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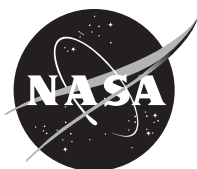
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Abstract

This paper reports XPS analysis of jet exhaust particulate from a B737, Lear, ERJ, and A300 aircraft during the APEX III NASA led field campaign. Carbon hybridization and bonding chemistry are identified by high-resolution scans about the C1s core-shell region. Significant organic content as gauged by the sp^3/sp^2 ratio is found across engines and platforms. Polar oxygen functional groups include carboxylic, carbonyl and phenol with combined content of 20 percent or more. By lower resolution survey scans various elements including transition metals are identified along with lighter elements such as S, N, and O in the form of oxides. Burning additives within lubricants are probable sources of Na, Ba, Ca, Zn, P and possibly Sn. Elements present and their percentages varied significantly across all engines, not revealing any trend or identifiable cause for the differences, though the origin is likely the same for the same element when observed. This finding suggests that their presence can be used as a tracer for identifying soots from aircraft engines as well as diagnostic for monitoring engine performance and wear.

Introduction

Soot chemistry is relevant to its environmental interaction and impact on human health (Pope et al. 2002). Soot can contain heteroelements. These may arise from the fuel, lube oil, engine wear or by the combustion process (Timko et al. 2010). Elemental content and concentration depends upon the contribution and partitioning of these sources to soot. Hence, their presence serves as a potential diagnostic and also is a potential means of apportionment. Heteroelements can participate in surface reactions (Countless et al. 1980). For example, Fe can generate reactive oxygen species, such as OH by the well-known Fenton reaction (Kennedy 2007).

Soot chemistry also pertains to oxygen functionality and organic content. In absence of condensed sulfate and volatile compounds, oxygen groups determine the acidity of the carbon surface and correspondingly its hydrophilic properties (Gysel et al. 2003). Three nominal classes, hydroxyl, carbonyl and carboxylic acid groups are the characteristic groups as distinguished by wet analytical methods (Boehm 1994). Therein it is quite logical to use the same group identification by XPS (Okpalugo et al. 2005). Soot chemistry also includes the carbon hybridization state, namely sp^2 versus sp^3 (Lascovich et al. 1991). Alkyl groups, as substituent groups on aromatic units and other hydrocarbon fragments from either fuel or oil can contribute to the latter (Yu et al. 1991). Secondary condensation of volatiles can contribute to both, and can usually be distinguished via TEM from the “solid” particle as a coating, or appear as a flattened droplet if formed as an independent secondary aerosol (Russell et al. 2002). Both aspects of surface chemistry impact atmospheric longevity of the soot, its propensity to condense gases such as SO_3 and NO_2 and to coalesce with other aerosols (Choi and Leu 1998).

To-date, reports on the chemistry aircraft exhaust particulate matter (PM) emission from full-scale engines (as opposed to sector or model combustors) burning actual fuels are few. Early work reported elemental speciation for PM from a CFM56-2C1 engine with a recent study analyzing soot collected from the NASA-DC-8 jet for element content (Kinsey and Hays 2011). Limited analysis has also been performed on particulate collected in chase experiments (Wuebbles et al. 2007). Performed relatively recently, these studies summarize the relatively few studies to-date.

Thus far most emphasis has been upon physical characterization of engine PM. Field campaigns with multiple teams have measured PM size and number distributions, with others calculating mass emission indices as function of power and fuel type (Wey et al. 2006). Specific techniques have included scanning mobility particle sizer (SMPS), aerosol mass spectrometers (AM), providing electric and aerodynamic mobilities, respectively, tapered element oscillator measurement (TEOM) for total PM mass and absorption for black carbon determination in an aethalometer or multi-angle absorption photometer (MAAP) instrument.

Characterization of actual aircraft engine PM is difficult; little is available and sampling opportunities from real systems few. Yet significant public exposure occurs at airports, and particularly for ground support personnel. On tarmacs, boarding ramps, and open terminals, if exhaust is smelled, likely soot, concurrent with emission is breathed. Therein the objective of this study was to obtain PM samples across a variety of jet engine platforms to compare the chemical composition of the combustion-generated particulate (solid and volatile) at realistic engine conditions, and contribute to existing data.

The goal of this study was analysis of a spectrum of soot for the aforementioned aspects of chemistry. With paucity of such data from real operating aircraft, this subset of analyses conducted on soot collected during the field campaign provides a baseline for the consistency or variability of these different chemical measures of jet engine PM. Given the varied aspects each with their own relevance, XPS was selected for its applicability to each.

Experimental

PM emissions are historically measured as the fuel emission index (EI), being the percent of PM mass per unit (mass) of fuel consumed. Filter based measurements have shown EI to peak at low and high engine thrust. The former is due to poor efficiency at idle operation (4 to 7 percent power) and the latter due to amount of fuel consumed at takeoff (85 to 100 percent power). These two modes are the primary operational regimes of jet engines at and near ground level, i.e., at airports, and hence are the operational regimes producing the PM exposure to travelers and the surrounding neighborhood. These are the thrust levels as which soot chemistry is characterized across a variety of jet engine platforms. Also these powers produce the majority of ground and near-ground level soot emissions. Samples were collected during the APEX III field campaign in the fall of 2005 at the NASA-Glenn Research Facility in Cleveland Ohio, immediately adjacent to the Cleveland Hopkins International Airport. This geographic proximity facilitated “loans” of the varied aircraft, with fuel, Jet-A, by Continental Airlines, coordinated by Hopkins personnel.

XPS measurements were performed on soot collected on quartz filters (at ambient temperature). These filters were type GF 10 used for absorption in a MAAP, manufactured by Thermo Electron. Further details may be found in a NASA Technical Memorandum for APEX I (Wey et al. 2006).

XPS Instrument and Analysis

The PHI 500 Series XPS is a conventional dual anode X-ray source (Mg & Al) with a 200 hemispherical electron energy analyzer and a multi-channel detector. Analyzer electronics have an energy scan range of 0 to 4800 eV with a resolution of 0.025 eV minimum step size, and the lens is an Omni-Focus III (Physical Electronics Inc. (PHI)). The mono-chromatic Al X-ray source has a variable energy range of 4 kV to 15 kV with 300 W power in continuous operation. The sample stage can be moved and focused in three dimensions.

XPS was performed on each sample using both a survey scan for all elements plus a multi-plex (high resolution) scan for carbon (and usually oxygen). The percent of each element, determined by the survey scan was measured to ± 0.1 percent was measured using a semi-quantitative program associated with the XPS software. The data was collected by a MATLAB (The Mathworks, Inc., Natick, MA) computer routine.

A high-resolution (multi-plex) scan was run for carbon, with a minimum of 10 sweeps and 7 cycles. The resultant high resolution C1s peak was curve fit using Gauss-Lorenz peaks and a Shirley fit. Because the carbon 1s peak was the peak of interest, attention was focused on this peak: its breadth, displacement and asymmetry. Soots were examined to determine if the carbon 1s peak had identifiable sub-peaks as established by a curve fitting routine attached to the XPS software. Any sample charging was taken into account by using the neutralizer during acquisition. The default limits to this program used a FWHM of 1.0 and a (%) Gaussian component of 20. An effort was made to fit a peak for the leading edge ($\sim 283\text{eV}^+$) of the curve and locate larger peaks with a minimum peak broadening. The exception to this was the area where the plasmon peaks are found, usually $>286\text{ eV}$. This area was often broad and poorly defined relative to baseline. Peak deconvolution was performed via the same MATLAB program after setting the background parameters. Peak assignments were made per the NIST compilation (NIST database), allowing for shifts due to sample charging. Precision of reported percentages of the different C1s components is judged to be ~ 5 percent as $\pm 1\text{s}$, this measure being based upon examination of residuals expressing goodness of fit upon variation of peak position or width.

Results and Discussions

Chemical Composition, Surface Chemistry, and Carbon Bonding State

As an analytical tool, XPS is of particular value in providing three complimentary chemistry measures of carbonaceous aerosol: elemental composition, surface chemistry and carbon bonding. Though a commercial fuel with up to 300 ppm sulfur content was used in all tests.

Variability in engine design have the potential to create very conditions for soot formation and oxidation. Examination of the soot chemistry by hetero-element content and carbon bonding can identify the impact or not, of engine differences. A secondary consideration is how different are such soots from common laboratory flame. Similarity would permit transfer of knowledge between the laboratory and actual systems whereas differences would point to the future need for individual studies at full scale.

Elemental Composition

In XPS a survey scan generally covers a very broad energy range in which element signatures are identified on the basis of the emitted photoelectron kinetic energy, as shown in Figure 1, for each of the four jet soots. Common to all soots is the significant content of N, S, and Na.

In the case of highly refined jet fuel (kerosene), light elements such as N and O will not arise from the fuel but rather from the air-supported combustion. Additional high resolution scans over the S2p, N1s and O1s regions confirm these elements to be in the form of oxides (Wey et al. 2006). The high N content suggests significant exposure and adsorption of NO_x species (Prince et al. 2002). NO or NO_2 could undergo radical addition to p bonds or to vacancies and edge sites in aromatic systems and the carbon lamella comprising the soot surface. Reaction will form—NO- intermediates on carbon, as is known by oxidation studies (Jeguirim et al. 2005), but NO_2 may not be prevalent relative to NO at exhaust temperatures. Alternatively surface oxygen groups (observed in the C1s scanned region) could participate in bonding with NO and NO_2 to again form surface bound nitrogen oxides (Seisel et al. 2005). No sulfur was detected in elemental form either but rather, consistent with N, in the form of oxides. Its adsorption is also attributed to bonding with surface oxygen groups. The role that water may play in facilitating adsorption of nitrate or sulfate compounds is not addressed by these measurements. Moreover these interpretations do not preclude the possibility that sulfur species yet may act as seed nuclei for soot

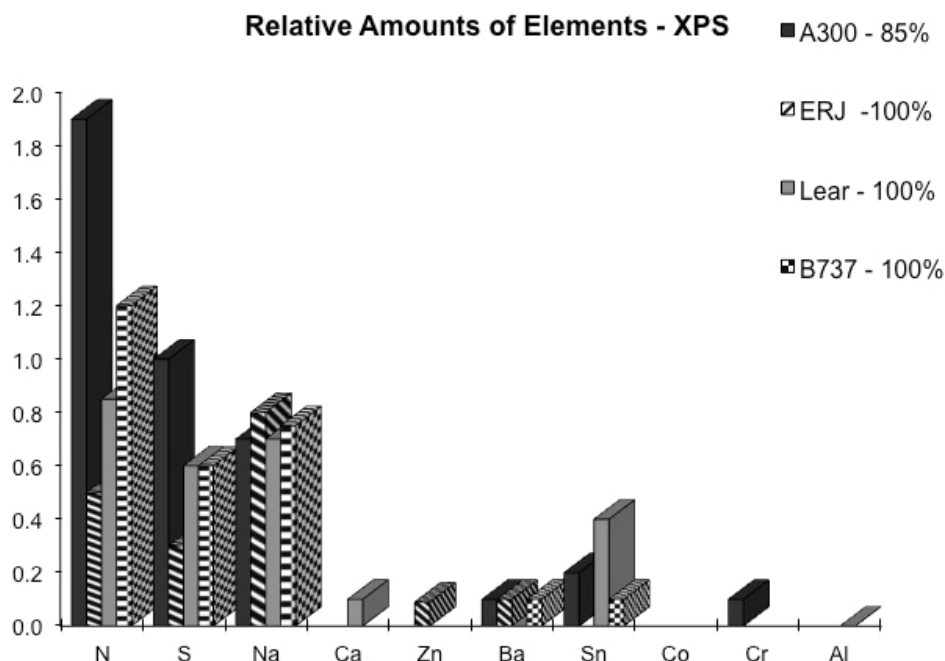


Figure 1.—The XPS global survey scan of A300, ERJ, Lear, and B737 derived soot.

(Karcher 1998), where at the particle core the (elemental) S would not be detectable. Other elements such as alkalis (e.g., Na) can arise from pre-treatment of the fuel by supported catalysts or absorbents, or may simply be the counter ion of organic or inorganic salts. The sum total of these factors determines the elemental composition of the soot.

Soot, particularly as produced by engines, often contains metals in addition to carbon (Kinsey and Hays 2011). Transition or heavier metals may arise from jet engine materials. Al is used in inlet ducts and Al_2O_3 is a bond coat material for thermal barrier coatings that are primarily composed of yttria (Y_2O_3) stabilized zirconia (ZrO_2) (Clarke and Phillopot 2005; Van Ben et al. 2010; Stover and Funke 1999). Elements such as Sr or Ba may be added to the ceramic for stability while transition elements such as Ni or Co are found in the underlying bond coat and are constituents of turbine fan blades (Stover and Funke 1999). Cr is a common stainless steel alloy element, e.g., used in stainless steel bearings. The presence of any of these elements would be indicative either of erosion, wear of these coatings or exposure of underlying alloys. The fact that such elements are present in the PM_{2.5} allows for source identification and illustrates XPS as a valuable diagnostic tool for monitoring engine health.

However, most of the elements can be attributed to lube oil additives (Kinsey and Hays 2011). Additives are substances formulated for improvement of the anti-friction, chemical and physical properties of base oils (mineral, synthetic, vegetable or animal) that enhance lubricant performance and extend equipment lifetime (Denis et al. 2000; Kashiki and Oshima 1971; Booser 1988). Combinations of different additives and their quantities are determined by the lubricant type (e.g., engine, gear or hydraulic oils) and the specific operating conditions (temperature, load, component, materials, environment, etc.). Additive content may reach 30 percent.

Additives serve a number of functions (Denis et al. 2000; Kashiki and Oshima 1971; Booser 1988). Tin may be present as an oil additive, usually in conjunction with lubricants containing molybdenum compounds, though it can also be used as an overlay for flashing of components. Barium compounds serve as corrosion and rust inhibitors; detergent; anti-smoke additive in fuels. Zinc dithiophosphate (ZDP) or dialky-dithiophosphate (ZDDP) are anti-wear, anti-oxidant, and corrosion inhibitors. Sodium (Na) and barium (Ba) are associated with detergents that neutralize strong acids, produced during the combustion process. Phenolates, sulphonates and phosphonates of alkaline and alkaline-earth elements, such as calcium (Ca), magnesium (Mg), sodium (Na) or barium (Ba) are used as detergents in lubricants. The

absence of phosphorous (P) is surprising since it is often used in tri-cresyl phosphate as an anti-wear additive that prevents direct metal to metal contact. Other organic additives include anti-oxidants, (e.g., alkyl sulfides, aromatic sulfides, aromatic amines, and phenols), rust and corrosion inhibitors, (e.g., organic acids, esters and amino-acid derivatives), and polymeric pour point depressants and anti-foaming additives such as silicon-based organics.

It is likely that combustion of the S- N- or Si-atoms containing compounds contribute to the oxides of these elements for those engines and associated PM in which other lube-oil elements were detected. Related work has found oil to contribute to secondary organics by overboard venting of the recirculation system through the engine nacelle (Yu et al. 2010) and also by fragmentation patterns of hydrocarbons of vented vapors within the core flow exhaust (Yu et al. 2012). Yet fragmentation patterns, under exhaust flow conditions can be masked given the vast array of other organics produced by incomplete combustion. Hetero-elements and their oxidation state as incurred by surface adsorption of vented oil or by full combustion of oil from leaking seals can provide a definitive signature.

Elemental content appears specific to each soot and associated engine. The distribution of metals depends upon engine age and maintenance. Those elements whose origin is the fuel, such as sulfur (S) and nitrogen (N) are omni-present as is the nitrogen arising from combustion produced NO_x . However a particular pattern or specific ratio is not apparent.

Surface Oxygen Groups

Figure 2 summarizes the peak intensities associated with the Lear soot at 100 and 7 percent power levels, as extracted by deconvolution of the nominal C1s scans. Surface oxygen groups are inherent to partial oxidation of the carbon surface and include phenolic (-OH), carbonyl (-C = O) and carboxylic acid (C-OOH) groups. The concentration of different functionalities represents a composite picture of the oxidative environment experienced by the soot particle in its post-growth environment. Species such as CO_2 , H_2O and in particular NO_2 can all partially oxidize the soot particle. Across this range of species and temperature, the surface oxygen concentrations are the steady-state levels resulting from surface oxidation processes and are not reflective of the rate or degree of oxidation. However to the extent that the post-combustion environments of different (engine) sources differ in temperature and chemical environment,

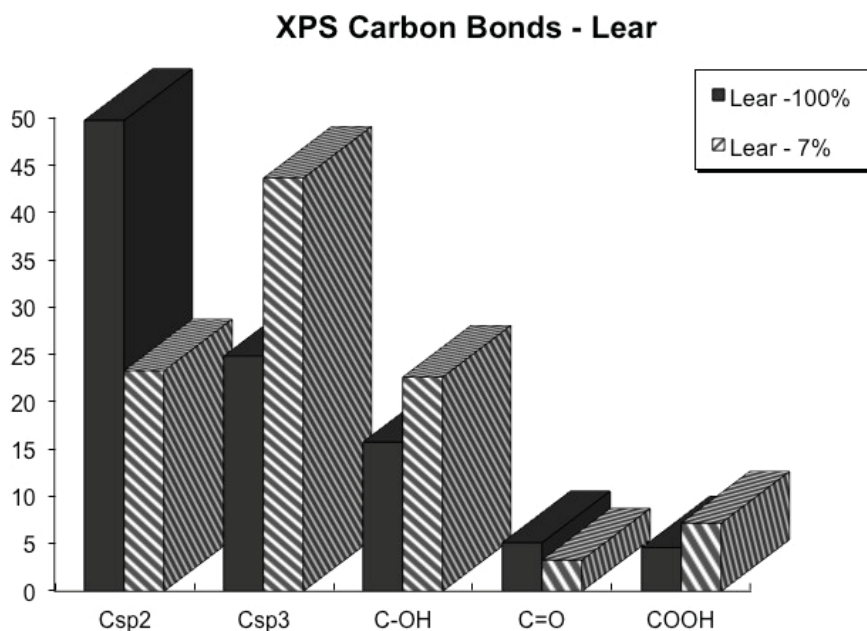


Figure 2.—Summary of peak intensities of C1s peak deconvolution from Lear 100 and 7 percent derived soot.

the identities and concentrations of these oxygen groups can also vary (Braun et al. 2008). It is interesting to note that with but a couple small exceptions, the carboxylic and especially the phenol concentrations uniformly are larger at lower engine power (85 or 65 percent) than at 100 percent. Across the jet engines observed in this study at equivalent power levels, the concentrations for these groups are similar. They are also equivalent to measurements made on soots from power plants and diesel exhaust particulate (Kinsey and Hays 2011). Therein these groups do not necessarily provide a robust signature distinguishing jet engine soots.

Nevertheless the significant concentration of these groups suggests that the emitted soot is far from hydrophobic, but rather quite hydrophilic. If as first order the carbon bonded to the oxygen functional groups is taken as the fractional monolayer coverage, relatively to purposefully assembled SAMs or even ordinary hydroxylated glass with less than 10 percent surface silanols, the soot should readily adsorb water and other polar compounds such as NO_x and SO_x. While no such films were observed in TEM, the evaporation of physically adsorbed species is likely in the high vacuum of such instruments. For this same reason the phenolic content is attributed to C-OH, and not bound water. Contributions from S-H or N-H, though coinciding with this energy region are not considered plausible given the combustion origin of the soot.

Carbon Chemical State

As illustrated in Figure 2, a dramatic change in sp²/sp³ content occurs between 100 and 7 percent power levels for the Lear soot. A similar shift in content is observed in the B737 soot between 100 and 55 percent power levels. These and results for other soots are summarized in Table 1. In each case the change reflects varied combustion environments at the different power levels. Soot is considered to be composed of both elemental and organic carbon (Matuschek et al. 2007). The main carbon C1s peak may be resolved into one or two peaks by deconvolution. The main position at approximately 284.5 eV corresponds to the sp² carbon while the peak centered near 285.4 eV may be interpreted as originating from sp³ hybridized carbon (Titantah and Lamoen 2005; Gilham et al. 2008). These two types of carbon bonding are integral to the overall soot nanostructure, representing the elemental and organic carbon, respectively. The amount and spatial relationship of these different hybridized components are intimately linked to the soot formation process. Nascent fuel composition, gas-phase pyrolysis processes and exposure to elevated temperature all play a role in determining the split between these components.

Of particular interest for the Lear soot at 7 percent power is the high sp³/sp² ratio, approximately 1:1.5, indicating significant organic content. A similar ratio of ~1.9, which indicates a significant organic content was found for the B737 soot, but at 55 percent power. It is not surprising that the organic content increases at lower power levels. Operating off optimal design, mixing is incomplete and combustion uncompleted. Fuel pyrolysis products becomes incorporated and retained within the soot. But for the ERJ and A300 soots, organic content exhibits the opposite trend, decreasing with decreasing power. Unburnt hydrocarbons in the exhaust stream can also condense upon the surfaces of the soot where they act as seed nuclei. Yet the HRTEM images did not reveal an organic coating upon the soot particles nor any liquid-like droplets upon the TEM grid used for direct capture—for any of the soots. In fact the TEM showed

TABLE 1.—SUMMARY OF C1S PEAK DECONVOLUTION COMPONENTS ACROSS SOOTS PRODUCED BY THE DIFFERENT AIRCRAFT

	ERJ - 100%	ERJ - 85%	Lear - 100%	Lear - 85%	Lear - 7%	B737 - 100%	B737 - 65%	A300 - 85%	A300 - 65%
<i>C</i> sp ²	6.63	6.72	49.72	12.87	23.28	36.21	-----	8.51	15.27
<i>C</i> sp ³	69.53	56.58	24.82	58.34	43.62	37.5	41.87	67.78	47.75
<i>C-OH</i>	10.49	22.49	15.75	18.53	22.61	15.39	34.29	13.21	23.4
<i>C = O</i>	5.1	6.33	5.13	-----	3.29	1.84	12.31	4.75	11
<i>COOH</i>	8.25	7.88	4.59	10.26	7.2	9.17	10.62	5.77	-----

that the particle surfaces were at least as structured if not more so than the core, ruling out a surface specific origin. This absence of visible organic material coupled with the evident oxidation of the particle suggests the organic content of the soot is matrix bound. And since it is unlikely to be trapped organics (again the HRTEM image does not suggest this), it is more likely in the form of alkyl groups as substituents on aromatic units (Cain et al. 2010).

Addendum

During the preparation of this article a complimentary one appeared in ES&T. Using X-ray (induced) fluorescence (XRF), PM elemental content was assessed from the three APEX campaigns. Collected on Teflon filters, exhaust plume samples from seven commercial turbofan engine models were collected on the ground at a distance of 30 m behind the engine exit.

For the aircraft and engines in APEX III results are available for only 2 of the 5 aircraft, the ERJ145 and the A300 jets. This limited overlap and different sampling position hinders comparisons. Our samples were not analyzed by XRF nor was HRTEM applied to those 2 PM samples. To note is that by XRF indicated high elemental sulfur content (54 percent for the ERJ and 89 percent for the A300, of total PM emission index) with >50 percent for both engines of the water soluble ion emission being sulfate. Such a high content suggests that sulfate aerosol served as the particle nuclei and/or coalesced with aggregates. Either case should be evident by TEM. Neither case was noted in our studies and samples. As known, sampling at distances of 30 m is a widely accepted practice that allows for the formation of volatile PM while maintaining plume integrity (Kinsey and Hays 2011; Onasch et al. 2009). A second point of commonality was the EC/OC determination using the prescribed NIOSH thermo-optical reflectance method on pre-fired quartz filters. No direct point of comparison is available, other than that the EC/OC ratio varies from less than 0.5 to well above 2.0 across the suite of engines for power levels 30 to 40 percent. Our values, denoted as sp^2/sp^3 inferred by XPS for full power operation are plausible, given this range (Kinsey and Hays 2011).

Conclusions

Techniques such as XPS and XRF excel in analyzing PM, particularly aerosols. Both techniques can analyze for elements including Na and above with 0.1 atomic percent detection limits. XPS is more sensitive than ion chromatography and can capture a broader range of elements in variable oxidation states. However it is strictly a surface sensitive technique, with penetration/probe depths in carbonaceous materials of only a few nanometers. For nanoscale materials such as soot, this outer surface band actually access ~20 percent of the particle volume, hence some volumetric portion of the particle is probed. Unlike ICP requiring gram quantities for carbon-based materials, XPS can analyze milligram—10 mg quantities, with similar accuracy and no sample preparation—certainly not the difficult sample digestion required by ICP for carbon.

XPS identified a suite of elements within the jet engine soots. The high fuel sulfur content led to soots with high sulfur contents (Onasch et al. 2009). Lube oil contributed elements such as Ca, Zn, and P by additives. Transition metals arose from chemical and/or mechanical wear. Light metals such as Al or Mg are integral to many engine components while Al, Ba, Y, and Zr are elements of bond coats on turbine fan blades. Alkali elements, particularly Na are the counter ion to organic salts within fuels. The presence and concentration of any particular element appears to be very dependent upon the specific engine and maintenance.

XPS also provides complimentary information regarding carbon bonding and surface chemistry. A near-surface sensitive measure of these characteristics is well suited for gauging environmental consequences of carbonaceous PM. Most combustion-generated soot possesses surface oxygen groups. Mainly in the form of -OH, hydroxyl groups, being the most stable thermodynamically, they are considered to arise by exposure to hot oxidizing gases such as H₂O and primarily O₂. Variable in percentage, the combined content relative to (unoxidized) carbon can extend to 20 percent, or more. It is

plausible that the extended time within the hot combustion exhaust leads to such concentrations before collection.

Of particular interest is the sp^2/sp^3 carbon bonding content, revealing that the soot is has significant organic content. Comparison to HRTEM images revealed no coating nor liquid-like droplets, suggesting that the organic content is matrix distributed. To note is that there does not appear to be a uniform trend in the sp^2/sp^3 with engine power. This may be understood or at least rationalized by the origin of the soot being from fuel-rich regions, or pockets where mixing is incomplete before combustion ceases or is quenched. How such regions vary across engines and with power level is unknown, but is likely different. Of value is that XPS can provide such measurements on microgram quantities of PM.

In summary, soot from jet engines operating at low and high power levels appears to be hydrophilic, acts to concentrate sulfur and nitrogen oxides, and may contain varied percentages of elements associated with lube oil—namely the metals from the organo-metallic additives. The impact to air quality surrounding airports can be assessed based on measured emission indices and jet operations, motivated by its chemically active nature as identified here.

Abbreviations

NASA National Aeronautics and Space Administration
TEM transmission electron microscopy
XPS X-ray photoelectron spectroscopy

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