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Gas Turbine Engine Non-volatile Particulate Matter mass emissions: Correlation with Smoke number for Conventional and Alternative Fuel Blends

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| 6 | *Simon Christie ¹ , Prem Lobo ^{1,2} , David Lee ¹ , David Raper ¹ |
| 7 | |
| 8 | ¹ Centre for Aviation Transport and the Environment, Faculty of Science and Engineering, |
| 9 | Manchester Metropolitan University, Manchester, M1 5GD, UK |
| 10 | ² Center of Excellence for Aerospace Particulate Emissions Reduction Research, Missouri |
| 11 | University of Science and Technology, Rolla, MO 65409, USA |
| 12 | |
| 13 | * Corresponding author E-mail address: s.christie@mmu.ac.uk |
| 14 | |
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17

18 ABSTRACT

This study evaluates the relationship between the emissions parameters of smoke number 19 (SN) and mass concentration of non-volatile particulate matter (nvPM) in the exhaust of a gas 20 turbine engine for a conventional Jet A-1 and a number of alternative fuel blends. The data 21 demonstrate the significant impact of fuel composition on the emissions, and highlight the 22 magnitude of the fuel-induced uncertainty for both SN within the Emissions Data Bank, as 23 well as nvPM mass within the new regulatory standard under development. Notwithstanding 24 25 these substantial differences, the data show correlation between SN and nvPM mass 26 concentration still adheres to the First Order Approximation (FOA3), and this agreement is 27 maintained over a wide range of fuel compositions. Hence the data support the supposition 28 that the FOA3 is applicable to engines burning both conventional and alternative fuel blends without adaption or modification. The chemical composition of the fuel is shown to impact 29 30 mass and number concentration as well as geometric mean diameter of the emitted nvPM, 31 however the data do not support assertions that the emissions of black carbon with small mean diameter will result in significant deviations from FOA3. 32

33

34 INTRODUCTION

Emissions from aircraft gas turbine engines include the combustion products carbon dioxide (CO₂) and water (H₂O), combustion by-products: oxides of nitrogen (NO_x) and products of incomplete combustion: carbon monoxide (CO), unburned hydrocarbons (UHC) and soot aerosol (or black carbon, BC). Each of these species are produced in different relative proportions and all impact or contribute to climate forcing and degradation of air quality^{1,2,3,4}.

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The International Civil Aviation Organization (ICAO) sets regulatory standards for NOx, 41 CO, UHC and Smoke Number, which are reported for all certified aircraft engine types 42 >26.7kN thrust in the Emissions DataBank⁵ (EDB). Emissions of BC are not currently 43 reported within the ICAO EDB, but may be inferred through the surrogate measurement of 44 Smoke Number (SN) at specific thrust settings that correspond to those used in the Landing 45 46 and Take-Off (LTO) cycle. SN is an optically based method that quantifies the change in the 47 reflectance of a Whatman #4 filter paper after sampling a fixed mass of engine exhaust per unit area at a given temperature⁶. The ICAO regulation of SN was originally introduced in 48 49 1981 as means to quantify aircraft exhaust plume visibility and to act as a driver to reduce 50 emissions. SN does not provide a characterization of BC emissions in terms of mass and 51 number concentration, size distribution, or chemical composition, and given its proxy nature, 52 cannot be used to directly determine the environmental impacts of aviation. Currently, there 53 is an initiative within ICAO to replace the SN with a regulatory measurement methodology 54 for non-volatile particulate matter (nvPM) emissions for aircraft engines certified for use in the commercial sector. In the meantime, SN remains the only measurement whereby BC 55 56 emissions can be estimated for environmental assessment activities.

57 A number of studies have reported the correlation between SN and mass concentration of black carbon (C(BC)) using a range of different hardware: Champagne⁷ reports a correlation 58 derived from exhaust samples extracted from a combustor rig based on a T56 turboprop 59 60 engine; Whyte⁸ presented a method to convert between SN and C(BC) from a study of kerosene alternative fuels; and Girling et al.⁹ report a correlation from an experimental study 61 using soot generated by a kerosene fuelled smoke generator amongst others^{10,11}. A critical 62 inter-comparison of these and other data, which agree to within 10%, was presented by 63 Wayson et al.¹². These correlations between SN and C(BC) form the basis of a method 64 endorsed by ICAO's Committee for Aviation Environmental Protection to estimate the mass 65

66 concentration and/or mass-based emission index of BC emitted from aircraft engines, referred 67 to as the 'First Order Approximation¹³ version 3' (FOA3). The FOA3 is intended for use as a 68 standard method to estimate PM mass-based emissions from certified commercial aircraft 69 engines within the vicinity of airports, and as an important assessment tool, there is a 70 commitment to improve FOA3 as new data become available until such time that the 71 methodology is rendered obsolete by a fully validated database of PM emission indices for 72 the commercial fleet.

73 Nevertheless, there has been criticism of FOA3, not least because of the potential for the SN measurement to be dependent upon the capture efficiency of the filter and thus particle 74 size distribution of the emitted BC. This potential for error was first alluded to by Dodds et 75 al.¹⁴, followed by Wayson et al.¹², Sevcenco et al.¹⁵, and most recently discussed by Stettler et 76 al.¹⁶, though any suggestion that the SN underestimates C(BC) would mainly be applicable to 77 78 more recent engine technology due to the reduced mean diameter of the emitted BC. However, as will be demonstrated and discussed later, the correlation between SN and C(BC)79 remains a good first order approximation, even when the emitted BC particles have a mean 80 81 geometric diameter of the order of 20nm.

82 Within the emissions inventory and modeling communities, sources of uncertainty in estimating the mass concentration of BC using SN values may arise when there is the need to 83 84 interpolate between data points at the four specific LTO thrust settings to determine intermediate values, and also more generally, from the error in the reported SN data itself 85 86 induced by both measurement uncertainty and the use of non-standardized fuel for certification tests on different engine types. Concerning this latter point, the hydrogen to 87 88 carbon ratio (H:C) and the aromatic content of the fuel used to produce the SN data for the specific engine type and in the specific emissions certification test are (mostly) recorded 89 within the EDB. The spectrum of reported values in the EDB legacy data of 1.85 - 2.00 for 90

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H:C ratio and 11.9% - 22.5% for aromatic content, covers a range that extends slightly 91 92 beyond the current recommended specification for fuel to be used in aircraft engine emission testing of 1.85 - 1.99 and 15% - 23%, respectively¹⁷. Nevertheless, even the current 93 94 'tightened' specification envelope allows for considerable variation in fuel properties, such that the known impacts of fuel composition upon SN are ostensibly not considered. The 95 96 variation in the fuel properties reported within the ICAO EDB reveal that aromatic content 97 may vary by \pm 3% at a given H:C ratio, and H:C ratio may vary by \pm 0.05 at a given aromatic content. And whilst a decrease in aromatic content is generally associated with an increase in 98 99 H:C ratio, the correlation between these two parameters is generally poor and insufficient to 100 define the fuel.

101 Since the introduction of SN, engine technology has made significant progress and certified SN's at take-off power have decreased from the 25 - 35 range in early data, to values for 102 newer engine technology that typically occupy the 0-5 range. However, a SN of zero is 103 104 clearly a problem for the application of FOA3 in air quality and climate models as it implies 105 that the mass concentration of BC is also zero. For these reasons, ICAO has committed to 106 develop a new direct nvPM standard, but with typical engine lifetimes exceeding 20 years, 107 older legacy engines will continue to contribute to overall emission levels and so both SN and 108 FOA3 may not be fully transitioned for some years to come.

The new ICAO regulatory standard under development for the measurement of aircraft gas turbine engine nvPM number and mass-based emissions uses the standard methodology specified in the Society of Automotive Engineers (SAE) Aerospace Information Report (AIR) 6241¹⁸. The development of this standard methodology for engine nvPM emission measurement was born out of the Aircraft Particle Emissions eXperiment (APEX) campaigns and many other similar studies^{19,20,21,22,23,24,25}. These studies highlighted the complexity of BC emissions measurement, and in particular the difficulty in obtaining repeatable and reliable

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measurement data. The data presented here have been obtained using the AIR6241 compliant
 system North American Mobile Reference System that has been developed and robustly
 characterized over several years through international collaboration²⁶.

The objective of this work was to compare SN measured using a SAE Aerospace 119 Recommended Practice (ARP) 1179d⁶ compliant system with the nvPM mass concentration 120 121 measured using the SAE AIR6241 compliant system for a conventional Jet A-1 and a number 122 of alternative fuel blends. In contrast to earlier FOA3 analysis where the correlation was 123 examined in terms of engine technology applicability, here we analyze the FOA3 correlation 124 from a fuel composition perspective. The gas turbine engine used in this study, a Garrett 125 Honeywell GTCP85-129 auxiliary power unit (APU), is not included within the EDB as its 126 rated output is <26.7kN. It is however a suitably close analogue to aircraft main engines that 127 provides a good model soot aerosol, and advances the methodologies previously used in the 128 development of the FOA3.

129 The chemical composition of the test fuels was managed by introducing various blends of Jet 130 A-1 and a Used Cooking Oil derived Hydrotreated Esters and Fatty Acids (UCO-HEFA) 131 kerosene. A complete range of fuels was investigated to allow full characterization of the data 132 within the FOA3 model, from low blend ratios (0 - 20%) that may be considered to be 133 essentially Jet A-1 variants, through to very high blend ratios that are distinctly paraffinic and 134 alternative in composition. Through this careful management of the fuel composition, it was 135 possible to vary SN in the range from 4 to >40, although the size distribution of the soot 136 aerosol is also present as a co-variable.

The significant impact of fuel aromatic content and/or fuel H:C ratio on nvPM emissions and measured SN, is highly relevant to both the recommended specification for fuel to be used in aircraft engine certification testing and the downstream effect on accurate emission estimates due to regional variability in commercially available aviation fuel. Furthermore, the

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potential impact of fuel compositional change becomes considerably more pronounced and 141 142 pertinent within the context of alternative fuels, and to the projected scale-up of sustainable alternative aviation fuel use (eg. EU Flightpath 2020^{27}), together with future fuel 143 certification, fuel diversification, and long-term fuel security. Sustainable alternative fuels are 144 anticipated to play a sizeable role in decarbonizing the aviation industry, and currently there 145 146 are no methods to quantify the much-reduced atmospheric burden of BC that results from their use²⁸. Any future update to FOA3 may need to incorporate a SN-fuel composition 147 148 response function.

149

150 BACKGROUND

151 Soot aerosol

Unfortunately the term 'soot aerosol' is rather imprecise in its definition, and terms such as particulate matter, soot, black carbon, graphitic carbon, refractive carbon and non-volatile particulate matter are often used synonymously. On occasions even the term carbon black is used, even though this is distinct in that it is a manufactured product²⁹. Efforts to develop precise nomenclature to distinguish between these terms are on-going, but these are often based on particular measurement techniques or light-absorbing properties^{30,31,32,33} and lack universal acceptance.

In recent years, the term black carbon (BC) has gained widespread usage within the climate and emissions measurement communities, although it is recognized that BC is in itself a generic term that describes a wide range of carbonaceous combustion derived substances from partly charred residues to highly graphitized soot³⁴. BC particles have highly variable physical properties and chemical compositions that very much depend upon their source^{35,36}. Indeed the disparate nature of BC from different sources is well established and has even been used in source apportionment studies. Physical properties such as size, morphology, heterogeneity, surface area, isotopic ratio and density are all variable, as is chemical composition with solvent extractable organic matter, and total carbon sometimes being primarily elemental carbon (EC), but more often existing as complex mixtures of EC and organic carbon (OC), with volatile and semi-volatile hydrocarbons, and other non-carbon species such as ionic species, sulphates, moisture and trace metals^{37,38,39,40}.

Laboratory-generated ultrafine EC particles such as those created in a diffusion flame are yet another distinct form of carbonaceous material. Overall, scientific studies need to clearly distinguish between these highly disparate EC-containing particles with care and precision to forestall the unwarranted extrapolation of properties and the transposition of inappropriate study conclusions from one material to another. Black carbon from one combustion source is not necessarily a model particle that is representative of the characteristics of an entirely different combustion source.

178 The focus of this work is to evaluate the correlation between current and forthcoming 179 regulated measurement techniques using the soot aerosol emitted from a gas turbine engine 180 burning a conventional Jet A-1 and a number of alternative fuel blends. The precise bounds 181 and classification of the emitted soot aerosol is therefore operationally defined by the 182 measurement technique employed. Within this text, the term black carbon is used to define 183 the measurand associated with the measurement of smoke number through SAE ARP1179d, 184 whilst the term non-volatile particulate matter is used to define the measurand associated with 185 the measurement of mass concentration, number concentration and size distribution through 186 SAE AIR6241, although it is recognized that size distribution is not a formal part of this 187 standard. The term soot aerosol is used elsewhere in the broader discussion to represent less 188 defined states.

189

190 Impact of fuel chemistry on soot aerosol formation

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Aviation Jet A-1 is a complex cocktail of thousands of different hydrocarbon component molecules, though these molecules are often categorized into four principal groupings: nparaffins, iso-paraffins, cyclo-paraffins and aromatics⁴¹. The former two groupings of n- and iso-alkanes typically dominate the class composition of all-fit-for-purpose petroleum derived fuels⁴².

Variability in the chemical composition of Jet A-1 (and other kerosene specifications such as Jet A, JP4, JP8, etc.) over both region and time is commonplace. The extent of this variation is largely reflective of variability in the feedstock crude and localized demand for other petrochemical distillation fractions. It is assessed on a regional level within fuel survey data such as Rickard⁴³ or the Petroleum Quality Information System⁴⁴ (PQIS). Furthermore, this diversity in the chemical composition of aviation kerosene is set to increase as alternative fuels from a variety of sources enter the market as blend components or substitute fuels.

203 Perhaps the most notable impact of low aromatic kerosene fuels, including Jet A-1 blended 204 with Fischer-Tropsch (F-T) or Hydro-processed Esters and Fatty Acids (HEFA) alternative fuels, is the very strong reduction in black carbon emissions^{45,46,47,48,49,50,51}. For example, the 205 Alternative Aviation Fuel Experiment (AAFEX) study using a CFM56-2C1 engine reported 206 207 concentrations of BC at the engine exit nozzle may be reduced by as much as 90% using F-T fuels⁵⁰. These reductions affect the mass concentration, number concentration and size of the 208 emitted BC aerosol^{46,47,51}. A detailed evaluation of the impact of small variations in the Jet A-209 210 1 / HEFA fuel blend ratio on the emission of nvPM is given in $Lobo^{52}$. Evidence that the 211 reduction in soot aerosol occurs due to the lower aromatic content of the fuel is becoming established, and aromatics are attributed as the class of compounds that primarily influence 212 the tendency to form BC and soot precursors during combustion^{42,45,53}. For example, 213 DeWitt⁴⁵ in an investigation of fuel composition, material compatibility and its relation to 214 emission characteristics showed that BC emissions increase with both increasing fuel 215

aromatic content and increased aromatic molecular weight when evaluated in a T63 turbo

- shaft engine. This increase in BC emissions was attributed to an increase in soot precursors.
- 218

219 **FOA3:** smoke number – mass concentration correlation model

The FOA3 model endorsed by ICAO, is often used to predict the mass concentration of BC in the exhaust emissions of a gas turbine engine from the surrogate smoke number measurement¹³. Such data is routinely required by atmospheric modelers and for the development of emission inventories.

For an engine with SN<30, the mass concentration of BC (mg/m^3) is predicted from the measured smoke number using the following FOA3 equation¹²:

226
$$C(BC) = 0.0694 (SN)^{1.24}$$
 (1)

- 227 Whereas for SN>30, the mass concentration of BC (mg/m^3) is predicted from the measured
- smoke number and using the following FOA3 equation¹²: 128

229
$$C(BC) = 0.0297 (SN)^2 - 1.802(SN) + 31.94$$
 (2)

In both of these equations, C(BC) is reported at standard temperature (273.15 K) and pressure (101.325 kPa), and the bounds of uncertainty for the correlation are dominated by the error in the measurement of the SN as errors in measurement of mass concentration are small in comparison¹².

234

235 EXPERIMENTAL METHOD

Gas turbine engine & operating conditions

The Garrett Honeywell GTCP85-129 gas turbine engine used in this study is often operated as an auxiliary power unit (APU) on Boeing 737 aircraft. APU gas turbine engines offer a good model of aircraft main engine combustion characteristics whilst being considerably more manageable and less costly to operate.

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In this work, three APU operating conditions were investigated: No Load (NL), 241 242 Environmental Control Systems (ECS), and Main Engine Start (MES). These conditions correspond to the normal operating conditions for an APU. For each experimental run the 243 244 APU was put through a warm up sequence using Jet A-1 before switching to the test fuel without interruption, and then stabilizing at the first condition. The test matrix followed a 245 246 successive step down in power from MES to ECS to NL condition, which represented 1 test 247 cycle. For each of the fuel blends evaluated, this test cycle was twice sequenced without 248 shutdown. The sequence stepped down in power to minimize possible differences in 249 operating temperature and therefore potential differences in the fuel vaporization rates that 250 could feasibly manifest themselves as measurement uncertainties. For each engine condition, 251 the emissions data were recorded over a 6 minute window once the APU was determined to 252 be stable (ie. when engine EGT, RPM, and fuel flow were established as consistent).

253 The different fuel blends of Jet A-1 and Used Cooking Oil based HEFA (UCO-HEFA) 254 used for the study were selected at random to mitigate possible systematic bias and drift. 255 Experimental runs with Jet A-1 were conducted at the beginning and end of the study, as well 256 as several times in between runs with different fuel blends to reaffirm baseline conditions. 257 Engine parameters such as fuel flow rate, RPM, air fuel ratio, and exhaust gas temperature 258 were also recorded. The engine was very stable at each operating condition and the 259 reproducibility of engine parameters was good due to the on-board engine management 260 system.

Ambient conditions of temperature, pressure, and relative humidity were also recorded throughout, and the range of values for these parameters was: 14.0 - 20.6 °C, 102.47 - 103.11kPa, and 61 - 85%, respectively.

264

265 Sampling system and instrumentation

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Two identical and almost collocated single-point probes, one for gaseous emissions and SN measurement, and the second for nvPM emissions measurement were place within $\frac{1}{2}$ nozzle diameter of the engine exit plane (~15 cm).

269 The sample line for gaseous emissions and SN was compliant with the specifications in ICAO¹⁷ Annex 16 Volume 2 and maintained at a temperature of 160°C. Gaseous species 270 271 were determined using a Binos Non-Dispersive Infrared Sensor (CO), a Signal Flame Ionization Detector (UHC), and an Eco Physics Chemi-Luminescence Analyser (NO_x), each 272 using appropriate span and zero gases between measurements. The SN was determined in 273 accordance with SAE ARP1179d⁶ using a Richard Oliver smoke meter to collect at least 274 275 three filter samples for each fuel and at each engine condition. The reflectance of the filter 276 samples was determined pre and post sampling using a BOSCH reflectometer. . Reported SN 277 data are the arithmetic mean of measurements from 6 filters (2 test cycles x 3 filters at each 278 condition) and uncertainty is conservatively estimated as ± 2 SN. This estimate of uncertainty 279 is consistent with the measured variability, with due recognition that the accuracy of an individual SN measurement is considered to be ± 3 SN⁶. 280

The nvPM emissions were measured using the AIR6241 compliant North American mobile 281 reference system^{18,26}. The probe line used to extract nvPM emissions sample was connected 282 to a 3-way splitter using a 7.5 m long, 7.9 mm internal diameter thin-walled stainless steel 283 284 tubing maintained 160°C. The nvPM sample was diluted with particle-free nitrogen gas via a 285 Dekati ejector diluter and carried to the measurement suite along a 25 m long, 7.9 mm 286 internal diameter, carbon-loaded and electrically grounded PTFE tube maintained at 60°C in 287 accordance with SAE AIR6241. The nvPM number-based emissions were measured using an 288 AVL Advanced Particle Counter, while nvPM mass-based emissions measurements were 289 obtained using an Artium Laser Induced Incandescence and an AVL Micro Soot Sensor 290 (MSS). Only the nvPM mass data obtained using the MSS is used in this analysis. The

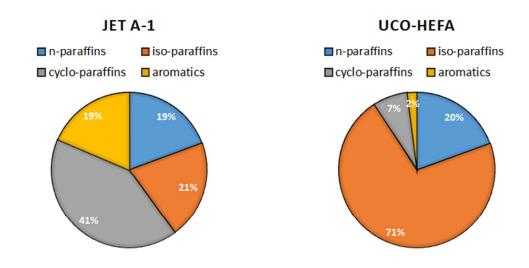
| 291 | particle size distributions of the nvPM, which are not specified in AIR6241, were measured |
|-------------------|---|
| 292 | using the Cambustion DMS500. The CO_2 concentration in the diluted nvPM line was |
| 293 | measured using a LiCor NDIR detector. The nvPM emissions data are reported at standard |
| 294 | temperature and pressure (273.15 K and 101.325 kPa), which is equivalent to mass |
| 295 | concentration data reported via FOA3. All nvPM emission concentration data was corrected |
| 296 | for dilution and thermophoretic loss in the sampling system. Measurement uncertainties in |
| 297 | nvPM emissions were calculated using 1σ standard deviation of the average data. |
| | |
| 298 | |
| 298 299 | Properties of test fuels |
| | Properties of test fuels The two kerosene fuels used in this study were Jet A-1 and UCO-HEFA. The Jet A-1 was |
| 299 | |
| 299 300 | The two kerosene fuels used in this study were Jet A-1 and UCO-HEFA. The Jet A-1 was |
| 299 300 301 | The two kerosene fuels used in this study were Jet A-1 and UCO-HEFA. The Jet A-1 was straight-run kerosene obtained from Air BP (Kingsbury, UK), while the UCO-HEFA was |

fuels: the Jet A-1 contains a substantial fraction of cyclo-paraffins and aromatics, whereas
these are much reduced for the UCO-HEFA fuel that is dominated by iso-paraffins.

shown in Figure 1. The figure shows the significant difference in the composition of the two

307

304



309 Figure 1. Summary of the GC x GC compositional analysis for the Jet A-1 and UCO-HEFA

kerosene fuels that were used to formulate the test blends.

311

312 A number of Jet A-1 / UCO-HEFA kerosene fuel blends were formulated in-house through 313 careful weighing and thorough mixing (blend ratios of 5%, 10%, 15%, 20%, 25%, 30%, 40%, 50%, 60%, 70%, 75%, 80%, 85%, 90%, and 95% by mass). The chemical composition of the 314 315 fuels varied linearly with fuel blend ratio, and test fuel H:C ratio varied from 1.89 to 2.14 316 whilst aromatic content correspondingly varied from 19.2% to 1.8% by mass. The Jet A-1 317 and UCO-HEFA fuels were fully miscible and the blended fuels were formulated at least 48 hours prior to use. It is recognized that several of these blends are outside of current ASTM 318 319 certification limits for HEFA fuel blends in operational aircraft, however these limits are no 320 longer applicable to the now ground based APU used within this study. Further details of the fuel properties for neat Jet A-1 and UCO-HEFA fuels are given in Lobo et al.⁵². 321 By introducing the hypothetical concept of an aromatic - H:C ratio space, these fuels can be 322 323 compared with fuels in the EDB, a world survey of the available JP8 fuels, and the nominal 324 bounds for JP8 jet fuel. The specification for JP8, a military grade kerosene made to more

exacting specifications than commercial jet fuel, is used in this context as a proxy, since H:C

ratio is not defined for checklist Jet A-1. This comparison is shown in Figure 2.

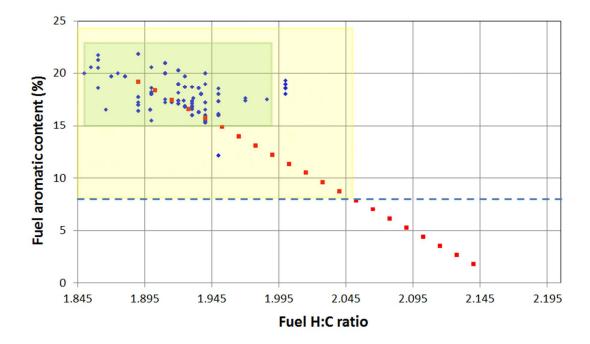


Figure 2. Comparison of aromatic content and H:C ratio of different fuels: Blue points: EDB engine certification data; Red points: Experimental fuel blends; Green shaded area: Bounds of ICAO engine test fuel specification¹⁷; Yellow shaded area: Bounds of PQIS world JP8 2013 survey⁴⁴; Chart area: Nominal bounds for JP8 jet fuel; Blue dashed line: ASTM D7566 minimum aromatic limit⁵⁴.

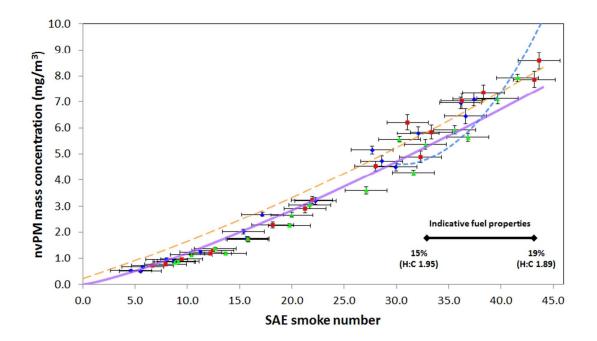
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328

335 RESULTS AND DISCUSSION

336 Correlation between nvPM mass concentration and SN

Figure 3 shows the measured nvPM mass concentration, corrected for dilution and thermophoretic loss¹⁸, as a function of SN. The different colored data points in the plot indicate the three different engine conditions, and the BC mass concentration as a function SN predicted by FOA3 for both SN<30 and SN>30 are also overlaid.



342

Figure 3. nvPM mass concentration as a function of smoke number. Colored data points indicate the three different engine operating conditions: Blue=MES; Red=ECS; Green=NL. The C(BC) as predicted by FOA3 using SN data is overlaid: Purple line = FOA Equation 1 (nominally applicable for SN<30); Dashed blue line = FOA Equation 2 (nominally applicable for SN>30); Dashed orange line = upper bound for Equation 1 generated using +3 SN error [Wayson et al.¹²]. An indication of the change in fuel aromatic content (H:C ratio) for ECS operating condition is inset.

350

The experimental data for the correlation between SN and nvPM mass concentration show close agreement with FOA3, particularly at SN<30. Furthermore this agreement is maintained over a wide range of kerosene compositions, and is largely independent of the engine operating condition. Lines of regression for the datasets representing the three engine conditions are practically coincident (not shown in the figure). The location of specific emissions data on the FOA3 curve is merely dependent upon the chemical properties of the fuel. Data points towards the left in Figure 3 represent measurements from fuel blends with

lower aromatic content and correspondingly greater H:C ratio. It is clear that the chemical 358 359 composition of the kerosene has a significant impact on the tendency to form nvPM. Fuel 360 aromatics have been identified as compounds that primarily influence the tendency to form soot aerosol during combustion^{45,46}, although it has long been suggested that fuel hydrogen 361 content may be a more fundamental parameter that is independent of molecular structure 58,59. 362 363 The data presented here cannot be used to differentiate between the impact of aromatics and 364 the impact of H:C ratio since both vary linearly in the two component fuel blends. 365 Experimental data using multi-component blends or surrogate fuels to adjust these parameters 366 independently is necessary to explore their relative authority. The magnitude of the 367 reductions in SN and/or nvPM emissions are comparable with data reported elsewhere for other gas turbine engines burning paraffinic fuels^{38,44,45,47,48}. 368

The nvPM mass concentration (C(nvPM)) and BC mass concentration (C(BC)) as defined by their respective measurement methodologies are not identical, and generally C(nvPM) \geq C(BC) since the former encompasses line loss correction factors that are not inherent in latter. The two standards are however closely related and these data support the supposition that C(nvPM) can be estimated from FOA3, but more significantly, that FOA3 can be used with alternative fuel blends of varying chemical composition without adaption or modification. The data indicate that the relation between C(nvPM) and SN is foremost represented by

FOA3 equation (1), even at SN>30. Using all data points in Figure 3 and a power law fit to

378
$$C(nvPM) = 0.048 (SN)^{1.55}$$
 (3)

Whilst using a constrained range of data points up to SN<30, the line of regression is givenby:

381
$$C(nvPM) = 0.058 (SN)^{1.27}$$
 (4)

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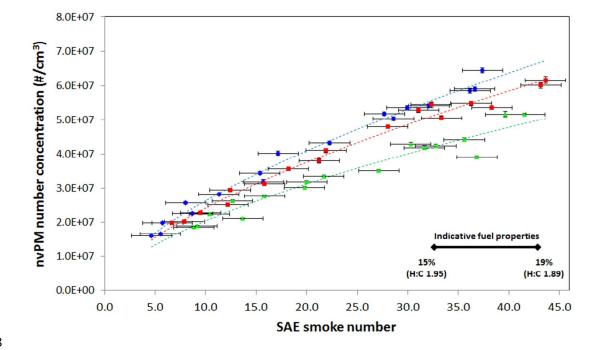
with the correlation coefficients of $R^2 = 0.979$ (n=51) and $R^2 = 0.965$ (n=33), respectively 382 383 (to simplify the representation of data, these lines of regression are not included in Figure 3). Figure 3 also shows a marker to indicate the 15% - 19% fuel aromatic range for the ECS 384 engine operating condition (markers for other engine conditions are of comparable magnitude 385 but offset relative to the SN axis). This marker corresponds to the mid-range and the lower 386 387 bound for aromatic content in the ICAO specification for fuel to be used for aircraft engine 388 certification testing. For this modest shift in fuel composition, the SN decreased by 30% and 389 C(nvPM) decreased by 45%. Hence the fuel-induced uncertainty in EDB SN or C(nvPM)390 derived through FOA3 is potentially twice this number, when considered in respect of the limits of fuel used for engine certification testing¹⁷ and typical commercial fuel variability⁴³. 391 392 SN data for a particular engine in the EDB is strictly only correct for the stated certification 393 test fuel and will increase or decrease in magnitude for fuel of different chemical 394 composition.

The data suggest that for engines with relatively large reported SNs the fuel-induced uncertainty could be significant and markedly greater than the nominal ± 3 SN uncertainty associated with the measurement of SN, whilst for engines with relatively small reported SNs the fuel-induced uncertainty will be captured within this same ± 3 SN measurement uncertainty. The proportional reduction in nvPM mass are consistent with data reported by Brem et al.⁵⁵ in a study evaluating the impact of fuel aromatic content on nvPM emissions from an in-production gas turbine engine.

402

403 **nvPM number concentration and size distribution**

Figure 4 shows the measured nvPM number concentration corrected for dilution and thermophoretic $loss^{18}$ as a function of the measured SN. Measurement uncertainties are as 406 previously described, and similarly the different colored data points in the plot indicate the



407 three different engine conditions.



Figure 4. nvPM number concentration as a function of smoke number. Colored data points
indicate the three different engine operating conditions: Blue=MES; Red=ECS; Green=NL.
An indication of the change in fuel aromatic content (H:C ratio) for ECS operating condition
is inset.

413

Data points towards the left in Figure 4 represent measurements from kerosene fuel blends of lower aromatic content and show a progressive reduction in the nvPM number concentration. In this case there is some distinction between lines of regression for the three datasets (shown in the figure) indicating that the relation between nvPM number concentration and SN may be dependent upon the engine operating condition.

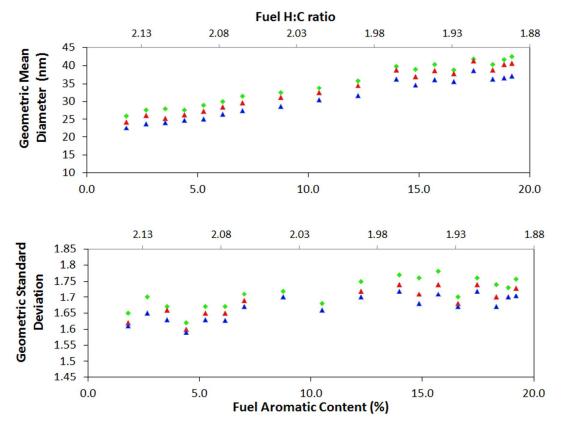
Figure 4 also shows a marker to indicate the 15% – 19% fuel aromatic range for the ECS
engine operating condition corresponding to the mid-range and the lower bound for aromatic
content in the ICAO specification for fuel to be used in aircraft engine certification testing.

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For this shift in fuel composition, SN decreased by 30% and the nvPM number concentration decreased by 22%. This would suggest that nvPM number concentration is also a strong function of fuel composition, an observation that is consistent with data reported elsewhere^{52,55}.

426 The nvPM size distribution parameters of geometric mean diameter (GMD) and geometric 427 standard deviation (GSD) for the fuel blends tested at each of the three APU operating 428 conditions are shown in Figure 5. The nvPM exhibited a characteristic lognormal size 429 distribution, which narrows and shifts the geometric mean diameter to smaller sizes as the 430 aromatic content of the fuel blend is decreased (correspondingly increased H:C ratio). For a 431 given fuel, the succession of nvPM GMD tracked the sequence NL>ECS>MES. Overall the 432 GMD varied from a minimum of 22nm for 1.8% aromatic fuel in the MES engine condition 433 to 42nm for 19.2% aromatic fuel in the NL engine condition. The corresponding GSD ranged 434 from 1.58 to 1.79. Hence on the microscopic scale, the fuel-induced reduction in the mass of 435 emitted nvPM corresponds to the emission of fewer and smaller units of particulate matter. These data are consistent with those reported for other gas turbine engines burning 436 conventional and alternative fuels^{21,26,47,49,50}. 437



439

Figure 5. Geometric mean diameter and geometric standard deviation for nvPM emission
from selected fuel blends. Colored data points indicate the three different engine operating
conditions: Blue=MES; Red=ECS; Green=NL. In both cases the upper secondary axis shows
the corresponding fuel H:C ratio.

444

When these nvPM GMD data are considered in relation to the C(nvPM) in Figure 3, it is 445 446 evident that the small nvPM with $GMD \sim 22nm$ that are characteristic of modern aircraft 447 engine emissions, do not result in significant deviations in the FOA3 estimation of mass concentration. Previously Stettler et al.¹⁶ published data that appears to show that the relation 448 449 between SN and C(nvPM) deviates significantly from FOA3 for nvPM with a GMD of the order of 20nm, with deviations of up to a factor 3. The data presented here do not support this 450 finding. The data presented by Stettler et al.¹⁶ do not represent a fair comparison with the 451 452 FOA3 method in three principal ways. Firstly, the applied methodology did not have a direct

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453 measurement of nvPM mass concentration, but rather estimated it from size distribution and 454 effective density measurements. In the current work, we directly measure nvPM mass. 455 Secondly, Stettler's experiments were based on laboratory measurements of propane 456 diffusion flame combustion, and the black carbon generated from a propane burner is not a model particle that is representative of the soot aerosol produced by a gas turbine engine. 457 458 Propane burners produce black carbon via a different mechanistic route (as chemically 459 dissimilar) that result in high EC fraction particulate matter with different physical and chemical properties. This assertion is supported by experimental data from Durdina et al.⁵⁶. 460 461 Thirdly, the SN measurement methodology employed by Stettler was not comparable with the 462 methodology that has been used to populate the data in the ICAO EDB. The use of a catalytic stripper to remove the semi-volatile OC from the line is not compliant with SAE ARP1179d⁶ 463 and will result in a relatively 'clean' source of soot aerosol to be impingent upon the SN 464 filter. The impact of volatiles to the measurement of SN was demonstrated by Rye et al^{60} . 465 The data in Stettler et al.¹⁶ do demonstrate that a 'clean' black carbon from a propane 466 467 burner is captured with a progressively decreasing efficiency as the geometric mean diameter 468 is reduced. However, the extrapolation that these data are applicable to the emission of nvPM 469 from an aircraft gas turbine engine cannot be justified because of the differences in both the 470 modeled source for BC / nvPM and the measurement methodologies employed. This is important since Stettler et al.¹⁶ claim that the FOA3 significantly underestimates aircraft 471 emissions of BC by a factor of 2.5 - 3 for SN ≤ 15 , and consequentially, propose a factor ~ 3 472 upwards revision of aircraft BC radiative forcing which would make it equivalent to $\sim 1/3$ of 473 the aviation CO_2 radiative forcing⁵⁷. On the basis of the measurements presented here and 474 critique of the Stettler et al¹⁶ methodology, such conclusions and extrapolations cannot be 475 476 supported.

| 477 | Significantly, this work develops a comparative framework between current and future |
|-----|---|
| 478 | regulatory standards for the measurement of soot aerosol from a gas turbine that incorporates |
| 479 | the quantitatively distinct emission from the combustion of alternative fuels, and places these |
| 480 | within the ICAO endorsed and widely accepted FOA3 methodology. With typical engine |
| 481 | lifetimes exceeding 20 years, older legacy engines will continue to contribute to overall |
| 482 | emission levels and so both SN as a surrogate measurement of BC, and FOA3 as a vital |
| 483 | assessment tool, may not be fully transitioned for some years to come. The importance of fuel |
| 484 | composition and the impact of its attendant variability may be particularly acute in the |
| 485 | application of EDB data to air quality modeling and the development of emission inventories. |
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| 487 | AUTHOR INFORMATION |
| 488 | Corresponding author *E-mail: <u>s.christie@mmu.ac.uk</u> |
| 489 | |
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| 494 | conclusions or recommendations expressed in this paper are those of the authors and do not |
| 495 | necessarily reflect the views of the sponsors. |

496

497 ABBREVIATIONS

BC, Black Carbon; C(BC), Concentration of Black Carbon; C(nvPM), Concentration of
non-volatile Particulate Matter; EDB, Emissions Data Bank; FOA3, First Order
Approximation (version 3); GMD, Geometric Mean Diameter; GSD, Geometric Standard
Deviation; ICAO, International Civil Aviation Organization; LTO, Landing and Take Off;
nvPM, non-volatile Particulate Matter; SN, Smoke Number; UCO-HEFA, Used Cooking Oil
derived Hydrotreated Esters and Fatty Acids.

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505 REFERENCES

506 (1) Lee, D.S.; Fahey, D.W.; Forster, P.M.; Newton, P.J.; Wit, R.C.N.; Lim, L.L.; Owen, B.;

Sausen, R. Aviation and global climate change in the 21st century. *Atmos. Environ.* 2009, 43
(22), 3520-3537.

- 509 (2) Lee, D.S.; Pitari, G.; Grewe, V.; Gierens, K.; Penner, J.E.; Petzold, A.; Prather, M.J.;
- 510 Schumann, U.; Bais, A.; Berntsen, T.; Iachetti, D.; Lim, L.L.; Sausen, R. Transport Impacts
- on Atmosphere and Climate: Aviation. *Atmos. Environ.* **2010**, 44 (37), 4678–4734.
- 512 (3) Stettler, M.E.; Eastham, S; Barrett, S.R.H. Air quality and public health impacts of UK
- 513 airports. Part I: Emissions. *Atmos. Environ.* **2011**, 45 (31): 5415-5424.
- 514 (4) Yim, S.H.L.; Lee, G.L.; Lee, I.H.; Allroggen, F.; Ashok, A.; Caiazzo, F.; Eastham,
- 515 S.D.; Malina, R.; Barrett, S.R.H. Global, regional and local health impacts of civil aviation
- 516 emissions. *Environ. Res. Lett.* **2015,** 10, 034001.
- 517 (5) ICAO Aircraft Engine Emissions Databank. European Aviation Safety Agency (EASA).
- 518 2015; https://easa.europa.eu/document-library/icao-aircraft-engine-emissions-databank

Page 24 of 32 ACS Paragon Plus Environment

| 519 | (6) Aircraft Gas Turbine Engine Exhaust Smoke Measurement. Aerospace Recommended |
|-----|--|
| 520 | Practice 1179d. Society of Automotive Engineers International (SAE). 2011. |
| 521 | (7) Champagne, D.L. Standard Measurement of Aircraft Gas Turbine Engine Exhaust |
| 522 | Smoke. ASME 71-GT-88. American Society of Mechanical Engineers, New York. 1971, 1- |
| 523 | 11. |
| | |

- (8) Whyte, R. B. Alternative Jet Fuels. AGARD Advisory Report no. 181, Vol. 2. *National Research Council*, Ottawa, Canada. 1982.
- (9) Girling, S.P.; Hurley, C.D.; Mitchell, J.P.; Nichols, A.L. Development and
 Characterization of a Smoke Generator for the Calibration of Aerosol Emissions from Gas
- 528 Turbine Engines. *Aerosol Sci. Technol.* **1990**, 13, 8–19.
- 529 (10) Hurley, C. D. Smoke Measurements Inside a Gas Turbine Combustor. AIAA, SAE,
- ASME and ASEE 29th Joint Propulsion Conference. AIAA, Monterey, CA. 1993, 1–9.
- 531 (11) Whitefield, P.D.; Hagen, D.E.; Siple, G.; Pherson, J. Estimation of Particulate
- 532 Emission Indexes as a Function of Size for the LTO Cycle for Commercial Jet Engines. *Proc.*
- 533 Air & Waste Management Association Annual Meeting. Pittsburgh, PA. 2001.
- (12) Wayson, R.; Fleming, G.; Iovinelli, R. Methodology to Estimate Particulate Matter
 Emissions from Certified Commercial Aircraft Engines. *J. Air Waste Manage. Assoc.* 2009,
 59 (1), 91–100.
- 537 (13) Airport Air Quality Guidance Manual. Doc 9889. International Civil Aviation
 538 Organization (ICAO), Montreal, Canada. 2011.
- 539 (14) Dodds, W.J.; Peters, J.E.; Colket, M.B.I.; Mellor, A.M. Preliminary Study of Smoke
- 540 Formed in the Combustion of Various Jet Fuels. J. Energy. 1977, 1 (2), 115–120.

Page 25 of 32 ACS Paragon Plus Environment

(15) Sevcenco, Y.A.; Bowen, P.J.; Johnson, M.P.; Hilton, M.; Welch, M.; Miller, M.N.
Mass and size distribution measurement of particulates from a gas turbine combustor using
modern mobility analyzer and particle sizer. 45th AIAA/ASME/SAE/ASEE Joint Propulsion
Conference & Exhibit. Denver, Colorado. AIAA 2009e4827. 2009.
(16) Stettler, E.J.; Swanson, J.J.; Barret, S.R.H.; Boles, A.M. Updated correlation between
aircraft smoke number and black carbon concentration. *Aerosol Sci. Technol.* 2013, 47, 12051214.

- 548 (17) ICAO Annex 16 Environmental Protection, Volume II. Third edition. Appendix 4.549 2008.
- (18) SAE Aerospace Information Report 6241 (AIR6241). Procedure for the Continuous
 Sampling and Measurement of Non-Volatile Particle Emissions from Aircraft Turbine
 Engines. SAE International, Warrendale, PA. 2013.
- (19) Lobo, P.; Hagen, D.E.; Whitefield, P.D.; Alofs, D.J. Physical Characterization of
 Aerosol Emissions from a Commercial Gas Turbine Engine. *J. Propul. Power.* 2007, 23, 919929.
- (20) Timko, M.T.; Onasch, T. B.; Northway, M.J.; Jayne, J.T.; Canagaratna, M.R.;
 Herndon, S.C.; Wood, E.C.; Miake-Lye, R.C.; Knighton, W.B. 2010. Gas Turbine Engine
 Emissions—Part II: Chemical Properties of Particulate Matter. *J. Eng. Gas Turbines Power*.
 2010, 132, (6) 061505.
- 560 (21) Lobo, P.; Hagen, D.E.; Whitefield, P.D.; Raper, D. PM Emissions Measurements of
- 561 In-Service Commercial Aircraft Engines during the Delta-Atlanta Hartsfield Study. Atmos.
- *Environ.* **2015**, 104, 237-245.

Page 26 of 32 ACS Paragon Plus Environment

(00) 77.

0010 DI

| 563 | (22) Kinsey, J.S.; Dong, Y.; Williams, D.C.; Logan, R. 2010. Physical characterization of |
|-----|--|
| 564 | the fine particle emissions from commercial aircraft engines during the Aircraft Particle |
| 565 | Emissions eXperiment (APEX) 1-3. Atmos. Environ. 2010, 44, 2147-2156. |
| 566 | (23) Anderson, B.E.; Beyersdorf, A.J.; Hudgins, C.H.; Plant, J.V.; Thornhill, K.L.; |
| 567 | Winstead, E.L.; Ziemba, L.D.; Howard, R.; Corporan, E.; Miake-Lye, R.C.; Herndon, S.C.; |
| 568 | Timko, M.; Wood, E.; Dodds, W.; Whitefield, P.; Hagen, D.; Lobo, P.; Knighton, W.B.; |
| 569 | Bulzan, D.; Tacina, K.; Wey, C.; Vander Wal, R.; Bhargava, A.; Kinsey, J.; Liscinsky, D.S. |
| 570 | Alternative Aviation Fuel Experiment (AAFEX). NASA. TM-2011-217059, Hanover, MD. |
| 571 | 2011. |
| | |

- 572 (24) Petzold, A.; Marsh, R.; Johnson, M.; Miller, M.; Sevcenco, Y.; Delhaye, D.; Ibrahim,
- A.; Williams, P.; Bauer, H.; Crayford, A.; Bachalo, W.D.; Raper, D. Evaluation of methods
 for measuring particulate matter emissions from gas turbines. *Environ. Sci. Technol.* 2011,
 45, 3562–3568.
- 576 (25) Marsh, R.; Crayford, A.; Petzold, A.; Johnson, M.; Williams, P.; Ibrahim, A.; Kay, P.;

577 Morris, S.; Delhaye, D.; Lottin, D.; Vancassel, X.; Raper, D.; Christie, S.; Bennett, M.;

578 Miller, M.; Sevcenco, Y.; Rojo, C.; Bowen, P. Studying, sampling and measurement of

aircraft particulate emissions II (SAMPLE II): Final Report. **2010**, EASA.2009.OP.18.

- 580 (26) Lobo, P.; Durdina, L.; Smallwood, G.J.; Rindlisbacher, T.; Siegerist, F.; Black, E.A.;
- 581 Yu, Z.; Mensah, A.A.; Hagen, D.E.; Miake-Lye, R.C.; Thomson, K.A.; Brem, B.T.; Corbin,
- 582 J.C.; Abegglen, M.; Sierau, B.; Whitefield, P.D.; Wang, J. Measurement of Aircraft Engine
- 583 Non-volatile PM Emissions: Results from the Aviation Particle Regulatory Instrument
- 584 Demonstration Experiment (A-PRIDE) 4 Campaign. Aerosol Sci. Technol. 2015, 49, 472-
- 585 484.

Page 27 of 32 ACS Paragon Plus Environment

(27) Flightpath 2050, Europe's Vision for Aviation. *European Union*, Belgium. 2011,
ISBN 978-92-79-19724-6.

- (28) Speth, R.L.; Rojo, C.; Malina, R.; Barrett S.R.H. Black carbon emissions reductions
 from combustion of alternative jet fuels. *Atmos. Environ.* 2015, 105, 37-42.
- 590 (29) Long, C.M.; Nascarella, M.A.; Valberg, P.A. Carbon black vs. black carbon and other
- airborne materials containing elemental carbon: Physical and chemical distinctions. Environ.

592 Poll. **2013**, 181, 271–286.

- 593 (30) Janssen, N.A.H.; Gerlofs-Nijland, M.E.; Lanki, T.; Salonen, R.O.; Cassee, F.R.; Hoek,
- 594 G.; Fischer, P.; van Bree Brunekreef, B.; Krzyzanowski, M. Joint World Health Organization
- 595 Convention Task Force on Health Aspects of Air Pollution Health Effects of Black Carbon.
- 596 World Health Organization, Regional Office for Europe, Copenhagen, Denmark. 2012.
- (31) Andreae, M.O.; Gelencsér, A.; Black carbon or brown carbon? The nature of lightabsorbing carbonaceous aerosols. *Atmos. Chem. Phys.* 2006, 6, 3419 3463.
- 599 (32) Petzold, A.; Ogren, J.A.; Fiebig, M.; Laj, P.; Li, S.M.; Baltensperger, U.; Holzer-Popp,
- T.; Kinne, S.; Pappalardo, G.; Sugimoto, N.; Wehrli, C.; Wiedensohler, A.; Zhang, X.Y.
 Recommendations for reporting "black carbon" measurements. *Atmos. Chem. Phys.* 2013, 13,
- 602 8365-8379.
- 603 (33) Lack, D.A.; Moosmüller, H.; McMeeking, G.R.; Chakrabarty, R.K.; Baumgardner, D.;
- Characterizing elemental, equivalent black, and refractory black carbon aerosol particles: a
 review of techniques, their limitations and uncertainties. *Analytical bioanalytical chem.* 2014,
 406, 99–122.
- 607 (34) Shrestha, G.; Traina, S.; Swanston, C. Black carbon's properties and role in the
 608 environment: a comprehensive review. *Sustainability*. 2010, 2, 294-320.

Page 28 of 32

ACS Paragon Plus Environment

| 609 | (35) Fernandes, M.B.; Skjemstad, J.O.; Johnson, B.B.; Wells, J.D.; Brooks, P. |
|-----|--|
| 610 | Characterization of carbonaceous combustion residues. I. Morphological, elemental and |
| 611 | spectroscopic features. Chemosphere. 2003, 51, 785–795. |
| 612 | (36) Fernandes, M.B.; Brooks, P.; Characterization of carbonaceous combustion residues: |
| 613 | II. Non-polar organic compounds. Chemosphere. 2003, 53, 447–458. |
| 614 | (37) Matuschek, G.; Karg, E.; Schroppel, A.; Schulz, H.; Schmid, O. Chemical |
| 615 | investigation of eight different types of carbonaceous particles using thermoanalytical |
| 616 | techniques. Environ. Sci. Technol. 2007, 41, 8406-8411. |
| 617 | (38) Kocbach, A.; Li, Y.; Yttri, K.E.; Cassee, F.R.; Schwarze, P.E.; Namork, E. |
| 618 | Physicochemical characterisation of combustion particles from vehicle exhaust and |
| 619 | residential wood smoke. Part. Fibre Toxicol. 2006, 3, 1-10. |
| 620 | (39) Report to Congress on Black Carbon. Office of Air Quality Planning and Standards, |
| 621 | Office of Atmospheric Programs, Office of Radiation and Indoor Air, Office of Research and |
| 622 | Development, Office of Transportation and Air Quality, US Environmental Protection |
| 623 | Agency (US EPA). Washington, DC. EPA-450/R-12-001. 2012. |
| 624 | (40) Huang, L.; Brook, J.R.; Zhang, W.; Li, S.M.; Graham, L.; Ernst, D.; Chivulescu, A.; |
| 625 | Lu, G. Stable isotope measurement of carbon (OC/EC) in airborne particulate: A new |

- dimension for source characterisation and apportionment. *Atmos. Environ.* 2006, 40, 26902705.
- 628 (41) Shafer, L.M.; Striebich, R.C.; Gomach, J.; Edwards, T. Chemical Class Composition
- of Commercial Jet Fuels and Other Specialty Kerosene Fuels. 14th AIAA/AHI Space Planes
- and Hypersonic Systems and Technologies Conference. AIAA Paper 2006-7972. 2006.

Page 29 of 32 ACS Paragon Plus Environment

631 (42) Dryer, F.L. Chemical kinetic and combustion characteristics of transportation fuels.

632 Proc. Combust. Inst. 2015, 35, 117–144.

- 633 (43) Rickard, G. The quality of aviation fuel available in the United Kingdom annual
 634 survey 2007. *Energy Institute*. Qinetiq/08/01656. 2008.
- 635 (44) PQIS 2013 annual report: Petroleum quality information system. US defence logistics636 agency. 2013.
- 637 (45) DeWitt, M.J.; Corporan, E.; Graham, J.; Minus, D. Effects of aromatic type and
 638 concentration in Fischer-Tropsch fuel on emissions production and material compatibility.
 639 *Energy & Fuel.* 2008, 22, 2411-2418.
- 640 (46) Timko, M.T.; Yu, Z.; Onasch, T.B.; Wong, H.-W.; Miake-Lye, R.C.; Beyersdorf, A.J.;
- 641 Anderson, B.E.; Thornhill, K L.; Winstead, E.L.; Corporan, E.; DeWitt, M.J.; Klingshirn,

642 C.D.; Wey, C.; Tacina, K.; Liscinsky, D.S.; Howard, R.; Bhargava, A. Particulate Emissions

- of Gas Turbine Engine Combustion of a Fischer-Tropsch Synthetic Fuel. *Energy Fuels*. 2010,
 24, 5883-5896.
- (47) Lobo, P.; Hagen, D.E.; Whitefield, P.D. Comparison of PM emissions from a
 Commercial Jet Engine burning Conventional, Biomass, and Fischer-Tropsch Fuels, *Environ. Sci. Technol.* 2011, 45, 10744-10749.
- 648 (48) Lobo, P.; Rye, L.; Williams, P.I.; Christie, S.; Uryga-Bugajska, I.; Wilson, C.W.;
- 649 Hagen, D.E.; Whitefield, P.D.; Blakey, S.; Coe, H.; Raper, D.; Pourkashanian, M. Impact of
- Alternative Fuels on Emissions Characteristics of a Gas Turbine Engine Part 1: Gaseous and
- Particulate Matter Emissions. *Environ. Sci. Technol.* **2012**, 46, 10805-10811.
- 652 (49) Cain, J.; DeWitt, M. J.; Blunck, D.; Corporan, E.; Striebich, R.; Anneken, D.;
- 653 Klingshirn, C.; Roquemore, W. M.; Vander Wal, R. Characterization of Gaseous and

Page **30** of **32**

ACS Paragon Plus Environment

Environmental Science & Technology

- Particulate Emissions From a Turboshaft Engine Burning Conventional, Alternative, and
 Surrogate Fuels. *Energy Fuels.* 2013, 27, 2290-2302.
- 656 (50) Beyersdorf, A.J.; Timko, M.T.; Ziemba, L.D.; Bulzan, D.; Corporan, E.; Herndon,
- 657 S.C.; Howard, R.; Miake-Lye, R.; Thornhill, K.L.; Winstead, E.; Wey, C.; Yu, Z.; Anderson,
- B.E. Reductions in aircraft particulate emissions due to the use of Fischer–Tropsch fuels.
- 659 *Atmos. Chem. Phys.* **2014,** 14, 11–23.
- 660 (51) Corporan, E.; Edwards, T.; Shafer, L.; DeWitt, M.J.; Klingshirn, C.; Zabarnick, S.;
- 661 West, Z.; Striebich, R.; Graham, J.; Klein, J.; Chemical, Thermal Stability, Seal Swell, and
- Emissions Studies of Alternative Jet Fuels. *Energy Fuels*. 2011. 25, 955-966.
- (52) Lobo, P.; Christie, S.; Kandelwal, B.; Blakey, S.; Raper, D. Evaluation of non-volatile
 PM Emissions Characteristics of an Aircraft Gas Turbine Engine with varying Alternative Jet
 Fuel Blend Ratios. *Energy & Fuel.* 2015, 29, 7705–7711.
- 666 (53) Christie, S.; Raper, D.; Lee, D.S.; Williams, P.I.; Rye, L.; Blakey, S.; Wilson, C.W.;
- 667 Lobo, P.; Hagen, D.; Whitefield, P. Polycyclic Aromatic Hydrocarbon Emissions from the
- 668 Combustion of Alternative Fuels in a Gas Turbine Engine. *Environ. Sci. Technol.* 2012, 46,
 669 6393-6400.
- 670 (54) Standard Specification for Aviation Turbine Fuel Containing Synthesized
 671 Hydrocarbons; ASTM D7566; *ASTM International*. West Conshohocken, PA.
- (55) Brem, B.; Durdina, L.; Siegerist, F.; Beyerle, P.; Bruderer, K.; Rindlisbacher, T.;
 Rocci Denis, S.; Andac, G.; Joseph Zelina, J.; Penanhoat, O.; Wang, J.; Effects of fuel
 aromatic content on non-volatile particulate emissions of an in-production aircraft gas
 turbine. *Environ. Sci Tech.* 2015, 49, 13149–13157.

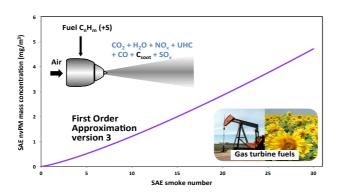
Page 31 of 32 ACS Paragon Plus Environment

- 676 (56) Durdina, L., Lobo, P., Trueblood, M.B., Black, E.A., Achterberg, S., Hagen, D.E.,
- 677 Brem, B.T., Wang, J., Response of Real-Time Black Carbon Mass Instruments to Mini-
- 678 CAST Soot. Aerosol Sci. Technol. 2016, 50, 906-918.
- 679 (57) Stettler, E.J.; Boies, A.M.; Petzold, A.; Barret, S.R.H. Global civil aviation black
- 680 carbon emissions. *Environ. Sci. Tech.* **2013**, 47, 10397 10404.
- 681 (58) Moses, C.A.; Callahan, T.J.; Cuellar, J.P.; Dodge, L.G.; Likos, W.E.; Naegeli, D.W.;
- 682 Valtierra, M.L. An Alternate Test Procedure to Qualify Fuels for Navy Aircraft: Phase II.
- 683 Naval Air Propulsion Center. Trenton, NJ. Report No. NAPC-PE-145C. 1984.
- 684 (59) Bowden, T.T.; Pearson, J.H.; Wetton, R.J. The Influence of Fuel Hydrogen Content
- Upon Soot Formation in a Model Gas Turbine Combustor. J. Eng. Gas Turbines Power.
 1984, 106, 789-794.
- 687 (60) Rye, L.; Lobo, P.; Williams, P.I.; Uryga-Bugajska, I.; Christie, S.; Wilson, C.W.;
- 688 Hagen, D.; Whitefield, P.; Blakey, S.; Coe, H.; Raper, D.; Pourkashaniand, M. Inadequacy of
- 689 Optical Smoke Measurements for Characterisation of Non-Light Absorbing Particulate
- 690 Matter Emissions from Gas Turbine Engines. *Combustion Sci. Tech.* **2012,**184, 2068-2083.

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