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**Fuel and Water Characterization in
Support of the CRC Panel on Engine
Component Deposits**

Final Report

May 2021



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Executive Summary

Due to infrequent but disruptive flight and pre-flight incidents, such as aborted take-offs and aborted on-ground engine starts in North America, several engine and airframe manufacturers have initiated investigations to try to determine the root cause of these incidents. They determined that these disruptions might have been caused by engine component deposits (often referred to as “water-soluble” deposits, however, the term can be misleading as not all deposits have been shown to be either fully or partially soluble in water). In spite of significant, detailed work to characterize the deposits, their source and mechanism remained unclear. Consequently, a systematic, yearlong fuel and sump sampling program from various airports across the continental United States—along with an array of fuel and water analytical testing—was initiated to provide information that might lead to a correlation to, or source of, these water-soluble deposits. The purpose of this document is to report the results of the sampling program

An extensive survey was conducted on the chemical composition of 93 jet fuel samples. In addition, any water present in the fuel samples was analyzed; if no water was found, a small amount of water was used to extract the fuel so that microbial determinations, metals, anions and cation concentrations could be determined. Fuel samples were received from 10 major, commercial airports distributed across the entire continental United States from December 2018 to January 2020. Fuel phase analysis included bulk hydrocarbon and trace polar chemical compositions, total heteroatomic content and thermal stability analysis by Quartz Crystal Microbalance (QCM). Only seven fuels were selected for thermal stability evaluation using the QCM due to program limitations. By taking this extensive survey of fuels and conducting these relevant experiments, data should be available to help determine relationships between fuel composition and the formation of the water-soluble deposits thought to lead to engine anomalies.

Results from the fuel portion of these samples indicated that: 1) several airports have received fuel that contained sufficient trace heteroatomic content to cause degraded thermal stability as evaluated via a QCM apparatus (ASTM D7739), and 2) these D7739 issues exist in spite of the fact that all fuels were assumed to have passed D1655 specification testing, including D3241 thermal stability evaluation. Five of seven samples tested using the QCM showed substandard thermal stability, but it is unclear how pervasive this observation is across the country/industry. These poor thermal stability fuels all contained elevated nitrogen, polars, and/or sulfur content. Findings were consistent with prior research that links heteroatom content to deposition. However, more specific/direct correlations between species concentration and deposition levels is not possible at this time.

Results from water testing have indicated that some biological activity is present in the samples received, but it is difficult to attribute the contamination to the fuel systems without consistent sampling protocols. In summary, almost half of the samples (42 of 88) tested showed some microbial contamination, either bacterial or fungal. Ion chromatography results indicate the presence of cations (notably sodium, ammonium, potassium, magnesium and calcium) and anions (notably sulfate and chloride) in the water phase, and while D7739 testing was only

conducted on fuel phase samples, there is no indication at this time that either microbial presence or ion levels are directly linked to fuel deposition tendencies.

Recommendations

It is clear that some airports are receiving fuel that contains sufficient trace heteroatomic content to cause degraded thermal stability characteristics, as assessed using the QCM; however, it is unclear how pervasive these concentrations are across the country/industry. It is assumed that all of the fuels tested met the ASTM D1655 specification, therefore, there is an open question about how the thermal stability requirements in D1655 relate to current aircraft demands. We recommend further study on the following points:

- Develop guidance for actionable levels of trace, heteroatomic species, e.g., polars and total nitrogen.

- Develop a thermal stability assessment and/or protocol that would be complementary to ASTM D3241.

- Determine a critical threshold(s) for carbon deposit rates of jet fuel under different “thermal loads,” i.e., time and temperature reaction conditions, which are relevant to current aircraft.

These points could be addressed by focused research studies to: increase the number of fuel samples that undergo both QCM and trace heteroatomic analysis; increase the number of samples that undergo combined QCM and D3241 analysis; and creating a working group of engine OEMs, aircraft OEMs, and relevant industry partners to coordinate aircraft fuel system design criteria with measured deposition rates.

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Background

Over the past few years, several Airlines have been subjected to disruptive incidents (such as aborted takeoff, AOG from engine start faults, etc.) in North America, involving several Airframe and Engine OEMs. As a result, a large investigation was launched, and a root cause analysis determined that engine component deposits (often referred to as “water-soluble” deposits) was the likely cause. Part of the investigation focused on the evaluation of jet fuel quality and fuel handling equipment and procedures at limited airport locations. Although chemical characterization of the water-soluble deposits has been performed [Bowman et al., 2015], the source and mechanism of deposition remains unclear. Therefore, it was desired to enact a systematic, yearlong fuel and sump sampling program from various airport locations across the continental United States—along with an array of fuel analytical testing—to provide information that might lead to a correlation or source of the elusive water-soluble deposits.

Experimental

Samples & Sampling Protocol

Fuel samples were received from the various airports in one gallon cans. Shipments came occasionally by air but more often by ground freight. Transit time ranged from one to two weeks and on several occasions nearly a month. Sample condition ranged from “dry fuel, clean and bright,” to 90% black water bottom with a thin layer of fuel. Sample volumes ranged from about ½ to one US gallon. Containers ranged from ‘like-new’ to old and dented; 2 cans were leaking slowly on receipt. Sixty-eight of the 97 samples received were “dry” (i.e., no visible water present). Water bottoms, when present, ranged in volume from about 5 to 10 mL, however, one sample contained more than 1 L of aqueous phase. The majority of fuel samples were analyzed for composition, however, not all samples could be processed for all analysis techniques. Appendix 1 outlines the protocol used to determine how some of the analysis were conducted, e.g., water extractions of fuel for subsequent ion chromatography (IC) and microbial analysis.

Bulk Hydrocarbon Type

Two-dimensional gas chromatography (GC×GC) was used to conduct the bulk hydrocarbon type analysis of the individual fuels examined for this study. This technique is well described previously [Striebich et al., 2014]. In this technique, a non-polar, primary column separation occurs followed by a repeated modulation of the effluent from the first column onto a short, polar secondary column. The separation from this shorter column occurs fast enough to keep up with the primary column separation. The result is a two-dimensional separation with zones containing a retention time having both primary column and secondary column coordinates, and response in the Z-axis. This response is measured with a traditional chromatographic detector, such as a flame ionization detector (FID), a mass selective detector (MSD), or both.

This version of GC×GC was conducted using an Agilent 5975 GC-MS system equipped with Capillary Flow Technology (CFT) flow modulation. A 20-meter, DB-5MS, 0.18-mm ID primary column and a 5-meter, DB-17MS, 0.25-mm ID secondary column were used. A programming rate of 1.5°C/minute was used to obtain the primary separation, and a six second modulation time was chosen. Both FID and MS data were taken simultaneously, using post-column splitting and short transfer lines to each detector. The primary column flow rate used was 0.4 mL/min, and the secondary column flow was 36 mL/min. This high flow through the secondary column allowed peaks from the polar column to be relatively narrow compared to other flows examined. Data were evaluated using GC Image software (Zoex, version 2.2b0). A template was developed for sample evaluation by close examination of MS results, and subsequent translation to the co-generated FID file. These templates, or two dimensional boundaries, included the following hydrocarbon classes: iso-paraffins, normal-paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes, cycloaromatics (i.e., indans and tetralins), and diaromatics. Quantitation of classes was performed by the total FID response of the compounds in each hydrocarbon class, as FID has been shown to respond linearly (with a large dynamic range) by number of carbons for a wide range of hydrocarbon types [Schofield, 2008].

Trace Heteroatoms

Measurement of trace sulfur, nitrogen, and oxygen species in fuel was conducted using a variety of techniques and methods. The ‘total nitrogen’ and ‘total sulfur’ content of fuel samples were determined via direct injection of the fuel sample on a GC-NCD/SCD system; while ‘polar nitrogen,’ ‘polar sulfur,’ and ‘total polars’ was determined by first performing a solid phase extraction (SPE) on the fuel sample prior to GC analysis. The SPE, with subsequent GC×GC-FID/MS analysis, allowed for both the speciation and quantification of trace oxygenate compounds (as well as speciation of most nitrogen compounds). The nitrogen chemiluminescent detector (NCD) and sulfur chemiluminescent detector (SCD) techniques do not allow for direct qualification (identification) of compounds, but do provide consistent quantification.

GC Chemiluminescence Detection

Total nitrogen and total sulfur in fuels, as well as solid phase extracts of fuels, were determined by gas chromatography with chemiluminescence detection. The system, purchased from Petroleum Analyzers Corporation (PAC), consisted of an Agilent 7890 gas chromatograph equipped with dual combustion furnaces and Antek 7090 chemiluminescence detectors for simultaneous selective nitrogen and sulfur analyses. Neat (undiluted) samples of fuels or SPE extracts (typically in methanol) were injected into the GC through the use of a 7693 autosampler. The GC column configuration was a 5-meter, 0.32-mmID fused-silica guard column, followed by a 30-meter, 0.32-mmID, 0.5 μ m film Rxi-1MS column that was split into identical transfer (0.5-meter, 0.1mmID) fused silica transfer lines heated to 250°C. Column effluent was oxidized at 950°C in the dual furnaces to convert organo-nitrogen and organo-sulfur compounds into NO and SO₂, respectively. Nitrogen and sulfur were subsequently detected and quantified with the chemiluminescent detectors. The emission from the detectors is specific and directly proportional to the concentration of nitrogen or sulfur.

Solid Phase Extraction (SPE)

In order to isolate, identify, and quantify the polar components in jet fuel, 20 mL of each fuel was subjected to a solid phase extraction (SPE) procedure with subsequent GC analysis as has been previously described [Shafer et al., 2015]. Briefly, a silica gel cartridge (1000 mg) was prepared by washing and prepping the silica bed with non-polar hexanes. Then 20 mL of fuel was put through the bed at a flow rate of approximately 1-2 mL per minute. The polar components in the fuel were retained by the silica gel. The bed was then rinsed with hexanes to wash off all of the non-polar components, leaving simply hexane and the polar components on the bed. The bed was then dried using a combination of vacuum and flowing nitrogen to remove the remnants of the non-polar material. Finally, the polar components still remaining on the bed were eluted with methanol to a final volume of 1 mL. Thus the concentration effect in isolating the polars is a factor of 20. These samples were analyzed using GC×GC-FID/MS.

The GC×GC-FID/MS instrument hardware was the same as for the hydrocarbon type analysis; however, operating conditions were modified slightly. The initial GC oven temperature of 50°C was held for 3 minute and a programming rate of 2°C/minute from 50°C to 240°C was used to obtain the primary separation; a six second modulation time was used. Sample was injected,

undiluted at an amount of 1.5- μ L into a split/splitless injector heated to 260°C at a 5:1 split ratio. The FID detector was heated to 270°C and the mass spectrometer transfer line was heated to 260°C. Both FID and MS data were taken simultaneously, using post-column splitting and short transfer lines to each detector. The primary column flow rate used was 0.4 mL/min, and the secondary column flow was 36 mL/min. Data were evaluated using GC Image software (Zoex, version 2.2b0). A template was developed for sample evaluation using a combination of examination of MS results from the analysis of various types of samples and standards containing neat components. The resulting FID template was divided into polar species groups, and also further divided by carbon number.

The FID has the advantage of having a wide linear range (six orders of magnitude) and consistent response factors for compounds of the same type. This made it possible to calibrate with only a few compounds from each polar species. Stock standards were prepared in methanol from representative compounds for each group-type of polar species and each carbon number that were readily available. Calibration standards were made from the stock standards. The concentrations of standards ranged from approximately 20 to 400 mg/L (before adjusting for concentration in the solid-phase extract). A second set of stock standards were used to prepare mid-level initial calibration verification standards. All standards were analyzed using the GC $\times$ GC–FID method above. The FID areas were used to generate the calibration curves from a minimum of four calibration levels for each concentration range. The standards prepared from the second stock standard were quantified using the calibration curves to verify the calibrations. The verification standards fell within ± 15 relative % of the actual value. Surrogate standards are generally used with the jet fuel (before conducting SPE) at a concentration of 16 mg/L in order to determine the efficiency of the extractions.

Microbial

Samples were evaluated to determine the level of microbial growth present. Since fuel samples were taken without regard to established microbial sampling protocols and were not shipped to the laboratory expeditiously, quantitation was not possible and only the presence or absence is reported. Water bottoms if present were plated to determine microbial Colony Forming Units (CFU) as well as fungal CFU. Samples without free water were washed with a buffer solution which was then plated to obtain a CFU count. In general, bacterial colonies will form within 2 to 3 days while fungal growth usually takes several days longer. In order to count fungal colonies without bacterial overgrowth, the media contains antibacterial additives. Several fungal culture plates supported bacteria suggesting that some of the bacterial populations were resistant to common antibiotics.

Metals

Metals concentration was measured in fuel samples via Inductive Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). In ICP-OES the sample is sprayed into a circular glass chamber where it is mixed with an Argon carrier. The chamber is constructed to induce a strong swirling motion which forces the larger droplets to the outer wall and leaving only the very smallest droplets and sample vapor to travel to the ‘torch’ region through a small capillary. The torch consists of a non-conducting quartz tube containing the capillary flow surrounded by

another layer of flowing Argon. Surrounding the tube is an induction coil carrying a high voltage 40MHz current that creates the plasma and a near total disassociation of the molecules in the sample stream. As the plasma—positively charged atoms mixed with free electrons—exits the RF field, electrons recombine with atoms to produce characteristic light emission which is recorded by the instrument.

The intensity of these characteristic emissions are proportional to the concentration which can be calculated from calibration curves for each element of concern. Unfortunately, in addition to element specific emission there is background emission to be dealt with as electrons combine with recently formed molecules. The thousands of possible recombination energies provide a highly variable background limiting the minimum level of detection and quantification. Dealing with a different background for each fuel requires the application of a technique known as sequential additions or standard additions. A response curve is constructed using at least 3 measured additions of the element in question with concentrations spanning the level of interest. If done with sufficient precision, the resulting curve will cross the concentration axis at the negative value of starting concentration. Due to the intensive level of effort necessary to perform sequential addition evaluations only 49 fuel samples were measured.

Fuel Thermal Stability/Deposition Characterization

Quartz Crystal Microbalance

Thermal stability characteristics of some jet fuel samples were assessed using a quartz crystal microbalance (QCM) apparatus in accordance with ASTM D7739. The QCM has been used extensively to characterize fuel thermal stability, and details of the apparatus can be found elsewhere [Klavetter et al., 1993; Zabarnick, 1994; Zabarnick et al., 1996]. Briefly, experiments were conducted by placing 60 mL of sample into a batch reactor. The sample was air saturated under ambient conditions, then closed and heated to 140°C. The reactor was well stirred for the test duration. Measurements of headspace oxygen, temperature, pressure, and mass accumulation were recorded, while the fuel sample was reacted isothermally for 15 hours. These experimental conditions were chosen to highlight the differences in oxidation and deposition tendencies of various jet fuel samples due to differences in trace chemical composition, e.g., heteroatomic species and dissolved metals content.

SEM/EDS Analysis

Deposit morphology and elemental composition on several QCM crystals was examined using a scanning electron microscope (SEM) and energy-dispersive X-ray spectrometry (EDS), respectively. SEM imaging was performed using a JEOL 6460 equipped with a tungsten filament. EDS spectra(um) and mapping was/were performed using IXRF's Iridium software package.

Ion Chromatography

Ion chromatographic separations were performed on a Dionex ICS-6000 DC with conductivity detection. The analysis of anions was performed using a Dionex IonPac AS23 RFIC analytical column (2x250mm) with a 2x50mm AG23 Analytical guard column at 30°C. The separation was

isocratic using a 4.5mM Carbonate/0.8mM Bicarbonate mobile phase at 0.25 mL/min. An AERS 500 carbonate ion suppressor (2mm, Dionex) was used at constant current (7uA) with electrochemical regeneration. Cations were separated using a Dionex IonPac CS12A-5um RFIC analytical column (3x150mm) with a 2x50mm CG12A-5um guard column at 30°C. The separation cations were also isocratic using a 20mN H₂SO₄ mobile phase at 0.5 mL/min. A CDRS 600 Cation suppressor (2mm, Dionex) was used at constant voltage (3.7V) with water as the external source of regeneration. The temperature of the suppressors were 30°C and the conductivity detectors were set to 35°C. The injection volumes were 10uL for both analyses. The analytes of interest were calibrated using the average conductivity response from four different concentrations of known external calibration standards.

Results

Analysis of jet fuel and water sump samples, collected from ten airport locations, was conducted over the course of 12 months during the calendar years 2019 and 2020 (see Table 1). The airport locations were all major, commercial airports across the continental United States. Fuel samples were subjected to both bulk (i.e., hydrocarbon type) and trace (e.g., polar heteroatomics, metals, and microbial) analysis procedures as outlined in the experimental section of this report. Aqueous samples were analyzed using ion chromatography and screened for the presence of microbes. Observations of those analyses are given herein, while analysis of the results are provided in the proceeding *Discussion* section.

Table 1. Sample Frequency by Location

Location Code	Total No. Samples	Sample Receipt Dates	
		Initial	Final
A	3	15-Feb-2019	26-Sept-2019
B	11	2-Apr-2019	3-Jan-2020
C	9	15-Mar-2019	8-Oct-2019
D	9	5-Mar-2019	2-Dec-2019
E	8	26-Mar-2019	5-Dec-2019
F	9	13-Dec-2018	13-Nov-2019
G	18	25-Feb-2019	3-Jan-2020
H	11	29-Apr-2019	6-Jan-2020
I	5	21-Mar-2019	11-Nov-2019
J	10	19-Mar-2019	10-Dec-2019

Bulk Hydrocarbon Type

Bulk hydrocarbon analysis was performed using a GC×GC-FID method [Striebich et al., 2014] for 93 of the jet fuel samples. Complete, detailed compositional information is listed in APPENDIX II. Figure 1 shows a box and whisker plot¹ of the major hydrocarbon species classes for all of the fuel samples examined. It can be seen that the paraffin classes, and the cycloparaffins in particular, exhibit the largest distribution in content, e.g., about 14 to 18 %wt range between the first and fourth quartiles. The cycloparaffin class also had the most outliers. The aromatic species classes exhibited very low variability, e.g., about 2 to 7 wt%, but also comprise the smallest percentage of the bulk fuel composition. Figure 2 shows a box and whisker plot of the total aromatic content, i.e., the sum of alkylbenzenes, cyclobenzenes, and diaromatics, by airport location. Mean values of total aromatic content range from about 15.5 to 22 %wt. The

¹ Footnote: Standard box and whisker plots are used throughout this report, i.e., the box bounds the upper and lower quartiles, the median is shown as a line within the box, an 'x' is used to mark the mean (optional), whiskers represent local maximum and minimum, and outliers (shown as circle markers) are outside of the upper/lower quartile by 1.5 times the interquartile distance. "Outlier" in this case refers to the relationship of the observed value to the other observations within the sample set, it does not imply the measured value is incorrect or outside the precision of the method used.

range of total aromatic values at a single airport location vary by typically 2 to 5 %wt. The consistency of the bulk fuel composition, at a given location, may or may not imply consistency in the trace composition as well. The bulk fuel composition is not believed to significantly impact fuel thermal stability; however, it can be used as an estimate of fuel variability at a specific facility.

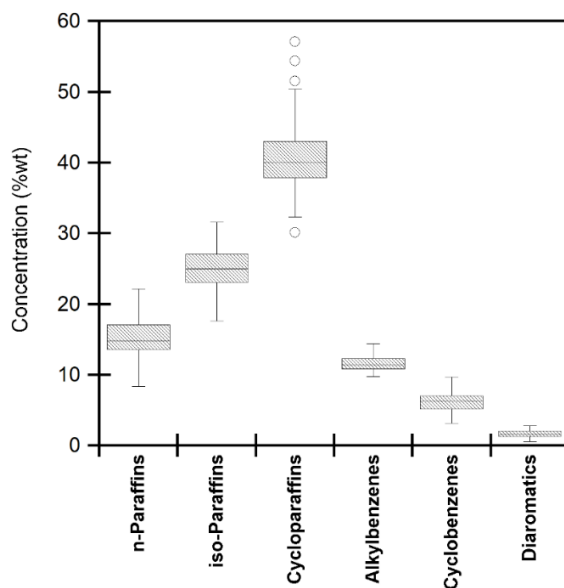


Figure 1. Box plot of major hydrocarbon classes for majority of fuel samples (n=93).

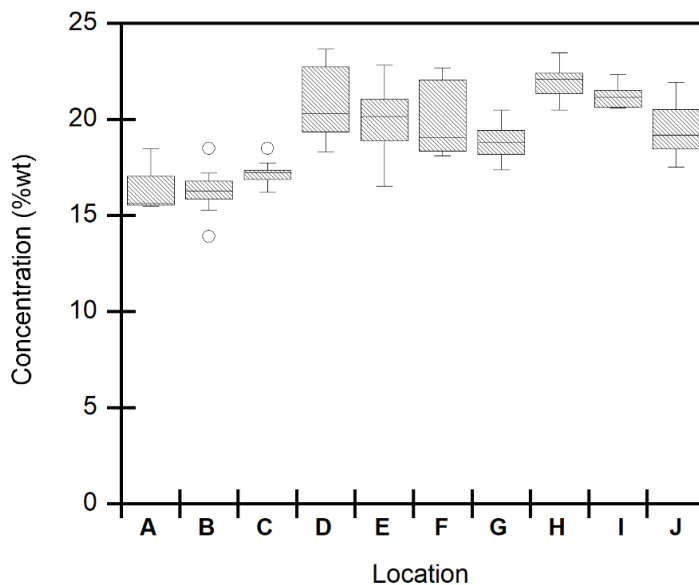


Figure 2. Jet fuel aromatic content (via GCxGC) by airport location (n ranges from 3 to 18 depending on location).

Trace Heteroatomics

The trace heteroatomic content, i.e., organic molecules containing oxygen, nitrogen, and/or sulfur atoms, was measured using multiple methods as outlined in the *Experimental* section. Solid phase extraction (SPE) followed by GC-NCD/SCD and/or GC×GC-FID/MS detection is capable of detecting (and identifying) the majority of the polar, heteroatomic compounds (typically containing either N or O functionality). Direct injection of fuel samples using GC-NCD/SCD is capable of detecting the total N and S content of the fuel (however, speciation of the compounds is unavailable). All of the results collected are tabulated in Appendix III.

Figure 3 shows a box plot of the oxygenated polar compounds found in the jet fuel samples via SPE-GC×GC-FID/MS. The single largest contributing class of oxygenates are phenols, with a median value of 148 mg/L, a maximum value of 365 mg/L, and a minimum value of 9 mg/L. The “other” category includes extractable polar compounds—believed to be mostly oxygenated compounds and/or compounds with multiple heteroatoms—that have not been positively identified by standards and/or mass spectrometry; however, these “other” polars compounds are significant contributors to the overall polar content. The remaining oxygenate classes vary in median concentration from 0 to 16 mg/L with occasional outlier concentrations of about 50 to 70 mg/L for some individual fuels.

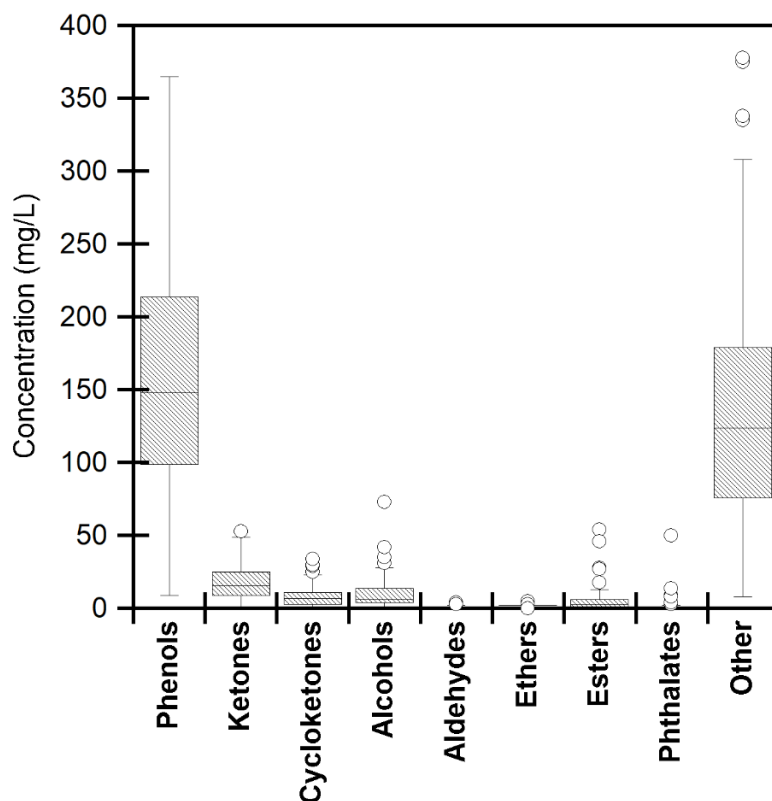


Figure 3. Distribution of speciated oxygenates via SPE-GC×GC-FID/MS in jet fuel samples (n=93).

The polar oxygenates shown in Figure 3 comprise approximately 86 to 98% of the total polar species determined by SPE-GC×GC-FID/MS. The remaining 2 to 14% of material are nitrogen containing organic species; Figure 4 shows a box plot of the organo-nitrogen species for the jet fuel samples. Quinolines exhibit the highest median concentration of 9 mg/L for the nitrogen compounds, however, anilines exhibited the highest maximum concentration of 56 mg/L. While the quinoline and aniline classes are the most abundant, of those shown in the figure, they also exhibit the greatest range in values.

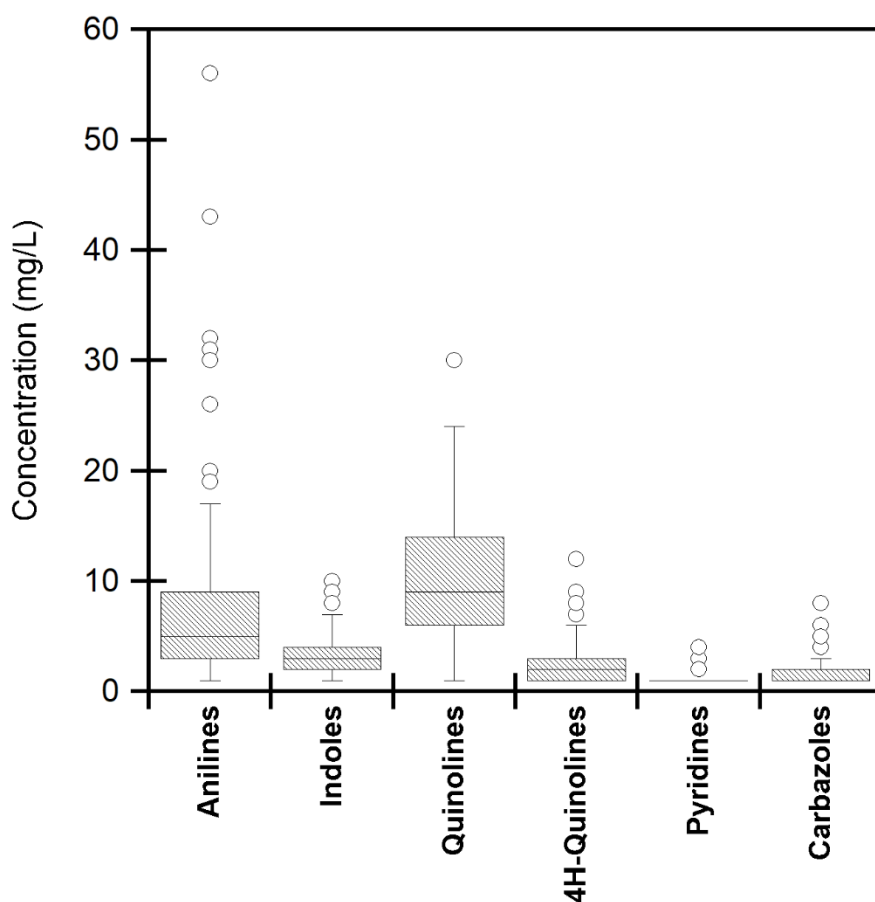


Figure 4. Distribution of speciated organo-nitrogen compounds via SPE-GC×GC-FID/MS in jet fuel samples (n=93).

Speciated polars data, as seen in Figure 3 and Figure 4, can provide insight into which classes of compounds might be implicated as deposit instigators. However, equally important is the total polars, total nitrogen, and total sulfur content found in jet fuel as shown in Figure 5 through Figure 7, respectively. The figures show these total concentrations with respect to airport location. Colorized shading for Figure 5 and Figure 6 has been used to indicate notional concentration levels of “high” (red), “mid” (yellow), and “low” (white); these levels are based on

prior UDRI experiences with aviation turbine fuels, however, they should not be interpreted as hard limits.

It can be seen in Figure 5 that two airport locations (H and I) exhibit median total polars concentrations greater than 600 mg/L and third-quartile concentrations greater than about 750 mg/L. Additionally, five other locations (A, C, D, E, G, and J) exhibit elevated polars levels where the median value is greater than about 300 mg/L. The remaining two airport locations (B and F) exhibit very low total polars concentrations.

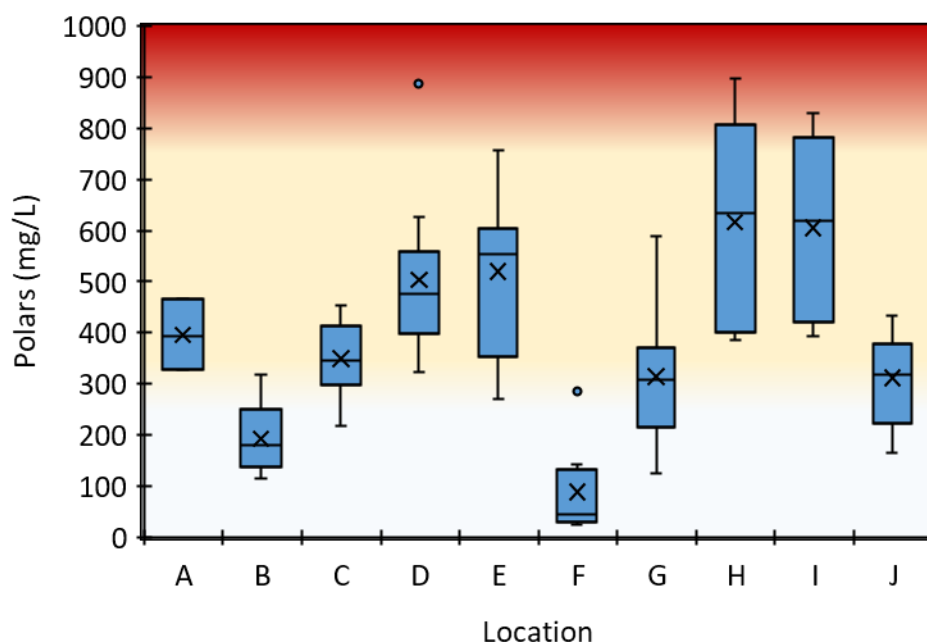


Figure 5. SPE polars content by location; red and yellow shading indicates nominal high and mid-level concentrations, respectively.

Figure 6 shows total nitrogen levels with respect to location (note that all parts per million [ppm] concentrations reported in this work are by weight, i.e., ppm = mg/kg). While nitrogen levels in jet fuel are not regulated by specification, organo-nitrogen compounds are known to instigate thermal instability reactions and therefore can be worthwhile to monitor. Location E stands out as the highest median concentration of 20.5 ppm N, while locations D, H, and I all have median concentrations greater than 10 mg/L. Location D gave a fuel with a very high total nitrogen (outlier) measurement of 34 ppm N. Location G gave a median value less than 10 mg/L, and samples from this site exhibit a large range of values from about 2 to 16 ppm N.

Finally, Figure 7 displays the total sulfur content of the fuel samples by location. Sulfur concentration is controlled by specification (ASTM D1655) and all samples received were within the maximum limit of 0.30 wt% or 3000 ppm S. The mean value of all samples was 685 ppm S. Location F gave the lowest median sulfur concentration of any airport at 106 ppm S; the other airport locations gave median sulfur values between about 400 and 1200 ppm S.

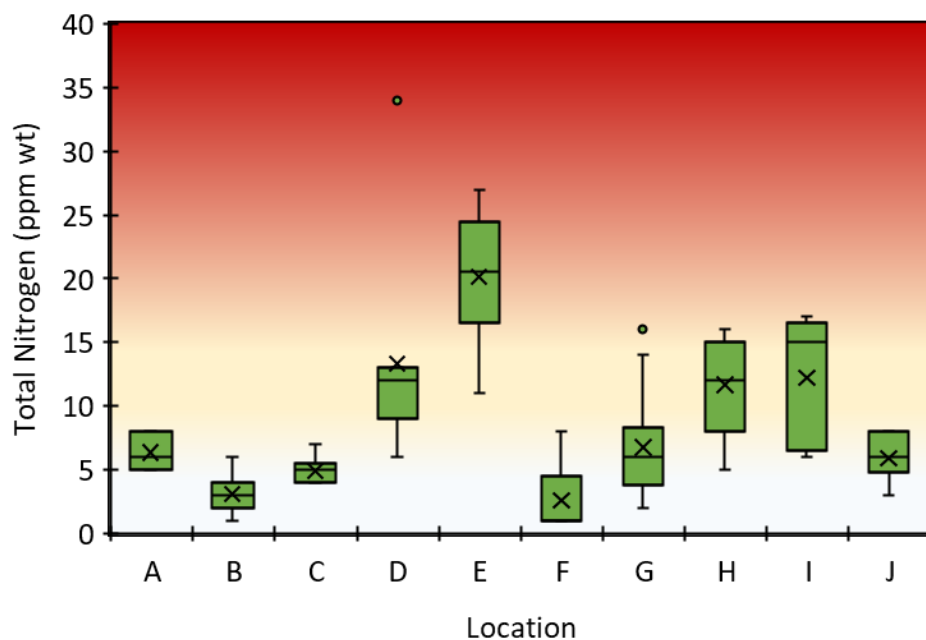


Figure 6. GC-NCD total nitrogen content by location; red and yellow shading indicates nominal high and mid-level concentrations, respectively.

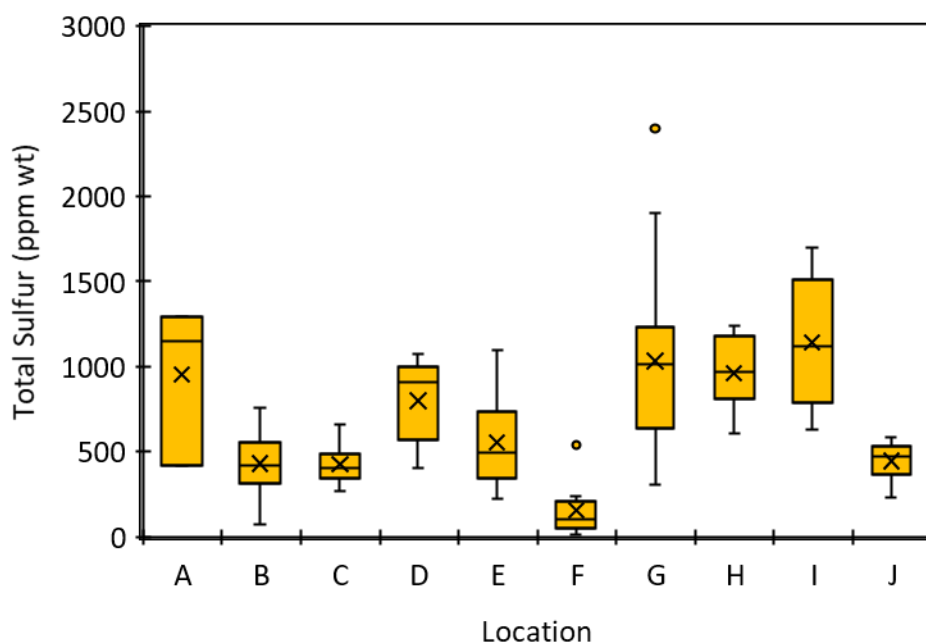


Figure 7. GC-SCD total sulfur content by location; orange and yellow shading indicates nominal high and mid-level concentrations, respectively.

Microbial

Table 2 lists test results from microbial assays of received water bottoms and/or aqueous extracts of fuel samples (see *Experimental* section for details). Forty-two of the 88 samples tested contained culturable microbes (either bacteria, fungus, or both). Without specific control over the sampling protocols at the airport locations it is difficult to determine what percentage of the positive tests reported were due to fuel microbes versus environmental sample contamination. Additionally, quantification of microbial levels was not possible with these samples as collected. Nevertheless, five airport locations (i.e., A, D, F, G, and J) reported a positive presence of bacteria and/or fungus for the majority of samples submitted. Systemic microbial contamination can negatively impact specific operations such as filtration, water coalescing, and corrosion; however, the authors are unaware of any studies directly linking microbial contamination and fuel thermal stability issues.

Table 2. Test Results Indicating the Presence/Absence of Microbes in Fuel Extract or Water Bottom Samples

Location	POSF ID	Bacteria	Fungus	Location	POSF ID	Bacteria	Fungus
A	13515	positive	positive	G	13523	positive	positive
	13765	positive	positive		13538	positive	positive
	13782	negative	negative		13580	negative	positive
B	13564	negative	negative		13608	positive	positive
	13609	negative	negative		13624	positive	positive
	13670	negative	negative		13672	positive	positive
	13675	negative	negative		13706	negative	negative
	13760	positive	negative		13768	positive	positive
	13773	negative	negative		13790	positive	positive
	13793	negative	negative		13852	positive	positive
	13854	positive	negative		13860	positive	positive
	13862	negative	negative		13868	positive	positive
	13867	negative	negative		13874	positive	positive
C	13878	negative	negative	H	13606	negative	negative
	13539	negative	negative		13607	negative	negative
	13540	negative	negative		13671	negative	negative
	13604	negative	negative		13707	negative	negative
	13623	negative	negative		13708	positive	negative
	13674	negative	negative		13767	negative	negative
	13762	negative	negative		13776	negative	negative
	13772	negative	negative		13794	negative	negative
D	13792	negative	negative	I	13859	negative	negative
	13877	negative	negative		13869	negative	negative
	13537	positive	positive		13872	negative	negative
	13605	positive	positive		13542	negative	negative
	13673	negative	positive		13764	negative	negative
	13761	positive	positive	J	13855	negative	negative
	13769	positive	positive		13875	negative	negative
	13783	positive	negative		13876	negative	negative
E	13853	positive	negative		13541	negative	negative
	13861	negative	negative		13625	positive	positive
	13873	positive	negative		13626	positive	positive
	13543	negative	negative		13642	positive	positive
	13669	negative	negative		13705	negative	negative
	13704	negative	negative		13709	positive	negative
	13774	positive	positive		13766	negative	negative
F	13791	negative	negative		13781	positive	positive
	13856	negative	negative		13795	positive	positive
	13865	negative	negative		13866	negative	positive
	13871	negative	negative				
	13505	positive	positive				
	13513	positive	positive				
	13563	positive	positive				
	13668	positive	positive				
F	13710	positive	positive				
	13763	positive	positive				
	13851	positive	positive				
	13857	positive	positive				
	13858	positive	negative				

positive = indicates presence of microbes
Negative = indicates absence of microbes
Shaded cells = sample subjected to QCM

Metals

Table 3 lists results of the elemental analysis using ICP-OES for 49 fuel samples. Of the four elements monitored, only copper was detected above the detection limits of the method (about 10 ppb). About 12% of the fuels analyzed contained trace levels of Cu (between 0 and 20 ppb), while about 24% of samples contained more than 20 ppb Cu. The maximum amount of Cu measured was 80 ppb in sample F13776.

Table 3. Results of ICP-OES Elemental Analysis

Location	POSF ID	Elemental Concentration (ppb)				Location	POSF ID	Elemental Concentration (ppb)			
		Mg	Cu	Fe	P			Mg	Cu	Fe	P
A	13765	-	40	-	-	G	13580	-	-	-	-
	13564	-	-	-	-		13608	-	BQL	-	-
B	13609	-	-	-	-		13624	-	-	-	-
	13670	-	-	-	-		13672	-	-	-	-
	13675	-	-	-	-		13706	-	BQL	-	-
	13760	-	-	-	-		13768	-	-	-	-
	13793	-	-	-	-	H	13790	-	-	-	-
C	13540	-	-	-	-		13606	-	30	-	-
	13604	-	-	-	-		13607	-	30	-	-
	13623	-	-	-	-		13671	-	-	-	-
	13674	-	-	-	-		13707	-	-	-	-
	13762	-	38	-	-		13708	-	-	-	-
D	13605	-	BQL	-	-	I	13767	-	50	-	-
	13673	-	-	-	-		13776	-	80	-	-
	13761	-	-	-	-		13794	-	35	-	-
	13769	-	50	-	-		13542	-	-	-	-
E	13543	-	-	-	-	J	13764	-	50	-	-
	13669	-	70	-	-		13541	-	-	-	-
F	13704	-	-	-	-		13625	-	BQL	-	-
	13563	-	-	-	-		13626	-	-	-	-
	13668	-	BQL	-	-		13642	-	BQL	-	-
	13710	-	-	-	-		13705	-	-	-	-
	13763	-	-	-	-		13709	-	40	-	-
LQL (ppb):		50	20	50	50		13766	-	-	-	-
							13781	-	-	-	-
							13795	-	30	-	-

LQL = lower quantitation limit, i.e., minimum quantifiable level.

BQL = below quantitation limit, i.e., element was detected in trace amount above baseline, but below the LQL.

“-“ = element was analyzed but not detected.

Shaded cells = samples subjected to QCM

Fuel Thermal Stability/Deposition Characterization

The thermal stability of seven fuel samples was assessed using a quartz crystal microbalance (QCM) apparatus operated at 140°C with a fuel stress duration of 15 hours (D7739). These thermal stress conditions differ from traditional D3241 testing in that the fuel is subjected to lower temperatures for longer residence times during D7739, while D3241 exposes fuel to very high wetted wall temperatures for very short residence times. The kinetics of fuel deposition chemistry is very sensitive to species concentrations, reaction time, and reaction temperature, e.g., Arrhenius kinetics, thus while both experiments attempt to characterize the stability performance of jet fuel, the results can sometimes differ as they examine different “time and temperature” phase spaces. Figure 8 shows mass accumulation (solid curves, open markers) and headspace oxygen profiles (dashed curves, solid markers) for seven fuels from the study. As the figure shows, mass deposition at 15 hours of thermal stress produced values ranging from 0.8 to 20.4 $\mu\text{g}/\text{cm}^2$ for fuel samples F13505 and F13776, respectively. Not only is this a very large range of deposition values, but within our experience fuels exhibiting deposition greater than about 6 $\mu\text{g}/\text{cm}^2$ after 15 hours of thermal stress duration are considered moderate to poor thermal stability fuels under these test conditions.

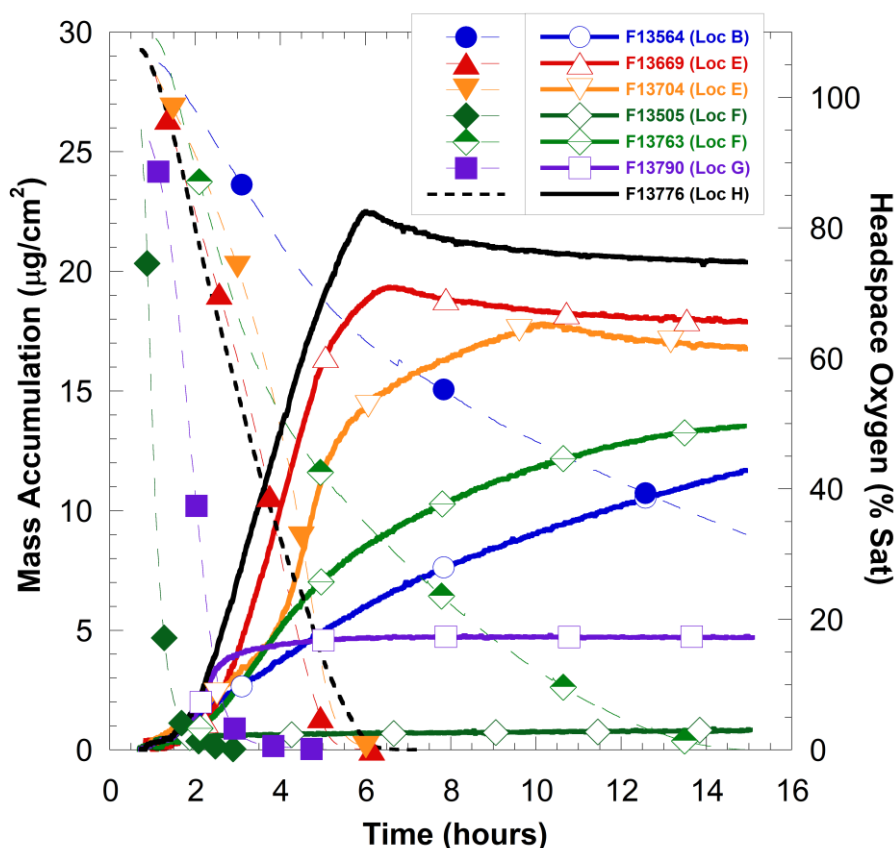


Figure 8. QCM profiles of mass accumulation (bold curves, open markers) and headspace oxygen (dashed curves, closed markers) of seven CRC fuels stressed at 140°C (see Table 6 for fuel chemical compositions).

New quartz crystals were installed for every QCM run. After each run, the crystal was carefully removed and saved for further analysis. Four of the seven crystals were photographed (see Figure 9) and inspected using SEM/EDS imaging (see Figure 10 through Figure 13). Photographs were taken after SEM analysis, thus some black tape residue remained on the upper (otherwise clean) portion of the affected crystals and should be ignored as an artifact from the photographs. As Figure 9 shows, the crystal corresponding to fuel F13505 appears visually clean (visibly comparable to the clean, new crystal), while the other three crystals have visible levels of deposit that could be characterized as fine to very fine, dark brown-black particles. Particles appear to be solids that adhere uniformly on the surface of the crystals for fuels F13669 and F13776. In contrast, the deposits from fuel F13790 contain numerous large spots that appear more like “waxy” particles. Visual observations corroborate QCM deposition values: a positive trend is seen between analytically measured surface deposits and qualitative visual assessment of total solids.

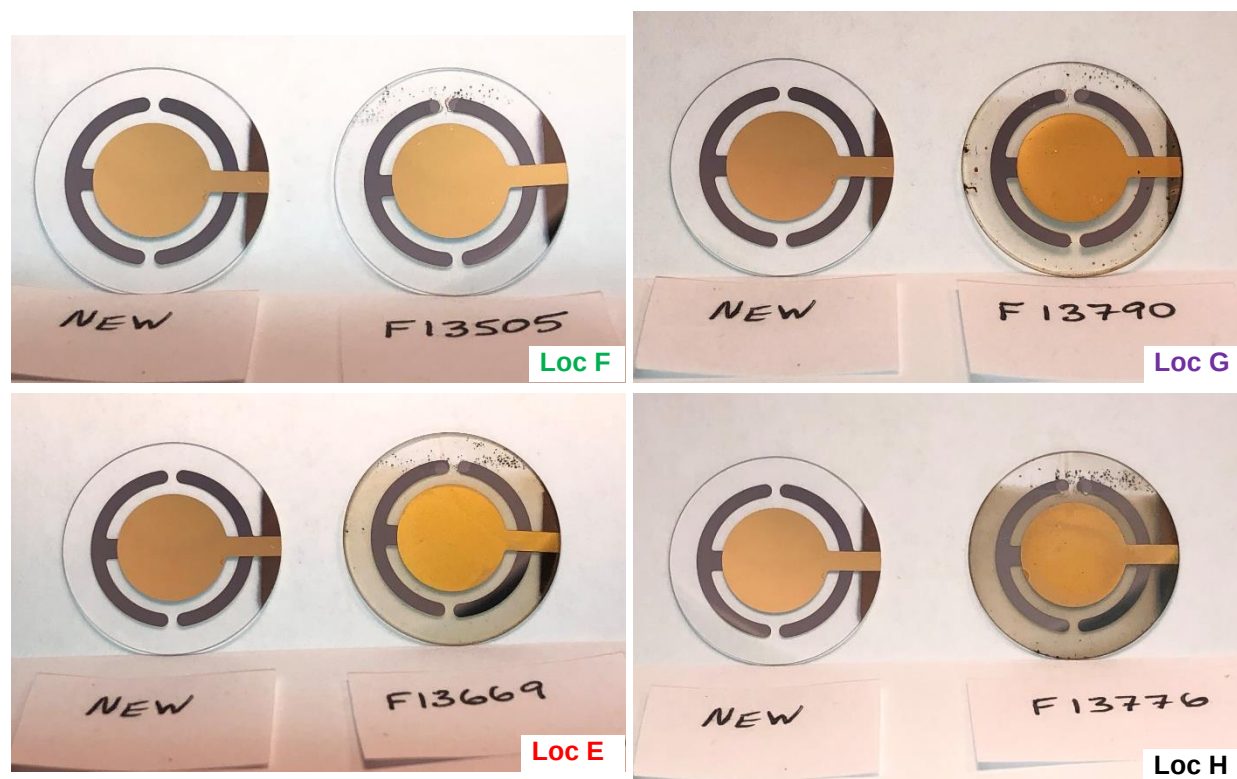


Figure 9. Photographs of new (left) and used (right) QCM crystals; black particles on upper ~20% portion of used crystals is residual carbon tape (from SEM analysis), brown-black discoloration of the lower ~80% of used crystals are deposits generated by thermally stressing jet fuel.

In addition to photography, SEM/EDS analysis was performed on the four crystal specimens and results are shown in Figure 10 through Figure 13. Few particle features were found on the sample generated from F13505, therefore, none are shown here. Figure 10 and Figure 11 show select SEM images (morphology) and EDS maps (elemental composition) from the F13776

sample. This fuel is the highest depositing of those sampled for QCM analysis, and therefore, deposit features are abundant and easily characterized on this sample. The features shown in Figure 10 are representative of the features investigated for this crystal sample. Deposits are found to be carbonaceous in nature, and appear similar in morphology to traditional thermal-oxidative deposits found in literature. While none of the QCM deposits interrogated in this report were tested for miscibility in water directly, prior research has demonstrated that QCM deposits can be water soluble [West, 2019]. Additionally, a highly polar organic tri-solvent, i.e., toluene:acetone:methanol 1:1:1 (v/v/v), is used to clean/remove carbonaceous deposits from the apparatus after every use. Therefore, it is assumed that all of the carbonaceous deposits shown herein would be effected, e.g., removable from surfaces, by water.

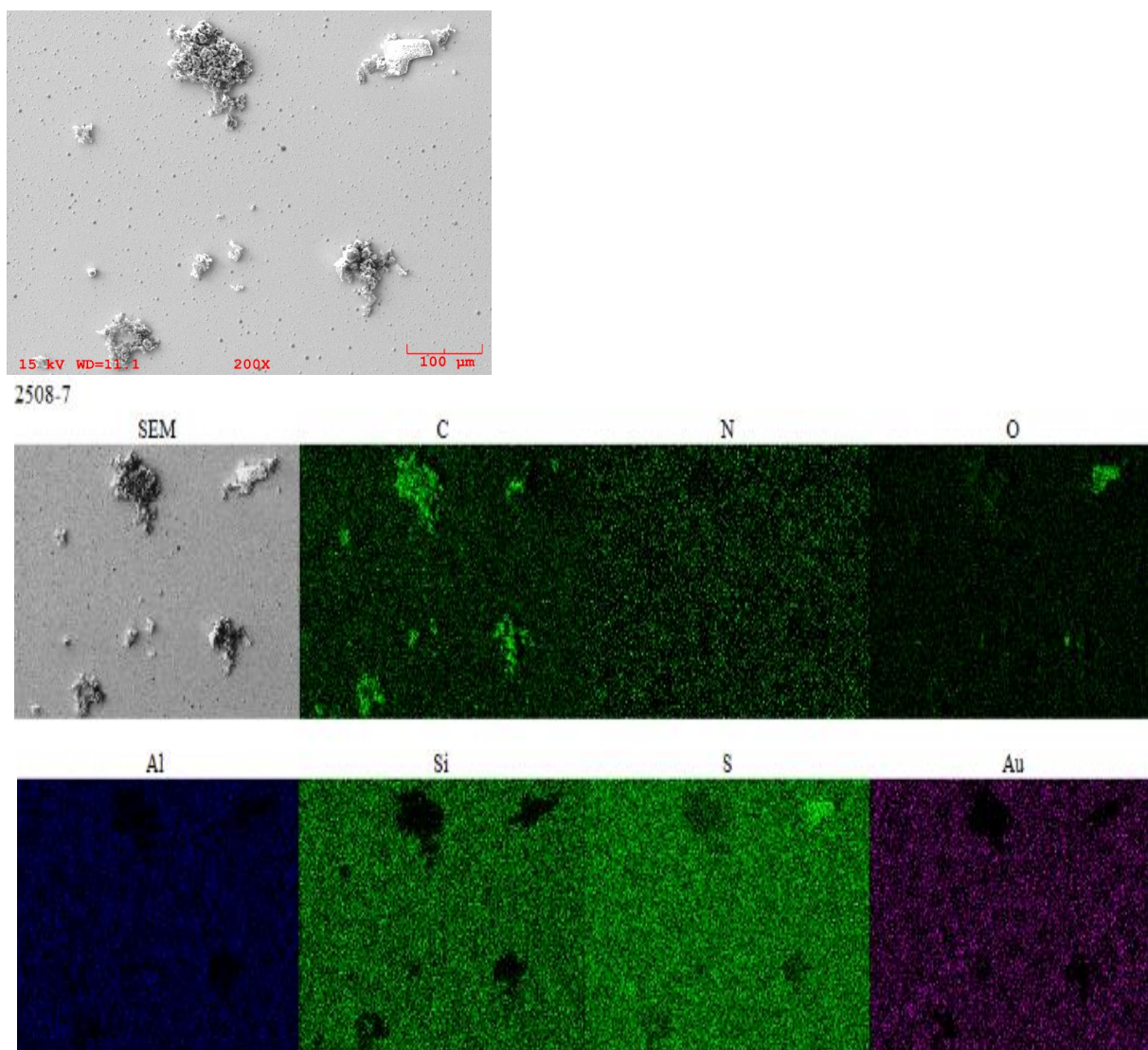


Figure 10. SEM (top) and EDS map (middle & bottom) images of quartz crystal generated from fuel sample F13776 (location H, see Figure 8 and Figure 9 for reference).

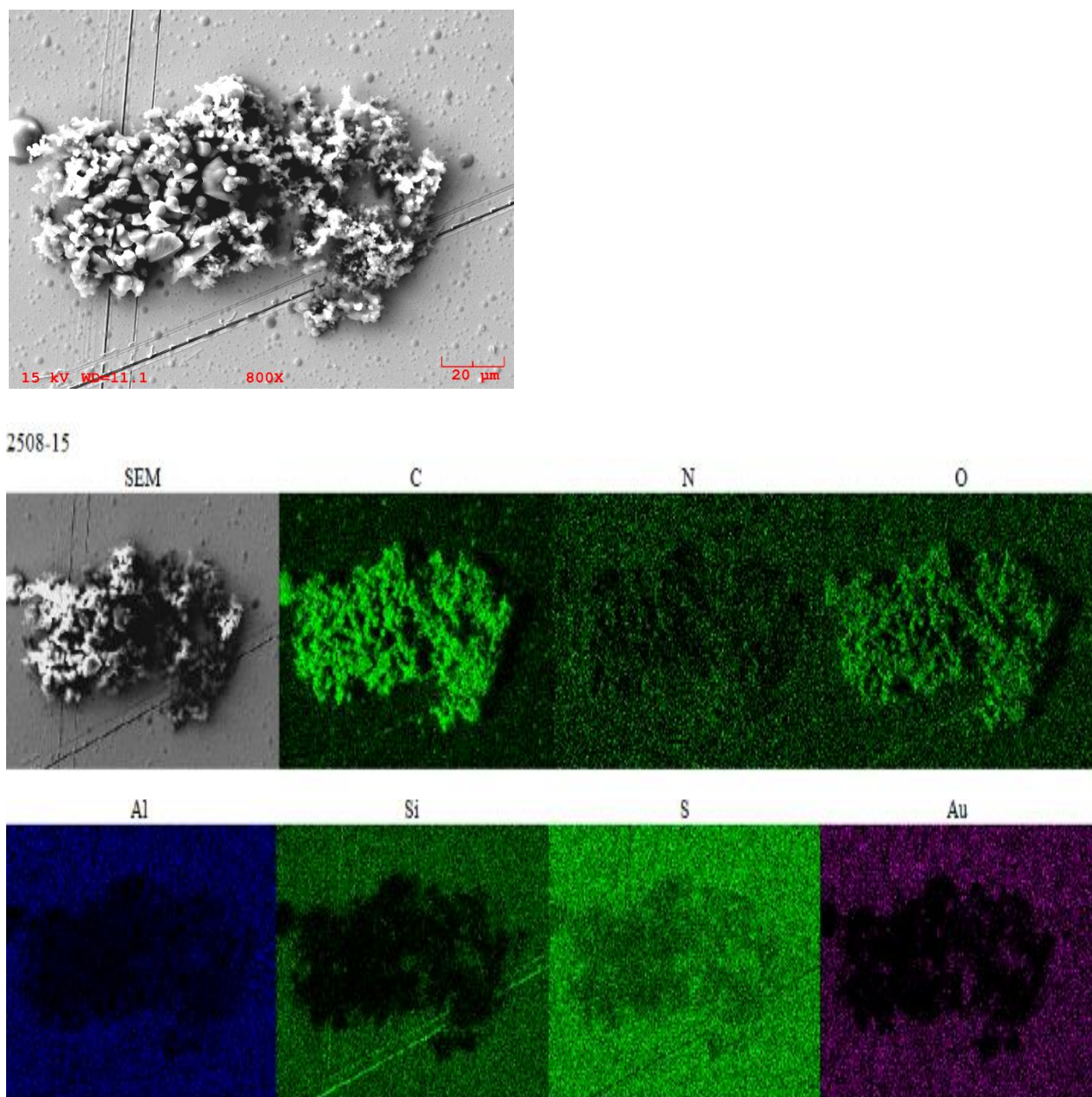


Figure 11. Typical particle morphology and composition—SEM (top) and EDS map (middle & bottom)—found on crystal surface from fuel sample F13776 (location H, see Figure 8 and Figure 9 for reference).

Figure 12 shows imaging of the quartz crystal from fuel sample F13790. Two features were analyzed, separately, using EDS and the maps are shown as feature ‘A’ and ‘B’. It can be seen that feature A is predominantly C, O, and N, while feature B has elemental contributions from C, O, Na, and S. The characteristics of feature A appeared to be more prevalent on the sample; feature B was considered an outlier. Figure 13 shows a representative SEM image from deposits generated using fuel F13669. Deposit features were again carbonaceous in nature.

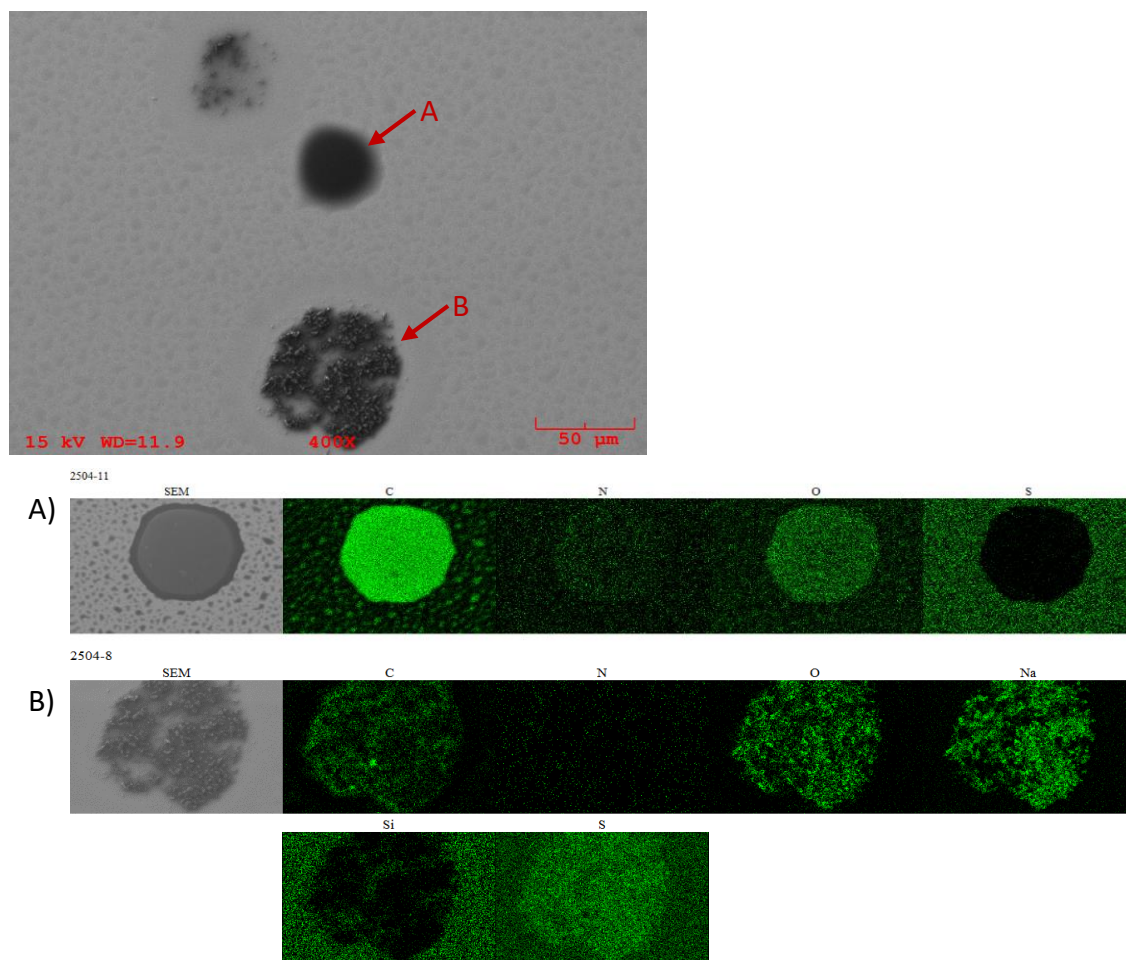


Figure 12. SEM image (top) and EDS maps of feature A (middle) and feature B (bottom) found on crystal surface from fuel sample F13790 (location G, see Figure 8 and Figure 9 for reference).

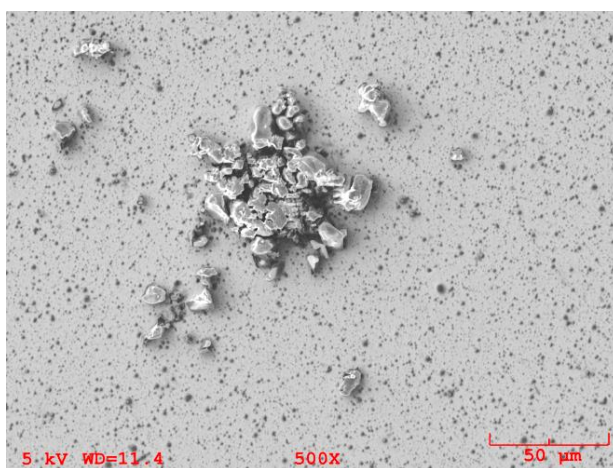


Figure 13. Representative SEM image from sample F13669 (location E, see Figure 8 and Figure 9 for reference).

Ion Chromatography

Table 4 and Table 5 list measured anion and cation concentration results, respectively, from collected fuel and water samples. Due to the nature of field fuel sample collection, e.g., the presence or absence of water in samples, and the possibility of water bottoms in bulk storage that were not sampled, it is not possible to directly compare absolute ion chromatography results between samples. Nevertheless, the presence or absence of certain ions in a particular sample as well as the relative amounts/ion ratios is of interest and may point toward handling issues upstream from airport storage.

The presence of measureable amounts of acetate and oxalate—common microbial metabolism products—also points toward significant amounts of microbial growth present in airfield or upstream distribution storage. Determining the source of these compounds was beyond the scope of this study as was their anticipated effect on thermal deposits.

Table 4. Anion Results of Aqueous Samples/Extracts

Location	POSF ID	Concentration (ppm)									Oxalate (mM)
		Fluoride	Acetate	Chloride	Nitrite	Bromide	Nitrate	Phosphate	Sulfate		
A	13515	4.7		1.4	8.2	7.4			39.1	12.8	
	13765	1.6	1.6	7.6	4.2	6.7	7.7	2.2	26.6		
B	13564			0.3		7.2	2.5				
	13670			0.3			7.1		1.		
	13675			0.3			3.1		1.		
	13760						7.2		1.		
	13862		0.11	0.31			0.02		0.14		
	13867			0.32		0.01	0.02		0.07		
C	13539										
	13540			0.5			2.		3.4		
	13674			0.1		6.5	7.1		1.		
	13762	1.			7.3				2.4		
D	13537	3.1	152.3			11.1	8.6		204.4	20.1	
	13673			0.2		6.5	7.1		1.		
	13761	1.		0.4		6.5	7.3		8.2	0.2	
	13769	1.		4.6	3.4	7.	8.		14.9	0.2	
	13853			1.6	0.	0.1	0.02		3.2	0.4	
	13861		0.12	0.28	0.01		0.04		0.23		
E	13669			0.3			7.1		1.7		
	13704			0.1					1.		
	13865	0.07	0.06	0.25		0.01	0.03		0.16	0.01	
	13871	0.09	0.01	0.44		0.01	0.03	0.02	0.16		
F	13505	3.4		21.		8.4	2.2	12.6	73.4	12.2	
	13513	3.		13.2	7.7	7.4	2.9	15.8	65.6		
	13563	9.	73.	51.8		7.7				17.5	
	13668	1.	0.4	51.	4.					0.3	
	13763	1.2		10.8	3.4	6.7	8.4	2.7	13.1		
	13857	0.5	0.4	25.1	0.1	0.1	0.3		19.6	0.03	
	13858	1.2	1.7	29.1		0.9	1.1		0.9	0.4	
G	13518						1.9		3.5		
	13519			0.	7.7		2.		3.9	11.8	
	13520			1.			2.	12.5	3.7	11.7	
	13521			0.6			1.9	12.4	5.3	12.1	
	13522						1.9		3.2		
	13523			6.7		7.6	2.2	12.6	27.	15.7	
	13608			165.3			1.04		486.8	0.8	
	13672	0.9		1.1		6.5	7.1		2.3		
	13706	0.9		0.			7.1		1.		
	13768	1.5		14.9	3.6	7.3	8.6		50.7	0.2	
	13790			24.					79.	3.2	
	13852	0.4		0.02	0.02						
	13860			1.9	0.01	0.05	0.05		3.95	0.42	
	13868			2.41	0.14	0.14	0.11		4.65	0.55	
H	13671			0.1			7.2		1.5		
	13707			0.8		6.5	7.5		2.8		
	13708			5.		6.6	8.4	2.3	4.5	0.2	
	13767	0.9		21.9		7.	7.7		6.6	0.2	
	13776			7.1					1.7		
	13859			0.56		0.64	0.17		0.24		
	13869			0.46	0.06	0.06	0.05		0.23		
	13872	0.01		3.66	0.01	0.05	0.04		0.89		
I	13764			7.3				1.3			
J	13625	0.5		0.2							
	13626	94.1		86.5					95.3		
	13642	82.7		232.7					123.1		
	13705	0.9		0.4			7.2		1.1		
	13709	0.9		0.4		6.5	7.4		1.3		
	13766	0.9		3.1	3.5	6.5	8.2		3.7	0.2	
	13781	3.3	2.8	4.9					3.8		
	13795	32.		41.					46.		
	13866	0.03	0.06	0.47			0.03		0.12		

Shaded cells = samples subjected to QCM

Table 5. Cation Results of Aqueous Samples/Extracts

Location	POSF ID	Cation Concentration (mg/l)					
		Li	Na	NH ₄	K	Mg	Ca
A	13765		12.5		3.9	0.2	17.5
	13782		7.1				3.7
	13609		7.5			0.4	
	13670		6.6			0.2	
	13675		6.6		1.6		
B	13760		5.8				
	13773		7.2				4
	13793		7.1				3.6
	13854		6.1				
	13862		6.4				3.9
	13867		5.9				3.7
	13878		5.8				
C	13604		9.3				3.9
	13674		6.7				
	13762		10.4		1.8	1.3	3.8
	13772		6.9			0.3	
	13792		6.9				4.3
D	13877		6.4				
	13673		5.4				4
	13761		6.6		5.6		9.9
	13769		9		2.9	0.1	6.6
	13783		8.2				
	13853		6.8		3.2		4.7
	13861		7.2				3.7
E	13873		38.8	88.2	50.9	13	3.8
	13669		7			0.2	
	13704		6.4			0.2	
	13774		8.6				4.2
	13791		7.7				4.1
	13856		6.2				
	13865		6.3				3.8
F	13871		6.2				
	13923		6.3				
	13710		6.8				
	13763		14.5		3	2.4	3.7
	13851		21.1		2.5	3.6	4.6
	13857		79		5.9	24	4.7
	13858		82.2		2.2	11.4	5.7
G	13924	0.3	63.4	49.4	25.9	13.3	5.5
	13538		75.7	139.7	55.7	23.7	4.4
	13672		13.9		2.4	6.2	
	13706		6.3		1.7		
	13768		11.6	1	19.7	2.9	
H	13790		16.3	18.1	2.9	4	
	13852		33.7	76.7	44.3	12.4	4.2
	13860		10.3		1.8	1.1	
	13868		11		1.9		5.8
	13874		35.3	187.4	50.8	0.6	7
	13607		7.8				
	13671		5.8		1.7		
I	13707		7.2		2.3	0.4	3.8
	13708		10.7		4.5		5
	13767		24		4.5	0.3	
	13776		12.3		2.1		4
	13794		7.9		1.9		
	13859		7.6		2.2		
	13869		6.9		1.7		3.7
J	13872		20.1		3.8		3.7
	13764		5.7		1.7	0.2	
	13855		5.1				
	13875		6.5			0.4	
	13876		5.7				
	13625		8.9		2	1.2	3.9
	13705		9.9		1.6	1.5	3.8
	13709		6			0.2	
	13766		50.7		2.7	5.4	
	13781		17.8		1.9	0.2	4.1
	13795		76.1	12.3	1.7	1	3.7
	13866		7				3.6
	13922		6.2				

Shaded cells = samples subjected to QCM

Discussion

It is well known that trace, heteroatomic species—comprised of oxygen, sulfur, and/or nitrogen containing organic molecules—found in aviation turbine fuels participate in thermal-oxidative reaction pathways that ultimately lead to surface and/or bulk deposits [Taylor, 1979; Hazlett, 1991]. Hazlett (1991) pointed out that “*Because of the variety of...jet fuels, and the different stress environments to which jet fuel is exposed, it is reasonable to state that deposits form by more than one mechanism. Thus, the definition of a universal process for insoluble formation is not likely.*” Nevertheless, we have experienced much success using a lumped, chemical mechanism to describe and model oxidation and deposition chemistry in jet fuel environments that accounts for many of the key trace compounds found in jet fuels [Kuprowicz et al., 2007; Sander et al., 2015]. With past experiences in mind, it was desirable to explore some of the known chemistry and thermal stability evaluation tools using current fuels.

The fuels selected for QCM analysis were chosen based on chemical composition (listed in Table 6), which place many of the fuels on the extreme concentration level for one or more trace component. Most of the fuels selected had elevated total nitrogen levels, e.g., ≥ 10 ppm wt, and moderate to elevated levels of total polars, e.g., 300–750 mg/L. Fuel samples F13669 and F13704 were from the same location and have similar polars, nitrogen, and sulfur content, however, F13669 is reported to contain a significant amount of copper while F13704 copper levels are below detection limits. Regardless of copper level, both fuels demonstrate poor thermal stability performance in the QCM giving between 16–18 $\mu\text{g}/\text{cm}^2$ of deposit (see Figure 8). Fuel F13505 has very low levels of heteroatomic species and shows very good thermal stability giving only 0.8 $\mu\text{g}/\text{cm}^2$ of deposit in the QCM. These results indicate a positive correlation between heteroatomic mixture content and fuel thermal instabilities, i.e., deposition tendency, however, direct correlation with the classes listed in Table 6 is difficult to determine with high certainty due to the relatively few samples. Nevertheless, the general observations made regarding trace, heteroatomic content and deposition are consistent with literature observations [Zabarnick et al., 2019; Zabarnick et al., May 2017 and Sept 2017; West et al., Mar 2017, April 2017, and Sept 2017; Zabarnick et al., 2016; West et al., 2016; Kuprowicz et al., 2007; Balster et al., 2006]. In addition, the elemental composition of QCM deposits analyzed herein appear to coincide with deposits from recent aircraft fuel systems [West, 2019]. It should also be noted that the presence or absence of microbes in these samples did not appear to correlate at all with QCM outcome.

While the data generated using both the QCM and SEM/EDS imaging was not comprehensive, it was very insightful. Five of the seven fuels tested on the QCM produce high levels of deposit ($>6 \mu\text{g}/\text{cm}^2$). In our experience these levels would be cause for concern. The majority of the deposits analyzed using SEM/EDS indicate the deposit material is carbonaceous in nature, which is in line with decades of research into thermal oxidative deposition of jet fuel. The elevated deposit levels are believed to be due to the elevated levels of trace, heteroatomic species that these fuels exhibit.

Table 6. Chemical Composition of QCM Fuel Samples

Location	POSF No.	[Polars] (mg/L)	[Nitrogen] (ppm wt)	[Sulfur] (ppm wt)	[Cu] (ppb wt)	Microbes Detected	QCM Deposit at 15 hrs ($\mu\text{g}/\text{cm}^2$)
F	13505*	24	1	15	n/a	+	0.8
B	13564	317	6	422	0	–	11.7
E	13669*	589	23	553	70	–	17.9
E	13704	544	25	373	0	–	16.9
F	13763	286	8	537	0	+	13.5
G	13790*	519	16	2400	0	+	4.7
H	13776*	858	16	1220	80	–	20.4

*Crystal inspected with SEM/EDS imaging and photography.

Summary

An extensive survey was conducted on the chemical composition of 93 jet fuel samples. Fuel samples came from 10 major, commercial airports within the continental United States over a year-long period from December 2018 to January 2020. Both bulk hydrocarbon and trace chemical compositions were evaluated for the majority of fuels. Average trace heteroatomic content of fuel samples was observed to vary based on location with some locations exhibiting elevated concentrations. This is of particular interest as trace heteroatoms are known to participate in thermal-oxidative processes, which lead to carbonaceous deposit formation.

Seven fuels were selected for thermal stability evaluation using the QCM. Five of the seven fuels displayed poor thermal stability; these poor thermal stability fuels all contained elevated nitrogen, polars, and/or sulfur content. Findings were consistent with prior research that link heteroatom content to deposition. However, more specific/direct correlations between species concentration and deposition levels is not possible at this time.

Recommendations

It is clear that some airports are receiving fuel that contains sufficient trace heteroatomic content to cause degraded thermal stability characteristics, as assessed using the QCM; however, it is unclear how pervasive these concentrations are across the country/industry. Presumably, all of the fuels tested met the ASTM D1655 specification, therefore, there is an open question about how the thermal stability requirements in D1655 relate to current aircraft demands. We recommend further study on the following points:

- Develop guidance on actionable levels of trace, heteroatomic species, e.g., polars, and total nitrogen.
- Develop a thermal stability assessment and/or protocol that would be complementary to ASTM D3241.
- Determine a critical threshold(s) for carbon deposit rates of jet fuel under different “thermal loads,” i.e., time and temperature reaction conditions, that are relevant to current aircraft.

These points could be addressed by focused research studies to: increase the number of fuel samples that undergo both QCM and trace heteroatomic analysis; increase the number of samples that undergo combined QCM and D3241 analysis; and creating a working group of engine OEMs, aircraft OEMs, and relevant industry partners to coordinate aircraft fuel system design criteria with measured deposition rates.

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APPENDIX I: CRC Airport Sampling SOP

1. Note approximate volume of fuel in can.
Take 3 fuel samples from the middle of can.
 - 1 sample – in glass vial – 40 ml – for fuel analysis.
 - 2 samples – in HDPE – 40 ml – for ICP.
2. Check for water bottom and record approximate volume.
IF YES → Collect and save in a small sterile bottle or 50 ml conical tube (volume dependent).
 - IF > 10 ml** → collect 1 ml in a 2 ml microcentrifuge tube for culturing, and filter sterilize 10 ml using a syringe, a syringe filter (0.2um) and a 15 ml sterile tube – label as “(sample #) water bottom filter sterilized”. Store remaining water bottom.
 - IF > 1 ml but < 10 ml** → collect 1 ml in a 2 ml microcentrifuge tube for culturing, add sterile water to a volume of 10 mls and filter sterilize using a syringe, a syringe filter (0.2um) and a 15 ml sterile tube – label as “(sample #) water bottom filter sterilized”
 - IF less than < 1 ml collected** → collect it and 10 ml of fuel from bottom in a 50 ml conical tube for extraction.**IF NO** → then collect 10 ml of fuel from bottom in a 50 ml conical tube for fuel extraction.
3. Fuel extractions from #2 (answer **NO** and **YES but less than < 1 ml collected**)
 - a. Add 2 ml of sterile water to 10 ml of fuel in 50 ml conical tube, vortex and let sit for 30 minutes
 - b. After 30 minutes, remove 1 ml and place in a 2 ml microcentrifuge tube for culturing, add ~40 ml water into the 50 ml conical tube, shake and pour 50 ml conical tube contents back into the fuel can
 - c. Let can sit for 30 minutes
 - d. Remove as much of the added water from the can as possible and place in a 50 ml conical tube
 - e. filter sterilize 10 ml of the retrieved water using a syringe, a syringe filter (0.2um) into a 15 ml sterile tube – label as “(sample #) filter sterilized extraction”
 - f. Save the remaining water in case needed.
4. Sample distribution:
 - a. Fuel samples – 1 glass vial for GCxGCxMS; 2 plastic vials for ICP analysis
 - b. Filter sterilized samples (either water bottoms or extractions from cans) – IC analysis
 - c. Microcentrifuge tubes (labeled as either water bottoms or fuel extractions) – culturing.

APPENDIX II: Bulk Hydrocarbon Type Data

See attached Microsoft Excel[®] file with tabulated data.

APPENDIX III: Trace Heteroatomic Results (Tabulated)

Table A.III.1. Total Polars, Nitrogen, and Sulfur Results

Location	POSF No.	Total Polars (mg/L)	Nitrogen (mg N/kg)		Sulfur (mg S/kg)	
			Total	Polar	Total	Polar
A	13515	393	6	5	1150	4
	13765	465	8	5	1290	2
	13782	329	5	5	421	1
B	13564	317	6	4	422	1
	13609	173	2	2	469	1
	13670	180	3	2	554	1
	13675	211	3	2	374	1
	13760	136	2	1	296	1
	13773	187	3	2	756	0
	13793	249	4	4	499	1
	13854	129	1	1	618	1
	13862	164	2	2	312	1
	13867	114	2	2	76	2
	13878	252	6	5	350	2
C	13539	296	4	4	491	3
	13540	453	5	5	454	2
	13604	373	5	5	406	2
	13623	345	5	4	388	2
	13674	359	4	3	658	1
	13762	300	4	3	319	1
	13772	454	7	5	267	1
	13792	218	4	4	375	1
D	13877	345	6	6	478	1
	13537	374	8	6	906	4
	13605	452	11	9	406	2
	13673	478	13	10	545	2
	13761	422	10	6	914	2
	13769	626	13	10	955	3
	13783	493	12	10	596	2
	13853	475	13	10	1040	4
E	13861	323	6	5	758	3
	13873	888	34	25	1070	7
	13543	270	11	11	430	3
	13669	589	23	16	553	3
	13704	544	25	17	373	2
	13774	608	20	14	769	1
	13791	756	18	17	1100	4
	13856	289	16	10	220	1
F	13865	547	27	21	335	1
	13871	560	21	17	641	3
	13505	24	1	1	15	0
	13513	29	1	1	31	0
	13563	32	1	1	118	1
	13668	33	1	1	63	0
	13710	45	1	1	104	1
	13763	286	8	5	537	2
G	13851	123	4	3	241	2
	13857	141	5	5	106	1
	13858	83	1	2	174	1
	13518	124	2	2	304	1
	13519	168	3	2	381	2
	13520	213	3	3	515	2
	13521	138	2	2	339	1
	13522	300	4	4	1030	2
H	13523	355	6	5	880	2
	13538	264	6	5	767	2
	13580	590	14	11	1440	4
	13608	327	7	6	1150	2
	13624	422	9	7	1328	2
	13672	214	4	3	674	1
	13706	316	8	5	1200	1
	13768	487	13	8	1900	1
I	13790	519	16	14	2400	2
	13852	299	6	6	999	2
	13860	318	5	5	1100	1
	13868	276	5	6	956	1
	13874	325	8	7	1190	2
	13606	470	8	6	1012	3
	13607	402	8	6	859	3
	13671	397	10	8	609	3
J	13707	385	5	3	970	2
	13708	634	15	13	758	3
	13767	728	13	8	1240	3
	13776	858	16	12	1220	2
	13794	807	16	14	971	3
	13859	898	15	13	1180	5
	13869	693	12	11	807	5
	13872	501	10	9	957	6
	13542	394	7	7	631	4
	13764	830	16	9	941	2
	13855	619	17	13	1320	5
	13875	735	15	13	1120	5
	13876	448	6	6	1700	12
	13541	434	8	8	494	7
	13625	218	5	3	483	5
	13626	361	6	4	581	7
	13642	329	8	5	569	7
	13705	307	6	3	453	3
	13709	223	4	3	351	2
	13766	430	8	5	515	3
	13781	292	5	5	367	6
	13795	164	3	3	227	3
	13866	353	6	5	403	3

Table A.III.2. Speciated Polars Results

Location	POSF No.	Concentration [†] (mg/L)														
		Phenols	Anilines	Indoles	Quinolines	4H-Quinolines	Pyridines	Carbazoles	Ketones	Cyclo-ketones	Alcohols	Aldehydes	Ethers	Esters	Phthalates	Other
A	13515	161	5	5	13	3	1	4	25	8	8	2	0	4	1	154
	13765	204	4	4	13	1	1	2	23	11	15	1	0	2	0	183
	13782	135	4	2	7	2	1	5	28	9	13	1	0	3	1	118
B	13564	122	5	4	11	1	0	8	24	2	11	0	0	2	1	125
	13609	88	2	1	7	1	0	2	10	1	7	0	0	1	0	52
	13670	101	2	0	9	0	0	1	9	2	6	0	0	3	0	48
	13675	94	2	1	8	1	0	2	18	4	11	1	0	1	1	66
	13760	65	1	0	3	1	0	1	8	2	8	1	0	3	0	44
	13773	116	2	1	4	2	0	0	4	2	5	0	0	2	0	50
	13793	99	3	1	5	1	1	2	21	7	11	1	0	6	0	91
	13854	66	1	0	2	1	0	1	6	2	4	0	0	1	1	45
	13862	78	1	0	5	1	0	1	17	3	8	1	0	1	0	50
	13867	54	1	0	2	0	0	0	12	2	12	1	0	1	0	30
	13878	110	4	2	4	2	0	5	19	3	10	0	0	1	1	93
C	13539	116	3	2	11	1	1	6	33	6	11	2	0	8	1	94
	13540	198	7	8	11	2	1	3	39	10	73	1	0	4	0	95
	13604	185	7	5	16	2	1	2	28	11	11	2	0	3	0	102
	13623	131	2	2	17	1	1	3	30	13	11	1	0	4	0	129
	13674	134	3	2	14	1	0	4	18	6	17	2	0	46	0	111
	13762	146	4	2	7	2	1	2	20	7	15	1	0	3	0	94
	13772	194	5	6	8	2	2	2	33	20	28	2	0	7	1	144
	13792	93	3	3	6	2	0	6	17	2	7	0	0	2	1	76
	13877	148	4	4	8	2	1	2	28	11	15	2	0	2	0	118
D	13537	170	4	4	15	3	1	2	17	12	5	1	0	2	1	137
	13605	255	17	8	13	2	1	1	9	9	2	1	0	1	3	129
	13673	212	17	8	15	4	1	1	8	9	3	1	0	2	50	148
	13761	214	13	4	7	1	1	2	13	9	3	1	0	2	9	143
	13769	346	19	8	10	4	2	2	15	11	3	0	0	2	1	204
	13783	223	6	3	9	4	1	2	16	13	12	1	0	2	8	195
	13853	203	3	5	9	8	1	1	12	20	2	1	0	2	0	208
	13861	144	2	2	6	3	0	0	12	11	6	1	0	2	0	134
	13873	365	12	8	16	8	4	3	28	34	24	3	5	27	14	338

Table A.III.2. Speciated Polars Results (cont.)

Location	POSF No.	Concentration [†] (mg/L)														Other
		Phenols	Anilines	Indoles	Quinolines	4H-Quinolines	Pyridines	Carbazoles	Ketones	Cyclo-ketones	Alcohols	Aldehydes	Ethers	Esters	Phthalates	
E	13543	117	20	4	6	3	1	1	11	6	3	0	0	1	1	95
	13669	219	32	5	9	6	1	1	16	11	3	1	0	9	1	276
	13704	211	43	5	8	9	1	1	16	12	6	1	0	2	0	230
	13774	261	31	7	10	7	1	1	16	16	6	1	0	13	1	237
	13791	333	15	4	17	5	2	2	24	18	20	2	0	5	0	308
	13856	109	30	2	4	4	0	1	9	6	4	0	0	11	1	110
	13865	188	56	4	7	4	1	1	19	15	4	1	0	6	0	241
	13871	254	26	8	10	6	1	1	12	17	3	0	0	6	0	215
F	13505	9	1	0	1	0	0	0	1	1	1	0	0	0	0	11
	13513	16	1	0	0	0	0	0	1	1	1	0	0	0	0	8
	13563	15	0	0	1	0	0	0	3	1	3	0	0	0	0	9
	13668	16	1	0	1	0	0	0	2	1	2	0	0	0	0	11
	13710	22	1	0	1	1	0	0	3	1	1	0	0	0	0	15
	13763	147	7	5	6	3	1	1	12	7	7	1	0	1	0	89
	13851	51	4	2	3	2	1	1	6	2	4	0	0	1	0	46
	13857	67	6	4	1	3	0	0	5	2	4	0	0	1	0	46
G	13858	30	2	0	2	1	0	1	6	2	2	0	0	0	0	38
	13518	49	3	1	2	1	0	1	7	1	4	1	0	10	0	43
	13519	71	4	2	3	1	0	1	11	2	5	1	0	10	1	57
	13520	90	6	2	5	1	1	1	11	3	6	1	0	13	3	66
	13521	58	3	1	2	1	0	1	6	1	3	0	0	12	0	50
	13522	141	8	4	6	2	1	2	9	3	3	0	0	6	2	113
	13523	165	9	5	7	3	1	2	14	4	6	1	0	10	1	126
	13538	128	8	4	10	2	0	2	10	3	4	1	0	1	0	93
	13580	266	15	10	30	5	1	4	16	6	5	0	0	1	3	229
	13608	150	11	5	12	5	0	2	8	3	3	0	0	3	0	125
	13624	210	9	6	16	3	2	2	11	5	5	0	0	2	1	150
	13672	99	8	2	12	2	1	1	5	3	3	0	0	2	1	76
	13706	143	7	4	12	3	1	1	7	3	2	0	0	4	3	126
	13768	211	11	7	16	4	1	2	12	5	6	0	0	2	0	212
	13790	254	13	9	21	12	1	3	14	7	6	0	0	3	0	277
	13852	129	5	3	10	4	0	1	8	3	3	0	0	1	0	131
	13860	161	4	3	6	2	1	0	7	4	5	0	0	1	0	124
	13868	127	4	2	7	2	0	1	9	3	5	0	1	1	0	113
	13874	136	4	3	8	2	1	2	12	4	6	0	0	3	2	143

Table A.III.2. Speciated Polars Results (cont.)

Location	POSF No.	Concentration [†] (mg/L)														
		Phenols	Anilines	Indoles	Quinolines	4H-Quinolines	Pyridines	Carbazoles	Ketones	Cyclo-ketones	Alcohols	Aldehydes	Ethers	Esters	Phthalates	Other
H	13606	212	3	2	24	4	1	2	18	11	6	0	0	11	2	172
	13607	214	12	5	13	1	1	2	15	8	4	1	0	3	1	122
	13671	151	10	6	15	4	1	2	14	10	4	1	0	54	0	126
	13707	204	7	2	8	1	1	1	13	9	4	1	0	7	0	128
	13708	219	31	3	16	5	2	2	39	25	22	2	0	3	0	264
	13767	328	5	2	14	2	1	2	36	18	20	3	0	18	4	273
	13776	342	11	3	16	4	2	2	38	29	27	4	0	6	0	375
	13794	334	4	3	13	3	2	3	39	30	35	4	0	3	0	335
	13859	353	7	3	17	5	2	3	53	30	42	2	0	4	1	378
	13869	307	13	4	12	3	1	3	32	19	22	2	0	27	1	250
I	13872	226	5	2	11	3	1	3	36	12	20	2	0	3	1	179
	13542	171	7	3	18	2	0	3	21	8	7	1	0	1	2	150
	13764	363	7	2	15	1	2	2	49	23	31	1	0	28	1	307
	13855	256	6	3	14	6	1	2	18	23	10	1	0	11	0	269
	13875	328	13	4	17	3	1	2	30	18	22	2	0	6	0	288
	13876	219	5	2	10	2	0	1	21	8	14	1	0	5	2	160
J	13541	244	9	4	15	0	3	3	24	7	11	2	0	1	2	108
	13625	79	5	1	10	1	2	2	22	4	16	1	0	3	2	70
	13626	150	6	3	17	1	2	2	37	8	18	3	0	3	2	109
	13642	116	2	2	19	1	1	2	30	8	18	3	0	4	4	118
	13705	108	1	2	8	1	1	2	28	8	12	2	0	3	1	130
	13709	74	2	1	7	1	1	2	21	6	13	1	0	5	1	90
	13766	153	1	2	10	1	1	2	38	11	42	2	0	4	0	163
	13781	106	1	1	5	2	1	1	26	11	21	2	0	1	2	113
	13795	54	3	1	4	1	0	1	17	4	14	1	0	2	1	62
	13866	148	6	1	7	1	1	2	36	13	21	2	2	3	0	109

[†]Concentration values of zero are non-detect; non-detection level is <5 mg/L for esters and <1 mg/L for all other species.