clouds which could produce positive radiative forcing (warming) of a magnitude similar to that of  $\text{CO}_2$ .<sup>3</sup> Therefore, a better understanding of the physical

and chemical properties of aircraft-generated PM is needed to more completely assess their impacts on local ambient air quality, human health, and the global climate.

Historically, scant PM emissions data were available for aircraft engines.<sup>4</sup> Recently, a number of studies have been conducted to provide PM emissions data for both civilian and military engines which includes both direct emission measurements<sup>5–7</sup> and airport studies of the advected plumes from operating aircraft.<sup>8,9</sup> However, these studies produced relatively little information on the detailed chemical composition of the

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fine PM, with most of the data derived from online particle mass spectrometers which provide only semiquantitative results.<sup>10–12</sup>

To address the need for improved chemical characterization of the PM emissions from aircraft turbines, the U.S. Environmental Protection Agency (EPA) participated in the Aircraft Particle Emissions eXperiment (APEX).<sup>13</sup> The APEX program is a major collaborative effort between the National Aeronautics and Space Administration (NASA) and a number of other research organizations. The EPA objectives for the three sampling campaigns (APEX-1, -2, and -3) were to improve emission estimates and chemical source profiles for aircraft-generated fine PM and, if possible, assess the effect of fuel properties and engine operating conditions on PM formation.

Presented in this paper are the detailed PM chemical characterization results generated by EPA from the three APEX campaigns. Exhaust plume samples from seven commercial turbofan engine models were collected on the ground at a distance of 30 m behind the engine exit. Sampling at distances  $\geq 30$  m is a widely accepted practice,<sup>5,12</sup> which allows for the formation of volatile PM while still maintaining plume integrity. Additional information, including the particle mass and number emissions and physical properties of the emissions, have been reported previously.<sup>14</sup> The following sections focus on the PM chemical composition in terms of the emission index (pollutant mass per mass of fuel burned) as determined by a carbon balance involving the percent carbon in the fuel and the concentration of carbon dioxide (CO<sub>2</sub>) measured in the sample stream.<sup>13</sup>

## ■ TEST ENGINES, FUELS, AND OPERATION

A total of 24 source tests were conducted during the three APEX campaigns. A CFM56-2C1 engine was used throughout the nine APEX-1 tests to investigate the effects of different fuel composition on emissions at various power settings. During APEX-2 and -3, other engine models were operated with the available Jet-A fuel normally used in commercial operations. Details of the specific engines and airframes tested, tests conducted, engine operating conditions, and fuels used during the three campaigns are provided in the Supporting Information. Also provided are the specifications for each engine with regard to bypass ratio, engine pressure ratio, etc., and whether the turbine core flow was mixed with the bypass air before (internally mixed flow) or after (externally mixed flow) being discharged to the atmosphere.

In general, the test engines were operated at a series of steady-state power conditions which were set for the environmental conditions using the expertise of the on-site engine company representative. During APEX-1, however, two engine testing matrixes were used: (1) the “EPA” test matrix which followed the four power settings of the landing and takeoff (LTO) cycle defined by the International Civil Aviation Organization; (2) the “NASA” test matrix designed to investigate the effects of engine operating parameters on particle emissions and included up to 11 power conditions. In APEX-2 and -3, the engines were operated in cycles encompassing a series of steady-state power settings to investigate their effects on particle emissions including those used during engine certification, simulated cruise, engine start/stop, and transitions between throttle settings. The thrust was changed in a stepwise fashion both up (“cold” condition) and then down (“warm” condition) in power.

For the time-integrated measurements, the time-weighted engine power (TWP) was calculated in terms of percent rated

thrust based on the amount of sampling time spent at each engine power point during the course of the test. As such, these samples represent a variety of engine operating conditions with the TWP used only as an approximate indicator of engine power.

## ■ EXPERIMENTAL SECTION

**Measurement Apparatus.** The APEX sample collection and measurement system was detailed previously.<sup>14</sup> Therefore, only a brief overview will be provided here with emphasis on chemical characterization of the PM<sub>2.5</sub> emissions.

The EPA Diesel Emissions Aerosol Laboratory (DEAL) was the sampling platform used in the three APEX campaigns.<sup>14</sup> The DEAL sample extraction system used a tapered probe anchored to the tarmac to collect emissions from a single point, primarily 30 m downstream from the engine exit plane at the exhaust plume centerline. Following collection, the plume sample passed through 18 to 26 m of 5-cm (outside diameter) stainless steel tubing at ambient temperature into a PM<sub>2.5</sub> “cut point” (i.e., particle diameter representing a 50% collection efficiency for equivalent unit density spheres  $\leq 2.5$   $\mu\text{m}$  in aerodynamic diameter) virtual impactor. It was then directed to a stainless steel sampling tunnel (9 m long, 15 cm inside diameter) and delivered to the various instruments via a series of “button hook” stack sampling nozzles (staggered in height inside the sampling tunnel) and custom designed four-way flow splitters. A similar system was also used for sampling the background atmosphere above the DEAL trailer.<sup>14</sup>

The typical DEAL instrumentation configuration used during the APEX campaigns for collection and speciation of both the engine exhaust and the ambient background air is provided in the Supporting Information along with a complete list of all measurement parameters, instrumentation, and test conditions. In this context, the term “speciation” refers to the determination of the gas- and particle-phase chemical composition by time-integrated sampling. Note that chemical speciation was only conducted in a limited number of tests and that certain samples and/or experimental results were eliminated or combined, as appropriate.

**Continuous Monitoring.** The concentration of black carbon (BC) and particle surface polycyclic aromatic hydrocarbons (PAHs) was continuously measured during the three APEX campaigns using two optical instruments: a Magee AE-2 aethalometer; and an EcoChem PAS 2000. The data from both instruments were background corrected by simple subtraction of the concentrations measured before and after each test. Although both instruments were designed for monitoring ambient air quality and are known to have certain biases and limitations,<sup>15,16</sup> they did provide useful data on emission trends.

**Time Integrated Sampling.** Time integrated PM sampling was conducted over the entire test period for selected engine/fuel combinations using Teflon filters, quartz filters, and polyurethane foam (PUF) plugs as outlined in the Supporting Information. This sampling included engine start/stop, power transitions, and steady-state operation. All samples were ambient background corrected using the separate sampling system described previously.<sup>14</sup>

**PM Analytical Procedures.** Following gravimetric analysis (see Supporting Information for details), the Teflon filters were analyzed using X-ray fluorescence (XRF) spectroscopy to quantitatively determine PM<sub>2.5</sub> elemental composition. In the XRF analyses performed for APEX-1, a Philips 2404 wavelength-dispersive

XRF spectrometer, running the UniQuant7 program, was used to determine elements greater than atomic number 9 present in the PM<sub>2.5</sub> sample.<sup>13</sup> For APEX-2 and -3, the analyses were conducted using a commercially available Kevex EDX-771 energy dispersive XRF which utilized secondary excitation from selectable targets or fluorescers. Although the net sample weights for the APEX-2 Teflon filters could not be determined, the samples were still valid and an XRF analysis was performed on these filters since the net sample weight is not needed for these analyses.

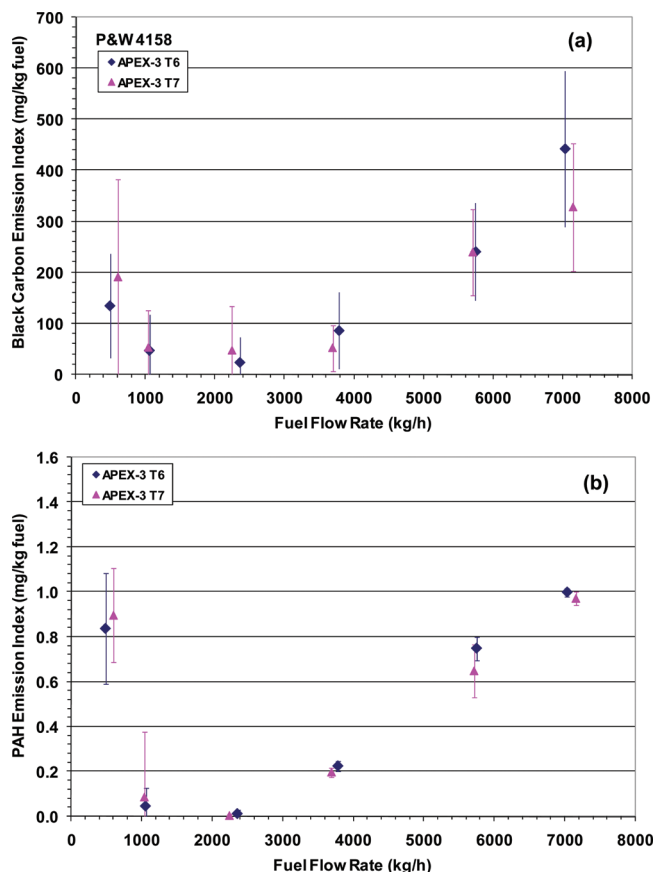
After performing nondestructive analyses (weighing and XRF), the Teflon membrane filter samples were further analyzed for water-soluble ions using ion chromatography [(IC) DX-120; Dionex Inc.]. Teflon filter sample extractions were performed in water (high pressure liquid chromatography-grade, low-conductivity) and aided by sonication (30 min). The extract was injected onto an ion-exchange resin column, on which an isocratic separation of water-soluble cations ( $K^+$ ,  $NH_4^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$ ) and anions ( $NO_3^-$ ,  $SO_4^{2-}$ ,  $NO_2^-$ , and  $Cl^-$ ) was performed with methanesulfonic acid- and  $Na_2CO_3/NaHCO_3$ -buffered water, respectively. The ions in the sample were measured with a conductivity detector and quantified using an external standard method.

The prefired quartz fiber filter samples were examined for organic carbon/elemental carbon (OC/EC) content with a thermal-optical carbon analyzer (Model 107-A, Sunset Laboratory, Inc.) using NIOSH Method 5040, subsequent to being analyzed for semivolatile organic compounds (SVOCs).<sup>17</sup> To remove the background OC, the quartz filters and aluminum foil petri dish liners were prefired in a kiln at 550 °C for 12 h before use. The SVOCs in the PM<sub>2.5</sub> collected on quartz filters were determined quantitatively for APEX-1 and -3 and APEX-2 using thermal extraction (TE)- and solvent extraction (SE)-GC-MS, respectively.<sup>13</sup> Earlier studies showed that the TE methodology is the more sensitive of the two techniques (ref 18 and refs therein).

Semivolatile organic compounds partition between the gas- and particle-phases. PUF plugs were installed downstream of the quartz filters for collecting the SVOC gases not adsorbed by the quartz filters. However, a thorough investigation of the PUFs revealed they were unsuitable for this type of research, and thus no data are reported for these analyses. Additional detail on all of the analytical procedures used is provided in the Supporting Information.

## RESULTS AND DISCUSSION

**Real-Time BC and Surface-Bound PAHs.** The emissions data from the real time instruments can be highly variable, at times unresponsive to changes in power, and generally compare poorly to the quartz filter results. Given these limitations, caution should be exercised when using these data to estimate emissions. However, an analysis of trends in the data is informative as illustrated in Figure 1 for the PW 4158 engine.<sup>13</sup> As reported previously for the total PM<sub>2.5</sub> emissions,<sup>14</sup> characteristic U-shaped curves of EI vs fuel flow were observed for turbofan engines, where the emissions are slightly elevated near idle, decrease to a minimum at midrange power, and then abruptly increase at climb-out or takeoff power. In the case of BC, the EI is normally greatest at higher power conditions, which is consistent with the results obtained by other investigators.<sup>5,10,12,19</sup> In contrast, the PAH emissions at idle and high power are somewhat similar depending on engine type.<sup>13</sup> Although the exact reason



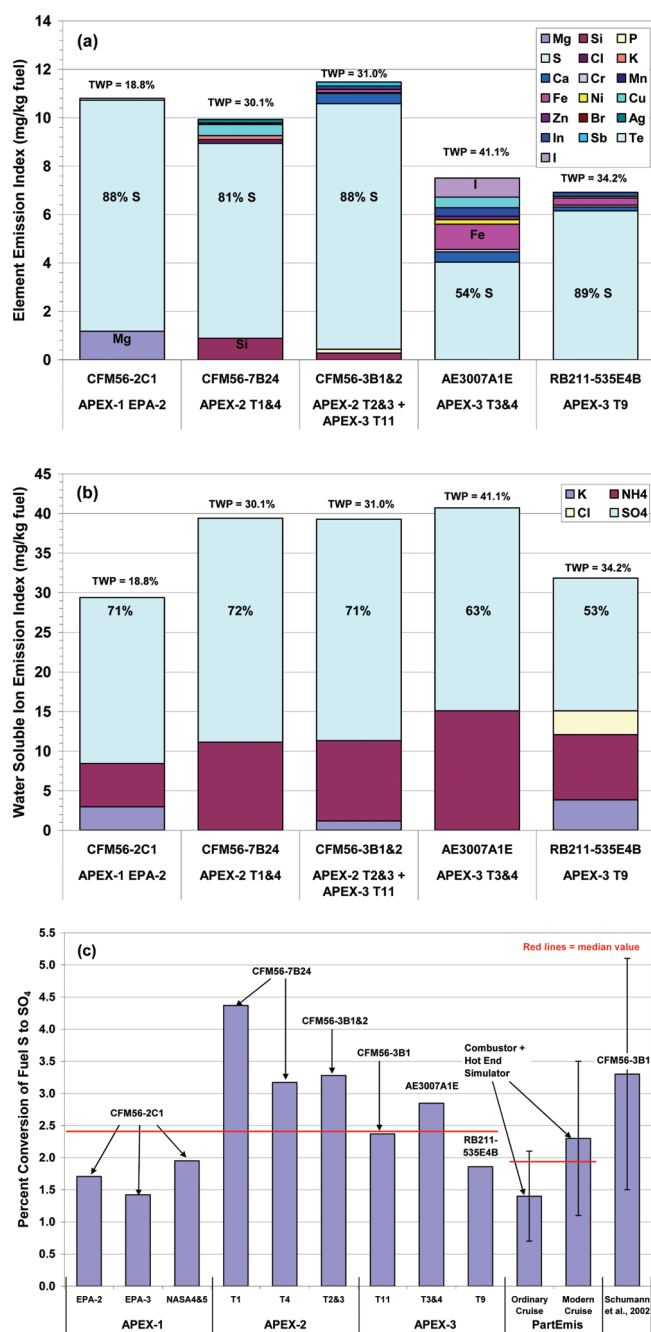
**Figure 1.** Mass emissions index for (a) black carbon, and (b) particle surface PAHs as determined for the PW 4158 engine.

for these trends is not clear, these observations are probably related to the operating conditions inside the combustor, especially with respect to pressure. Near idle, it might be expected that lower flame temperature and more fuel-rich zones are present with reduced burn-out of PAHs and carbonaceous soot. During high power, the pressure is much greater both potentially extending flammability limits, thus producing soot in regions normally too rich to burn, and possibly accelerating chemical reaction rates where combustion is initiated earlier and a larger proportion of the fuel is burned fuel-rich.<sup>19</sup>

**Element and Ion Emissions.** Various trace elements in the PM<sub>2.5</sub> emissions are thought to originate from fuels, lubricating oils, engine wear and corrosion, the sampling line, and fugitive dust. The EIs determined from the XRF analysis of the Teflon filters with the same engine and base or fleet fuel were averaged and the elemental emissions from different engines compared in Figure 2a. Note that data are not reported for elements less than three times their analytical uncertainty and that each value represents test averages over all engine power conditions. Data were also eliminated for those tests adversely affected by crosswinds (EPA-1 test in APEX-1 for the CFM56-2C1) or for filter contamination influencing the background correction (PW 4158 engine in APEX-3).

The results show that the total elemental emissions produced from the externally mixed flow CFM56 engines were generally similar but higher than those produced from the internally mixed flow AE3007A1E and RB211-535E4-B engines even accounting for differences in TWP. In addition, the detected elements





**Figure 2.** Time-integrated emission indices for (a) elemental composition, (b) water-soluble ions, and (c) percent conversion of S(IV) in the fuel to PM S(VI). All data are background-corrected. Also shown in a and b is the time-weighted engine power (TWP) expressed in terms of percent rated engine thrust.

contribute about 2–7% w/w to the total  $PM_{2.5}$  mass for these engines.<sup>13</sup> Figure 2a also shows greater than 80% of the XRF-measured elemental mass as S for all engines except the AE3007A1E (54% sulfur). Also note that fugitive dust had an impact on the results for some tests. This was especially true during APEX-2 where concrete cuttings produced during the mounting of the probe stands were entrained in the plume resulting in crustal elements such as Si, Ca, etc., appearing in the samples collected even after background correction. If these

elements were removed, the total elemental EIs would be reduced and the percent S increased.

The comparable water-soluble ion EIs determined by IC are shown in Figure 2b. The average ion EIs range from ~30 to 40 mg/kg fuel and are dominated by  $SO_4^{2-}$  and  $NH_4^{+1}$  which make up 90% of the total ion mass measured by IC. Similar to the elemental composition,  $SO_4^{2-}$  is the largest single component varying between 53% and 72% of the total ion EI. In addition, although it appears that the percent S found in the samples (Figure 2a) was inversely proportional to TWP, the  $SO_4^{2-}$  EIs do not exhibit a similar relationship to engine power. The lack of dependence of the  $SO_4^{2-}$  EIs with engine power is consistent with other reported data<sup>11</sup> which indicate only relatively minor power dependence.

Using the time-integrated data, the conversion of S(IV) to S(VI) was calculated from the fuel S and the experimentally determined  $SO_4^{2-}$  EI using the procedure outlined by Wayson et al.<sup>4</sup> The results are shown in Figure 2c, where they are compared to results of the European PartEmis program<sup>20</sup> and the landmark study by Schumann et al.<sup>21</sup> The IC results indicate that approximately 2–4% (median ~2.4%) of the S in the fuel was converted to water-soluble  $PM\ SO_4^{2-}$ , consistent with other published data.<sup>12,20,21</sup> Also, if the percent conversion of S(IV) to S(VI) calculated from the XRF data are compared to that determined from the  $SO_4^{2-}$  results, the average relative percent difference (RPD) between the two analytical methods for the nine sample sets is 18%, indicating a reasonably good agreement.

**Organic and Elemental Carbon.** Analysis of the quartz filters ( $Q_f$ ) was complicated by the fact that gas-phase organic species may have adsorbed onto the  $Q_f$  during sampling, resulting in an overestimate of the actual OC concentrations. Although there is no way to completely compensate for this artifact, a quartz filter ( $Q_b$ ) was installed behind the Teflon filter using the approach developed by Turpin et al.<sup>22</sup> The OC concentration was then obtained by difference ( $Q_f - Q_b$ ). The EC in PM is typically considered refractory and nonvolatile, and therefore no correction procedure was needed for the EC EI calculation.

For comparison purposes, uncorrected, background only-corrected, and background- and artifact-corrected OC and EC EI values are provided in Table 1. For the EPA 2 test, both the  $Q_f$  and background filter were damaged after sample collection and thus could not be analyzed for OC/EC content. However, these samples could be analyzed by GC-MS for individual organic compound speciation. Also, during APEX-3 T3 and -4 and T6 and -7, unusually high EC and OC concentrations were found in the background air due to poor ambient wind conditions. For this reason, only uncorrected EIs are provided for APEX-3 T3 and -4 and T6 and -7 in Table 1.

For the samples that could be artifact and background-corrected, the EIs obtained in this study generally ranged from 37 to 83 mg/kg of fuel burned for OC and 21 to 275 mg/kg for EC, depending on engine type and test conditions, with the EC to OC ratio ranging from ~0.3 to 7. This range of EC/OC values is reflective of the variety of engine technologies, power conditions, and fuels evaluated in the program.

Looking at just the artifact and background-corrected EC EIs, the emissions appear to be divided into three general groups: 21 to 32 mg/kg for the CFM56-2C1 and -7B24; 92 to 98 mg/kg for the CFM56-3B1/2; and 275 mg/kg for the RB211-535E4-B. Thus, the CFM56-2C1 and -7B24 produce the lowest amounts of EC, with the RB211 generating the greatest amount. Of these engines, the RB211 is somewhat unique in that it is both an

Table 1. Organic and Elemental Carbon Emission Indices for Each Test

campaign	test no.	engine model	time-weighted engine thrust (percent) <sup>a</sup>	time-weighted average fuel flow (kg/h) <sup>a</sup>	background and artifact corrected EIs			only background corrected EIs		EIs without any correction	
					OC (mg/kg)	EC <sup>b</sup> (mg/kg)	EC/OC Ratio	OC (mg/kg)	EC <sup>b</sup> (mg/kg)	OC (mg/kg)	EC (mg/kg)
1	NASA2 and 3	CFM56-2C1	18.8	770	83.2	21.1	0.253	100	21.1	179	27.9
	EPA3		20.4	797	37.1	26.1	0.703	21.1	26.1	188	40.2
	NASA4 and 5		35.7	1221	50.7	32.4	0.640	80.7	32.4	137	48.2
2	T1	CFM56-7B24	30.1	1264	82.0	28.1	0.342	132	28.1	225	37.4
	T4		30.1	1264	42.2	25.1	0.595	76.8	25.1	176	33.5
	T2 and 3		31.0	1200	50.4	91.9	1.82	69.3	91.9	120	95.4
3	T11	CFM56-3B1	31.1	1161	54.7	98.4	1.80	77.5	98.4	113	98.4
	T3 and 4	AE3007A1E	41.1	537	—	—	—	—	—	118	63.4
	T6 and 7	PW4158	32.0	2640	—	—	—	—	—	10.9	0.652
	T9	RB211-535E4-B	34.2	2473	39.2	275 <sup>c</sup>	7.02	57.0	275 <sup>c</sup>	89.9	275 <sup>c</sup>
Timko et al., 2010		all APEX engines	30								2–140 <sup>d</sup>
Petzold et al., 1999		SNECMA M45H Mk501	30								118–149
Anderson et al., 1998		multiple high bypass engines	at altitude								10–350

<sup>a</sup> Percent rated thrust and fuel flow integrated over entire test period. <sup>b</sup> Quartz filters will not adsorb EC; therefore, the EC data before and after artifact correction should be the same. <sup>c</sup> Note that this value has been corrected from that shown in Table 13-7 of ref 13. <sup>d</sup> Averaged over all available probe locations including 1, 15, 30, 43, and 50 m downstream of engine.

internally mixed engine and has the lowest bypass ratio (and possibly higher specific fuel consumption) of the turbofan engines tested. In addition, the CFM56-3B series tend to have a slightly lower engine pressure ratio and higher EC emissions as compared to the other CFM56 engine models tested, thus representing older engine technology. A similar trend in the total nonvolatile particle number and mass emissions was also found for the CFM56 series engines during APEX as described by Whitefield et al.<sup>5</sup> where the -3B1 > -2C1 > -7B24. It appears, therefore, that the EC EI is engine technology dependent even considering differences in TWP and fuel.

Also shown in Table 1 are BC EIs determined by other investigators as found in the literature.<sup>12,23,24</sup> As can be seen, our BC data are within the same general range as other published results, as determined both on the ground and at altitude. This is of interest because BC has been identified as a potential contributor to the formation of contrails and contrail-induced cirrus at cruise altitude.

**Particle-Phase Semivolatile Organic Compounds.** The SE- and TE-GC-MS methods used for identification and quantification of trace organic species are described in the Supporting Information. Filter samples from APEX 1 and 3 were analyzed using TE-GC-MS, and APEX 2 filters were composited and analyzed with SE-GC-MS. Results of the SVOC analyses are provided in Table S6 of the Supporting Information, which includes all SVOC concentration data ( $N = 174$  observations) that could be background and artifact corrected. Comparisons of log-transformed SVOC emission index means were conducted using an analysis of variance (ANOVA) model and the Tukey–Kramer HSD (honestly significant difference) test at  $\alpha = 0.05$  (JMP Version 7.0; SAS Institute Inc., Cary, NC). The ANOVA model was used to test if the multiple engine sources had roughly the same average SVOC emissions. The Tukey HSD test was applied to find precisely which engines produced average SVOC emissions that were significantly different. Zero values were taken as real and thus omitted from the statistical analysis.

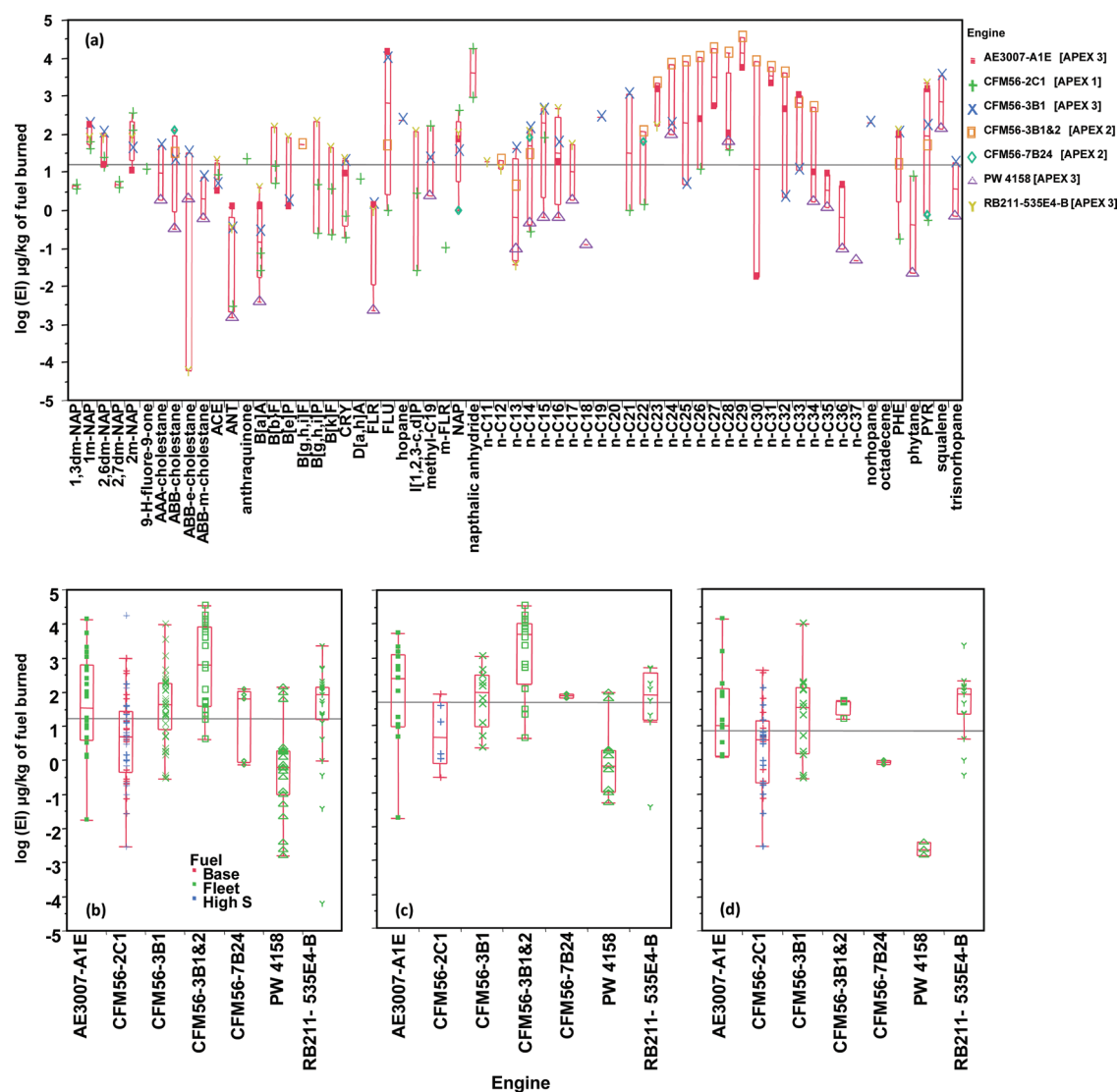
Figure 3a shows the EI values obtained for the individual SVOC compounds in the engine emissions which can also be

used as a composite chemical profile for these engines. Total GC-MS quantified SVOC emissions were near the low end of the range of total organic matter estimates produced with a continuous time-of-flight MS for these same tests.<sup>12</sup> Emissions ranges for the individual SVOC compounds in the *n*-alkane, PAH, and sterane/hopane compound classes were 0–95  $\mu\text{g/kg}$ , 0–63  $\mu\text{g/kg}$ , and 0–11  $\mu\text{g/kg}$ , respectively. The PAHs are a toxicity concern, and molecules within these SVOC classes are frequently used in air quality and source apportionment studies.<sup>25</sup> Hopane and sterane molecules in lubrication oils are used as organic markers of vehicle emissions.<sup>26</sup> While recent studies show that aerosolized lubrication oils are routinely vented from aircraft engine systems,<sup>27</sup> this is the first direct evidence of the presence of hopanes and steranes in aircraft engine emissions. Timko et al.<sup>12</sup> have confirmed the presence of synthetic lubrication oils in aircraft emissions using the  $\text{C}_5$ – $\text{C}_{10}$  esters of pentaerythritols.

Individual SVOC emission factors shown in Figure 3a varied by as much as 2 orders of magnitude, and no individual SVOC was emitted by all six engine types. This variability in SVOC emissions partly reflects the fact that the engine technologies tested (Supporting Information Table S3) had extensive age, bypass ratio, engine pressure, and thrust range differences. The variability is also reflective of the variety of operating cycles used across the APEX program (see Supporting Information Table S4).

Data in Figure 3b–d are color-coded by fuel type (Supporting Information Table S5). The influence of fuel technology on SVOC emissions cannot be thoroughly vetted within the current test matrix because only the CFM56-2C1 model in APEX-1 was examined with two fuels. Fuel and power cycle differences among the CFM56-2C1 tests do contribute to the variability observed in Figure 3a. However, in the CFM56-2C1, combustion of the high S and base fuels did not appear to influence the average SVOC emission factors ( $p = 0.7$ ). Overall, significantly higher ( $p = 0.02$ ) PAH emissions were associated with using the fleet fuel ( $N = 56$ ) rather than the high S fuel ( $N = 16$ ) or base fuel ( $N = 14$ ). However, further emissions testing will be needed to verify this result.

Figure 3b groups the individual SVOCs emitted according to engine model, ANOVA testing indicated a significant



**Figure 3.** Log-transformed emission index composites as shown: (a) for 64 individual semivolatile organic compounds; (b) by engine type; (c) for n-alkane chemical compounds; (d) for PAH chemical compounds. The reference line indicates the grand mean. Note that b–d are color coded by the fuel type shown in b. Abbreviations are provided in Table S7 of the Supporting Information.

difference ( $p < 0.001$ ) in the mean SVOC levels among engine types regardless of fuel type, confirming that the engine model affected SVOC emissions. Tukey HSD comparisons for all engine pairs show significantly lower SVOC emissions for the PW4158 (a newer engine operated here at lower nominal thrusts) than for all other engines except the CFM56-2C1 and newer CFM56-7B24, which had relatively fewer SVOC observations ( $N = 5$ ). The combined CFM56-3B1 and -2 tests using older 737-300 aircraft showed significantly higher SVOC emissions than all other engines excluding the AE3007-A1E (which was operated at relatively high thrust levels up to 100%) and the CFM56-7B24.

Figure 3c and 3d group individual n-alkane and PAH SVOCs detected in the PM emissions according to engine model. In combustion source and atmospheric aerosols, the n-alkanes are ubiquitous. For the present study, unburnt fuel or lubrication oil from the aircraft engine are potential n-alkane sources.<sup>12,27</sup> The PW4158 engine emits significantly lower n-alkanes than the AE3007-A1E, CFM56-3B1, and CFM56-3B1&2. The average n-alkane emissions from the CFM56-3B1 and -2 were significantly

higher than the RB211, CFM56-2C1, and of course PW4158. It should also be noted that the PW4158 uses a different lubrication system as compared to the other engines tested.

The ANOVA model again shows that average PAH emissions from these engines are significantly different ( $p < 0.001$ ). The Tukey HSD results show that the PW4158 engine, operating at relatively lower thrusts despite its higher ratings, emits significantly less PAH than all engines except the relatively new CFM56-7B24. The RB211 and CFM56-3B1 and -2 showed the highest PAH emissions on average. The RB211 engine had the lowest bypass ratio (likely increasing specific fuel consumption) and emitted significantly more PAH on average than the CFM56-2C1, the oldest engine in the group. Also recall that the RB211 had substantially higher BC emissions. For the CFM56-3B1 and -2 tests, the observed differences were insignificant.

Despite the inherent sampling and analytical limitations, the APEX program was able to provide detailed information on the chemical composition of aircraft engine PM emissions. Such data



are critically important to improving our understanding of air quality, climate, and health impacts.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Information on instrumentation, the experimental matrix, engines, fuels, and detailed organic speciation results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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