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ORIGINAL ARTICLE

Reflective spectra of gasoline, diesel, and jet fuel A on sand substrates under ambient and cold conditions: Implications for detection using hyperspectral remote sensing and development of age estimation models

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Abstract

Fuel spills are a very common occurrence globally and the traditional methods of identification and remediation can be expensive, hazardous, and time consuming. Hyperspectral remote sensing is a technology that utilizes images from a variety of air vehicles or satellites where each pixel in the image contains a quantitative reflected light spectrum that is a function of the materials in view. Laboratory and field experiments are desirable for building an effective reflective spectra library. This project evaluated the reflective spectra of gasoline, diesel, and jet fuel A on the spectrally bright Ottawa sand and a darker silica-rich sand from New Mexico (New Mexico 15) under room temperature and cold weather conditions. For the room temperature experiments, gasoline was only detectable to 90 min after initial application, diesel fuel was detectable out to 11 weeks on Ottawa sand, as well as the New Mexico 15 samples. Jet fuel A was detectable out to 5 weeks on Ottawa sand and the New Mexico 15 samples. For all cold condition experiments, gasoline was identifiable on substrates up until the 72-h mark largely and diesel fuel and jet fuel A were identifiable on each substrate out to 5 weeks. Regressions were fit to vaporization curves for room temperature and cold weather conditions and all were logarithmic in nature except for jet fuel A under lab and cold weather conditions which were best fit by power functions. Unexpectedly, diesel fuel evaporated more under cold weather conditions. Results indicate that fuel-substrate experiments can provide critical data for hyperspectral remote sensing investigations and future detailed work on fuels and other organic compounds is warranted.

Keywords Reflective spectroscopy · Hyperspectral remote sensing · Fuel spills · Petroleum pollution delineation

Introduction

Fuel spills are a very common occurrence globally (e.g., Song et al. 1990; Squillance et al. 1996; Gallego et al. 2001; USEPA 2004; Liang et al. 2011; Natural Resource Defense Council, 2015). These events are associated with normal operation of petroleum product systems and with accidents such as vehicular collisions, storage leaks, mechanical failure, extreme weather, and general accidents in transporting and extraction. Spills occur at a variety of scales and types.

Traditional identification and remediation methods for fuel spills can be expensive, hazardous, and time consuming, commonly taking days to prepare and begin clean-up efforts (e.g., USEPA 2019). Aerial panchromatic photography has issues discriminating petroleum from water especially in terrestrial conditions (e.g., Allen and Krekeler 2011, 2010). Hyperspectral imaging is now becoming more common for quick and reasonably accurate identification and quantification of contaminated soils (e.g., Correa Pabón et al. 2019) and more broadly in other environments (Ahmed et al. 2018; Asadzadeh and de Souza 2017; Del'Papa Moreira Scafutto and de Souza Filho 2016). The ability to monitor fuel spills using remote sensing technology has the potential to enable informed decisions to be made by first responders,

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environmental consultants, petroleum companies and governmental agencies. This would result in better response and lesser environmental and human health impacts. Such an approach is advantageous because direct, on the ground monitoring of fuel spills is hazardous owing to potential combustion and explosion hazard and a full spatial view of the event is often not possible from the ground.

Hyperspectral remote sensing is a technology that utilizes images from a variety of air vehicles or satellites where each pixel in the image contains a quantitative reflected light spectrum that is a function of the surface features, chemical composition and atomic structure of materials in view. Each spectrum can then be analyzed against a library of spectra from known reference materials that have previously been characterized in the laboratory to identify the materials both individually and combined with other materials. In theory, all materials reflect and absorb light as a function of their chemical and physical properties and thus hyperspectral data can serve as a powerful diagnostic tool.

As hyperspectral technology becomes more accessible, greater potential exists for use as a tool for responding to fuel spills. To exploit hyperspectral remote sensing effectively, a detailed hyperspectral library that captures objects and materials of interest is needed. As fuel spills are dynamic in time, measurements of how fuel spills age over time are also highly desirable for detailed remote sensing. Little work has been done in this area (e.g., Allen and Krekeler 2010) and to our knowledge, no work has been done assessing aging under cold weather conditions.

Detailed hyperspectral studies of fuel may also be of use beyond basic environmental investigations. Additionally, fuel spill detection and discrimination through hyperspectral approaches may be useful in locating downed aircraft, aircraft debris including fuel spills, locating ships, fuel or cargo spills from damaged, sunken ships or downed aircraft, as well as proving context for locating lost persons at sea or lost or injured outdoorsman in near shore settings. Fuel spill detection and discrimination may also be associated and provide context for locating bodies, clothing articles or blood from fresh and aged crime scenes, monitoring borders in numerous contexts (humanitarian migration, human trafficking, and drug trafficking), locating people after a natural disaster such as a hurricane or earthquake, and locating people after a terrorist attack.

There has been increasing interest in using hyperspectral remote sensing techniques to study petroleum and related products. (e.g., Correa Pabón et al. 2019; Ahmed et al. 2018; Asadzadeh and de Souza 2017; Del'Papa Moreira Scafutto and de Souza Filho, 2016). Comprehensive spectral data of fuels on well characterized geologic substrates, however, are not common. Furthermore, detailed laboratory studies of how spectra change over time on substrates are also limited (e.g., Allen and Krekeler 2010). This study investigates reflective spectra of gasoline, diesel and jet fuel A on substrates under two different temperature conditions.

Allen and Krekeler (2010) investigated crude oils and a variety of refined petroleum products on ten common substrates to provide a diverse set of hydrocarbon–substrate combinations. Experiments ran for at least 90 days unless liquids evaporated beforehand. They found for lower molecular weight products such as gasoline and E85 fuel, the sample spectra changed considerably with time as vaporization progressed. Functionally, this led to a gradual return to the original substrate spectra. Larger molecular weight products, such as diesel fuel and crude oils vaporized sufficiently to cause significant change to the initial hydrocarbon–substrate spectra. Stable products such as motor oil and the heavy crude changed very little over the observation period. Allen and Krekeler (2010) demonstrated, that it is possible under controlled conditions to effectively distinguish these hydrocarbons from one another and from water based on reflective spectroscopy alone. They concluded that while many of these liquids can be discriminated spectrally, based on the location and shape of absorption features (e.g., ethanol from motor oil), others cannot (e.g., diesel fuel from motor oil). They further demonstrated that ability to measure a sample over time, however, can provide distinguishing characteristics for some of these difficult combinations and note that observing semi-volatile diesel fuel for 1 week provided sufficient distinction to separate it from motor oil, which changed very little over the observation period. The work of Allen and Krekeler (2010) also indicates that substrates play an integral role in identifying these liquids and distinguishing them from one another. Substrates that are spectrally bright and have few absorption features that interfere with hydrocarbon absorptions are ideal backgrounds (e.g. Ottawa sand). Others provide insufficient contrast to detect hydrocarbon absorptions due to low overall reflectance (e.g., highly organic soil) or in some instances due to absorption features that interfere with the location of expected hydrocarbon absorptions (e.g., gypsum).

The results of Krekeler and Allen (2010) were the first to explore a variety of organic liquids and geologic substrates. Although individual experimental combinations were replicated, there was not extensive work comparing fuels on the common substrate of sands. Common silica-rich sands of different types or admixtures were not investigated. No study of temperature variation was made by Krekeler and Allen (2010). Furthermore, jet fuel A is an important fuel that was not investigated by Krekeler and Allen (2010).

The hypotheses to be evaluated in this investigation are that:

1. fuel types can be easily discriminated from each other as liquids but will share similar features;

2. fuel types will behave variably on different substrate sands;
3. fuels types will vaporize demonstrably less at lower temperatures.

Materials and Methods

Two representative sand substrates were used for this investigation. Ottawa sand was purchased from Fischer Scientific and used as received. New Mexico (NM) 15 is a silica-rich darker sand obtained from near the US–Mexico border. Gasoline and diesel fuel were purchased from retail outlets and jet fuel A was obtained from the Warren County Airport in Ohio. Properties of these fuel types are provided in supplemental materials. Sands used for experiments were characterized using a Zeiss Supra VP 35 Scanning electron microscope (SEM) operated in variable pressure mode and were analyzed using standard US sieves for grain size analysis with a Gibson Mechanical shaker and digital scale.

For reflective spectroscopy work, specimens were analyzed using the ASD (PANalytical) FieldSpec 4 Hi-Res spectroradiometer using the RS^3 software. The ASD FieldSpec 4 is both a bench-top laboratory instrument as well as a portable field instrument that is very well recognized in the remote sensing community as the standard spectroradiometer. Measurements were made in an open path configuration with a fiber to sample distance of approximately 50 cm. The ASD FieldSpec 4 Hi-Res spectroradiometer has a spectral range of 350–2500 nm with spectral resolutions of 3 nm at 700 nm and 8 nm at 1400 nm and 2100 nm. The instrument is equipped with a post dispersive system for extremely low stray light which is at $< 0.02\%$ for 350–1000 nm and $< 0.1\%$ for 1000–2500 nm. The instrument uses a modular silicon array as well as a Peltier cooled InGaAs detector spectrometer platform. The values for low noise equivalent delta radiance (NeDL) are 1.1×10^{-9} W/cm^2/sr/nm at 700 nm for UV/VNIR, 2.8×10^{-9} W/cm^2/sr/nm at 1400 nm for NIR and 5.6×10^{-8} W/cm^2/sr/nm at 2100 nm.

For pure liquid fuels, spectra were obtained by placing the fuel in a large ~ 15 cm diameter Pyrex petri dish which was placed directly on the white reference for measurement after calibration. Experiments involving substrates were conducted using 100-mm-diameter flat black spray-painted plastic petri dishes. Painted petri dishes with substrates were weighed and 5 ml of each fuel was applied. Reflective spectroscopy measurements were made over periods of several minutes to weeks and sample dishes were weighed commensurate with each reflective spectroscopy measurement as long as the fuel was detected.

For ambient lab room temperature experiments, fuel and substrate combinations were kept in a chemical hood at approximately 22 °C. For cold weather experiments, the fuel and substrate combinations were kept in an aluminum mesh cage that was weighted so as to not be disturbed or destroyed by the wind. The cage was secured on a rooftop and samples would be retrieved by cart for measurement to provide a more controlled, and safe experimental environment. The average temperature for the first 72 h of experiments was − 10 to − 5 °C, which then became more variable and warmed to near 0 °C thereafter.

Results

End member properties

Reflective spectra of liquids are shown in Fig. 1 and interpreted cause of major features that would be resolvable in hyperspectral imagery is listed in Table 1. As all three compounds are hydrocarbon and are of similar weight, they have spectra of similar topology. There are some differences where diesel has a pronounced ramp in the visible, gasoline has a much smaller ramp in the visible that starts at a higher reflective value, and jet fuel A has no discernable ramp or much smaller ramp in the visible compared to the other fuels. Gasoline differs from the other fuel types by having more pronounced adsorption features beyond 2000 nm.

Substrate characteristics are shown in Fig. 2 and spectral features that would be likely resolvable in hyperspectral imagery are listed in Table 2. The Ottawa sand is > 99% quartz, minor garnet and zircon can be found however these grains are rare. The average diameter of Ottawa sand grains is typically between 500 and 800 μm. The NM 15 sand sample has more feldspars which are angular grains in the SEM image and accordingly has more aluminum. The NM 15 sand also has a minor component of Fe oxides. The average diameter of NM 15 sand grains is typically between 100 and 1000 μm.

Room temperature experiments

Spectra sets for room temperature experiments are provided in Fig. 3 for the Ottawa sand substrate and Fig. 4 for the NM15 substrate. At times near initial application, most fuel features could be observed on all substrates for all room temperature experiments. However, for the room temperature experiments, gasoline was only detectable to 90 min after initial application. For room temperature experiments, diesel fuel was detectable out to 11 weeks on Ottawa sand, as well as the NM15 samples. Notably, signals at ~ 2310 and 2350 nm were not observed on the Ottawa sand samples until the 5-week time point, while they were consistently observed on the NM15samples for all time points. For room temperature experiments, jet fuel A was detectable out to 5 weeks on Ottawa sand and the

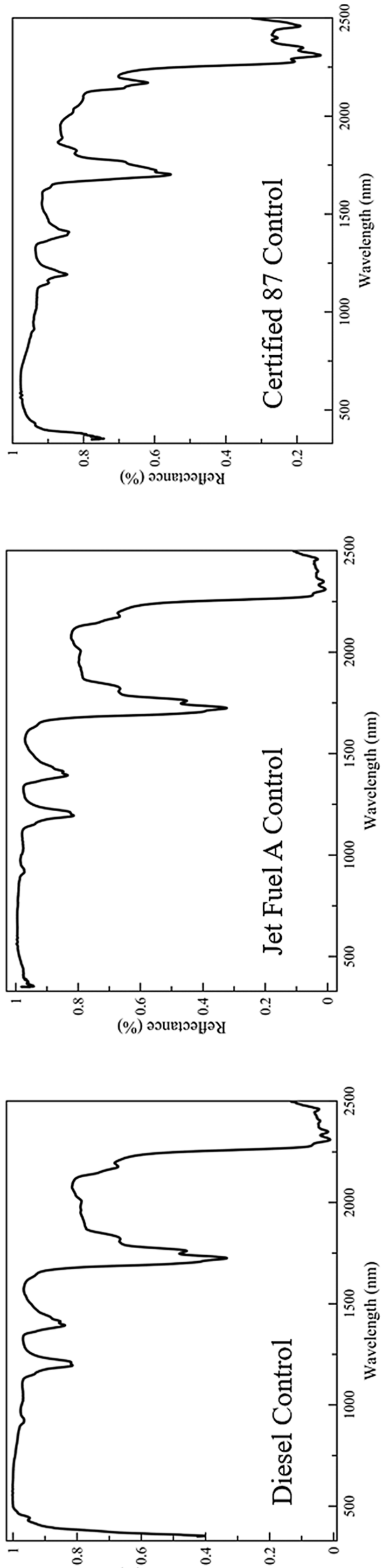

Fig. 1 Reflective spectra of fuels used in this study

NM15 samples. Similar to the diesel fuel, signals at 2310 and 2350 nm were not observed on the Ottawa sand with jet fuel A initially, but were detected 12 h after application, much sooner than the diesel fuel + Ottawa sand sample.

Cold weather experiments

Spectra sets for cold weather experiments are provided in Fig. 5 for the Ottawa sand substrate and Fig. 6 for the NM 15 substrate. For all cold condition experiments, gasoline was identifiable on substrates up until the 72-h mark. After this time point, the fuel was no longer clearly identifiable. Absorption features that are contributions from the gasoline and not the substrate include features between 1140–1200 nm, 1640–1770 nm, 2130–2180 nm, and 2300–2450 nm. Each of these regions noticeably dissipate between each time point and are not detected after 72 h. A faint absorption doublet occurs at 581 and 597 nm and is only observed during the 0-min time point. The first main feature observed is the doublet at 1140 and 1190 nm. The asymmetric triplet at 1702, 1720, and 1760 nm is caused by CH_2 and CH_3 stretches and bends in the first overtone region, preceded by a shoulder at 1642 nm (Cloutis 1989). A doublet at 2140 and 2170 nm is attributable to a C–C stretch, and while the feature at 2170 nm is broad and has some overlap with the substrate feature at 2205 nm, the gasoline feature is much more pronounced earlier in each experiment, while the substrate feature becomes more pronounced after the 1-week time point.

For all cold condition experiments, diesel fuel was identifiable on each substrate out to 5 weeks. Signals consistent with diesel did undergo slight changes during this time period but overall remained present and allowed for the identification of fuel on each substrate. Spectral ranges which are distinctly generated from diesel fuel include signals between ~ 560–600 nm, ~ 1160–1230 nm, ~ 1650–1830 nm, and two noticeable features at ~ 2310 and ~ 2350 nm. Unlike the gasoline, features from the diesel fuel did not completely dissipate over time. However, features did appear to alter slightly in intensity and shape between some time points.

For all cold condition experiments, jet fuel A was identifiable on each substrate out to 5 weeks. Features consistent with jet fuel A did undergo slight changes during this time period but overall remained present and allowed for the discrimination of fuel on each substrate. Regions which are distinctly generated from jet fuel A include signals between ~ 560–600 nm, ~ 1160–1230 nm, ~ 1650–1830 nm, and two noticeable signals at ~ 2310 and ~ 2350 nm. Similar to the diesel fuel, features from jet fuel A did not fade over time, while they did appear to alter slightly in intensity and shape between some time points.

Table 1 Recognized absorption features consistent with those observed in Ottawa Sand and NM 15 sand

Wavelength	Units	Interpreted cause	Example compound	References
~ 1.454	μm	Water	$2\nu1+\nu3$ vibration modes	Hunt (1977)
~ 1.5	μm	Fe^{2+}	Broad feature	Hunt et al. (1971a)—III
1.5–2.5	μm	Aluminum oxygen bonds	Broad features which will produce the overall fall-off in intensity	Hunt et al. (1971a)—III
2.17	μm	Hydroxyl groups	Combination of 2.76 and 10.55 um	Hunt et al. (1971a)—III
2.17	μm	Al–O–H	Fundamental stretch combined with fundamental Al-O–H bend	Hunt et al. (1971b)—IV
2.2	μm	Hydroxyl with aluminum present	In phyllosilicates—where dioctahedral members—OH- coordinated around aluminum	Hunt et al. (1973)—VI

Substrate variability on fuel detection

Substrate type significantly impacts spectra features of fuels. While grade 87 gasoline, diesel, and jet fuel A were all able to be identified on each substrate. Ottawa sand allowed for stronger fuel features to be observed from all three types of fuels. The NM 15 sand causes more suppression of fuel features. These results are consistent for both the cold and warm experiments and are expected owing to the overall spectral brightness of the substrates.

Vaporization plots

Plots of vaporization for Ottawa sand and the NM 15 sand are shown in Figs. 7 and 8, respectively. The duration of plots shown was limited to 72 h because this is likely the response time of a spill and temperatures increased and weather became irregular for cold experiments after 72 h. Regressions were fit to the data for each condition and these regressions were logarithmic in nature, except for both cases of jet fuel A under lab conditions which were best fit by power functions.

For Ottawa sand and fuel combinations, the gasoline and jet fuel A combinations evaporated faster than their cold weather equivalents; however, cold weather diesel evaporated faster than the lab equivalent. For the NM 15 sand, the gasoline and jet fuel A combinations also evaporated faster than their cold weather equivalents; and the cold weather diesel evaporated faster than the lab equivalent. Jet fuel A has a similar weight to diesel and thus the disparity in the behavior between the two is unexpected. This may be attributed to wind conditions and placement of the samples on the roof; however, the structure was built with uniform perforated sides to protect the samples from excessive wind.

Discussion

Choice of substrates

Substrates were chosen to represent a range of silica-rich sands of a variety of types. Ottawa sand was chosen as it is a widely used geologic and environmental media. NM 15 sand was selected because it represents areas near the US–Mexico border and represents arid regions. It is spectrally darker than Ottawa sand. Given the nature of these sands, they are broadly translatable or comparable to many sands in the US and elsewhere. These substrate choices represent a reasonable selection and darker sands were not used owing to the overall low reflective nature.

Comments on general detection

In each substrate—fuel combination explored in this work, the fuel was clearly identifiable from the substrate. While some fuel features do overlap with substrate features, in many cases the overlap drastically changes the spectral characteristics observed in those regions, and there are still a significant number of fuel specific features which allow clear identification of the fuel on the substrate. The results support previous work regarding the detection of hydrocarbon compounds on substrates (Allen and Krekeler 2010) and in imagery (Allen and Krekeler 2011). Numerous fuel features are observable in the reflective spectra however brighter substrates qualitatively make these features more prominent.

The impact of spectral brightness differences is noted with the darker substrate muting spectral features of the fuels. This relationship has potential to be explored further and it is predicted that there would be a cut-off on

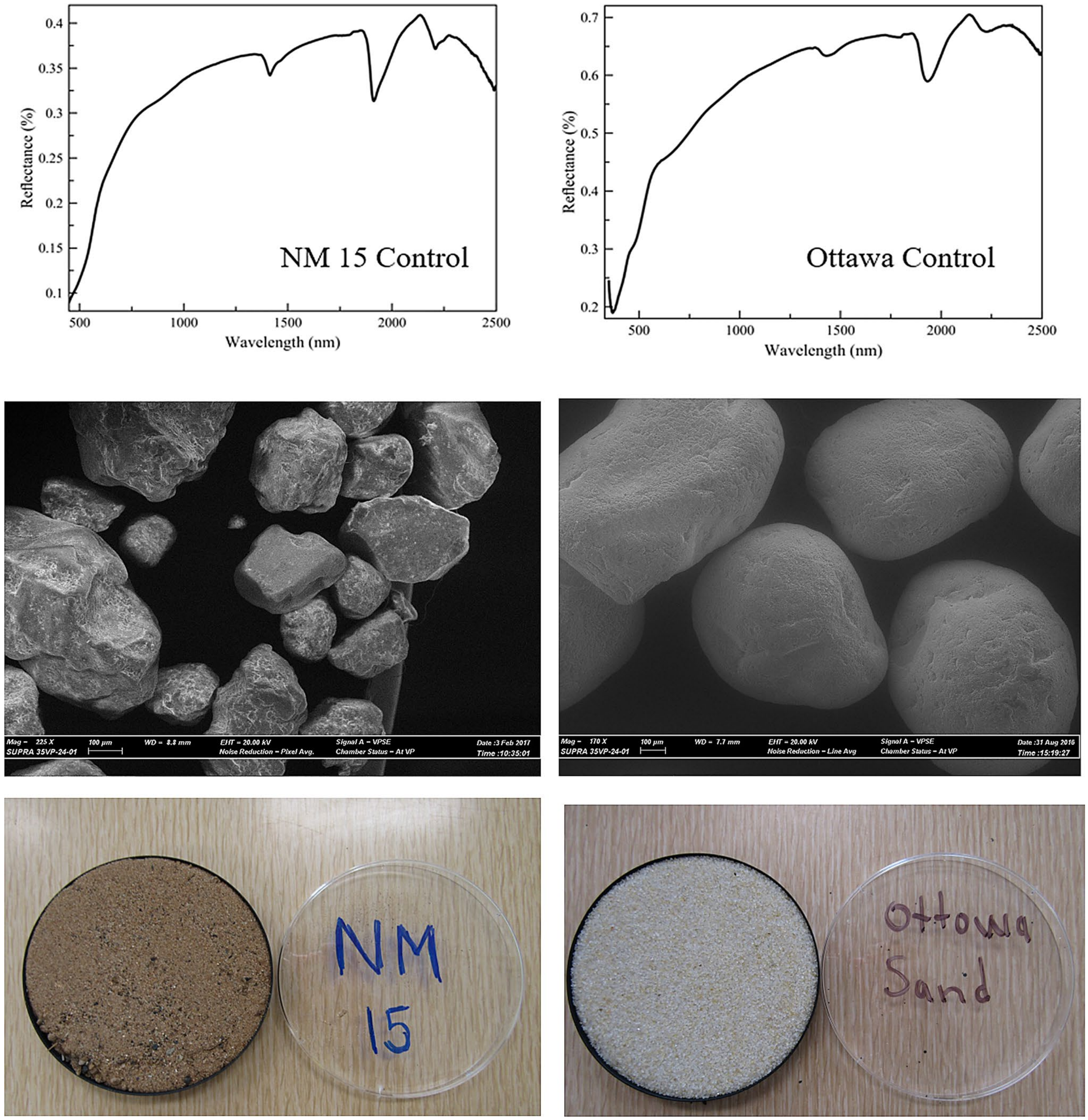

Fig. 2 Reflective spectra, SEM images and sample images of sands used in this study. NM 15 data is on the left and Ottawa sand data is on the right. Note the similarity on overall topology of the spectra however the NM 15 spectra is darker than the very silica-rich Ottawa sand

the ability to detect fuels on darker sands. Future work is planned to explore this relationship with basaltic sands, intermediate colored and bright white carbonate sands. It might be possible to predict the aforementioned cut-off with bulk Fe content measured in sands with X-ray fluorescence coupled with reflective spectroscopy and taking into account grain size.

Comments on vaporization plots and implications

The nature of vaporization of jet fuel A in the lab setting both fit power functions with reasonably high r^2 values but with high p values that are attributed to the scatter observed on the upper half of the curves. Cold weather curves for jet fuel A were irregular with most of the scatter

Table 2 Recognized absorption features for hydrocarbon and related organic compounds consistent with those observed in fuels of this study

Wavelength	Units	Interpreted cause	Example compound	Reference	Gasoline	Diesel	Jet Fuel A
0.93	μm	C–H stretch, third overtone	Oil	Curran (1989)	~	~	~
1.04	μm	C–H stretch, C–H deformation	Oil	Curran (1989)	~	~	~
1.12	μm	C–H stretch, second overtone	Lignin	Curran (1989)	X	X	X
1.42	μm	C–H stretch, C–H deformation	Lignin	Curran (1989)	X	X	X
1.45	μm	First overtone, C–H stretch, C–H deformation	Starch, sugar, lignin, water	Curran (1989)	X	X	X
1.68	μm	C–H stretch, asymmetric CH2 stretch	Alkene, aromatic C–H stretch at 3030 cm^{-1} and asymmetric CH2 stretch at 2920 cm^{-1}	Cloutis (1989)	X	X	X
1.69	μm	Asymmetric C–H3 stretch	Second overtone of asymmetric CH3 stretch at 2950 cm^{-1}	Cloutis (1989)	X	X	X
1.69	μm	C–H stretch, first overtone	Lignin (strong), starch, protein, nitrogen	Cloutis (1989)	X	X	X
1.70	μm	C–H stretch	Alkene, aromatic C–H stretch at 3030 cm^{-1} and symmetric CH2 stretch at 2850 cm^{-1}	Cloutis (1989)	X	X	X
1.71	μm	C–H stretch	Second overtone of asymmetric CH2 stretch at 2920 cm^{-1}	Cloutis (1989)	X	X	X
1.72	μm	C–H stretch	Asymmetric CH3 stretch at 2950 cm^{-1} and symmetric CH3 stretch at 2875 cm^{-1}	Cloutis (1989)	X	X	X
1.73	μm	C–H stretch	Asymmetric CH2 stretch at 2920 cm^{-1} and symmetric CH2 stretch at 2850 cm^{-1}	Cloutis (1989)	X	X	X
1.74	μm	C–H stretch	Second overtone of symmetric CH3 stretch at 2875 cm^{-1}	Cloutis (1989)	X	X	X
1.75	μm	C–H stretch	Second overtone of symmetric CH2 stretch at 2850 cm^{-1}	Cloutis (1989)	X	X	X
2.20	μm	C–H stretch, C–O stretch	Symmetric CH2 stretch at 2850 cm^{-1} and carbonyl-carboxyl C-O stretch at 1700 cm^{-1}	Cloutis (1989)	X	x	x
2.21	μm	C–H stretch, C–C stretch	Asymmetric CH2 stretch at 2920 cm^{-1} and aromatic carbon stretch at 1600 cm^{-1}	Cloutis (1989)	X	x	x
2.25	μm	C–H stretch, C–C stretch	Symmetric CH2 stretch at 2850 cm^{-1} and aromatic carbon stretch at 1600 cm^{-1}	Cloutis (1989)	X	x	x
2.27	μm	C–H stretch, C–H bend	Asymmetric CH3 stretch at 2950 cm^{-1} and asymmetric CH2, CH3 bend at 1450 cm^{-1}	Cloutis (1989)	X	x	x
2.32	μm	C–H stretch/CH2 deformation	Starch	Cloutis (1989)	X	x	x
2.33	μm	C–H stretch, C–H bend	Symmetric CH2 stretch at 2850 cm^{-1} and asymmetric CH2, CH3 bend at 1450 cm^{-1}	Cloutis (1989)	X	x	x
2.34	μm	C–H stretch/C–H deformation	Cellulose	Curran (1989)	X	x	x
2.35	μm	CH2 bend, second overtone	Cellulose, protein, nitrogen	Curran (1989)	X	x	x
2.35	μm	C–H stretch, C–H bend	Symmetric CH3 stretch at 2875 cm^{-1} and symmetric CH3 bend at 1375 cm^{-1}	Curran (1989)	X	x	x

Symbols of (~) indicate minor adsorption feature (x) moderate adsorption feature and (X) indicates major contributor to adsorption feature for respective fuels. Note that many features are close and overlap and contribute to the same adsorption feature and may not be resolvable. Others show doublet or triplet adsorptions

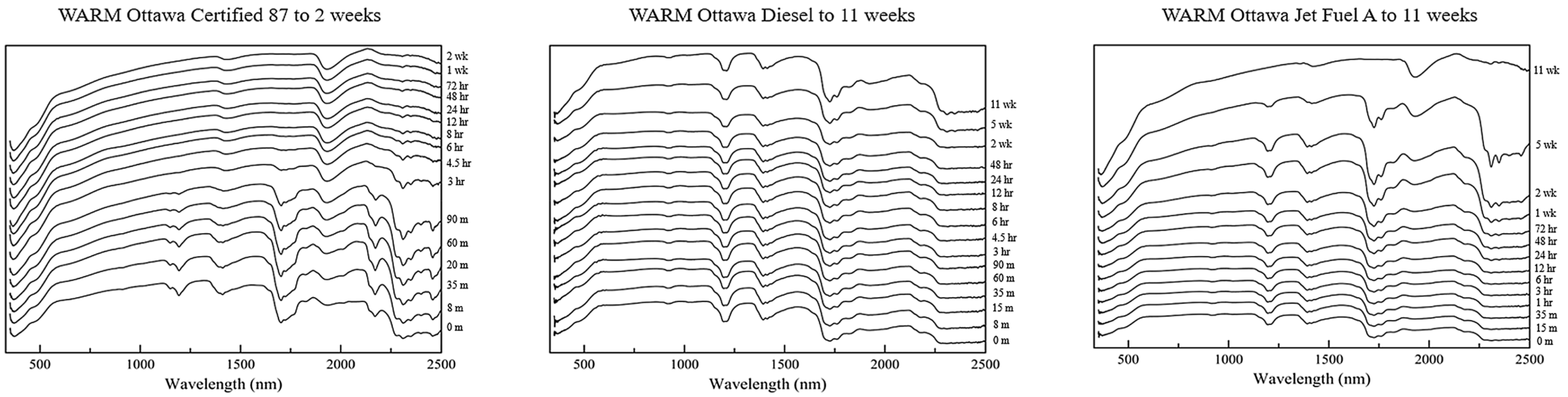

Fig. 3 Ambient lab room temperature experiments using Ottawa sand as a substrate. Left is using grade 87 gasoline as the fuel, center uses diesel fuel, and right uses jet fuel A. For grade 87 gas, bottom to top spectra were collected at 0, 8, 20, 35, 60, 90 min, 3, 4.5, 6, 8, 12, 24, 48, 72 h, and 1 and 2 weeks. For diesel fuel, bottom to top spectra were collected at 0, 8, 15, 35, 60, 90 min, 3, 4.5, 6, 12, 24, 48 h, and 2, 5, and 11 weeks. For jet fuel A, bottom to top spectra were collected at 0, 15, 35 min, 1, 3, 6, 12, 24, 48, 72 h, and 1, 2, 5 and 11 weeks

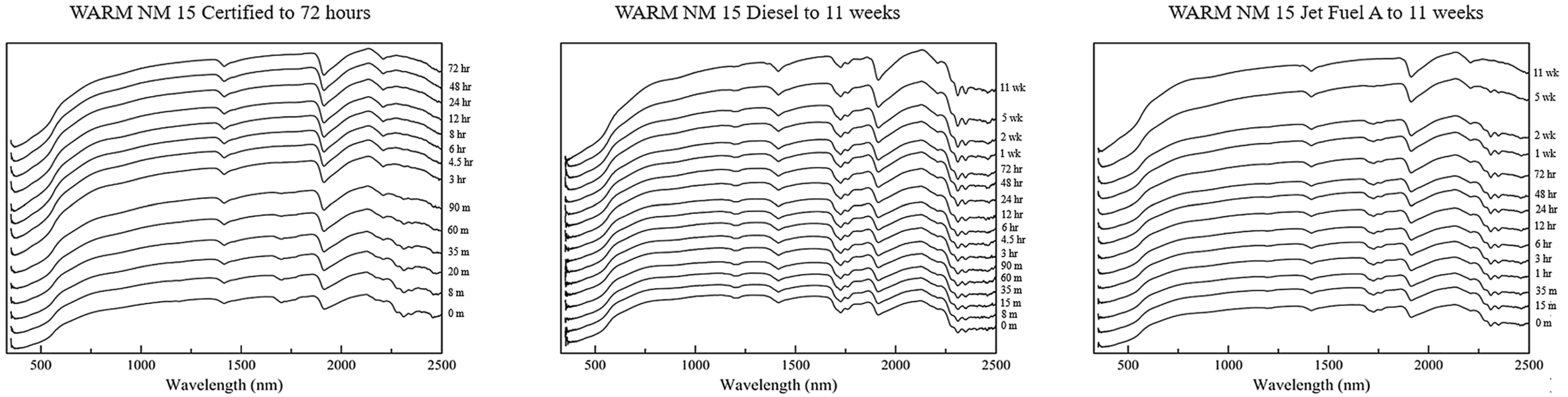

Fig. 4 Ambient lab room temperature experiments using NM 15 material as a substrate. Left is using grade 87 gasoline as the fuel, center uses diesel fuel, and right uses jet fuel A. For grade 87 gas, bottom to top spectra were collected at 0, 8, 20, 35, 60, 90 min, 3, 4.5, 6, 8, 12, 24, 48, and 72 h. For diesel fuel, bottom to top spectra were collected at 0, 8, 15, 35, 60, 90 min, 3, 4.5, 6, 12, 24, 48, 72 h, and 1, 2, 5, and 11 weeks. For jet fuel A, bottom to top spectra were collected at 0, 15, 35 min, 1, 3, 6, 12, 24, 48, 72 h, and 1, 2, 5, and 11 weeks

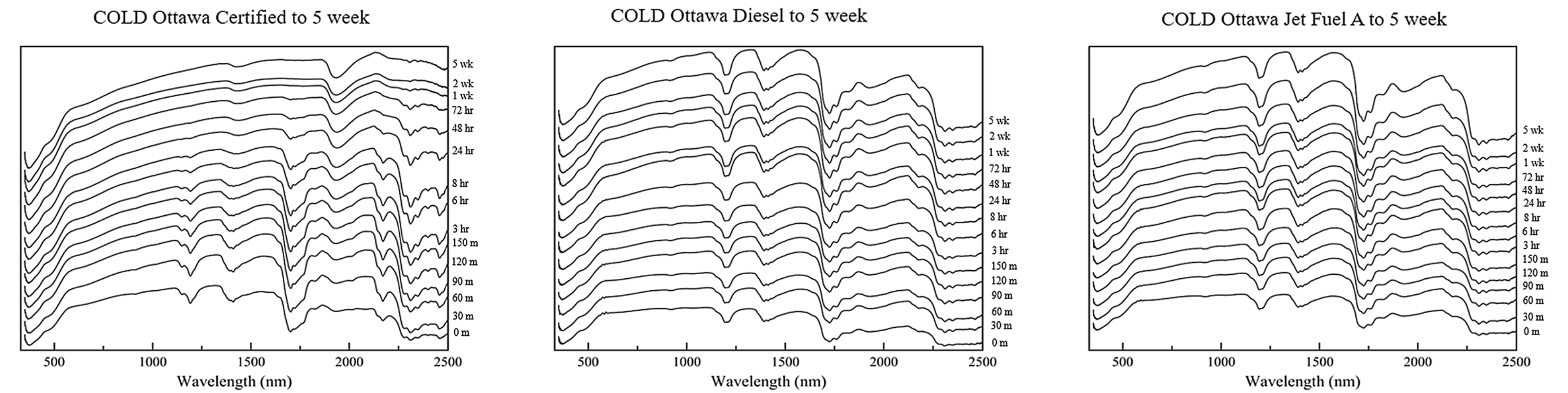

Fig. 5 Cold experiments using Ottawa sand as a substrate. Left is using grade 87 gasoline as the fuel, center uses diesel fuel, and right uses jet fuel A. From bottom to top, spectra were collected at 0, 30, 60, 90, 120, 150 min, 3 6, 8, 24, 48, 72 h, and 1, 2 and 5 weeks

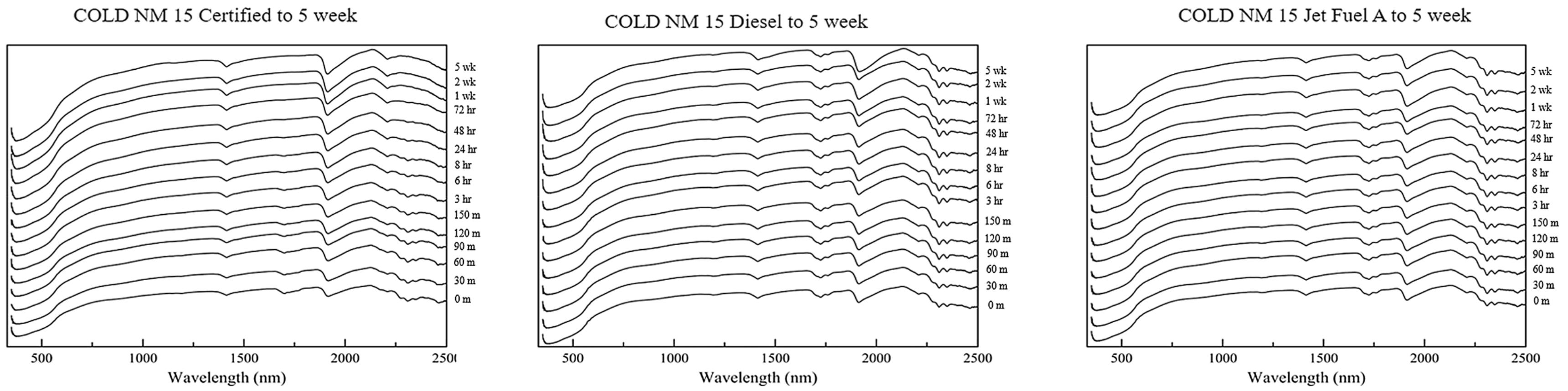

Fig. 6 Cold experiments using NM 15 material as a substrate. Left is using grade 87 gasoline as the fuel, center uses diesel fuel, and right uses jet fuel A. From bottom to top, spectra were collected at 0, 30, 60, 90, 120, 150 min, 3 6, 8, 24, 48, 72 h, and 1, 2 and 5 weeks

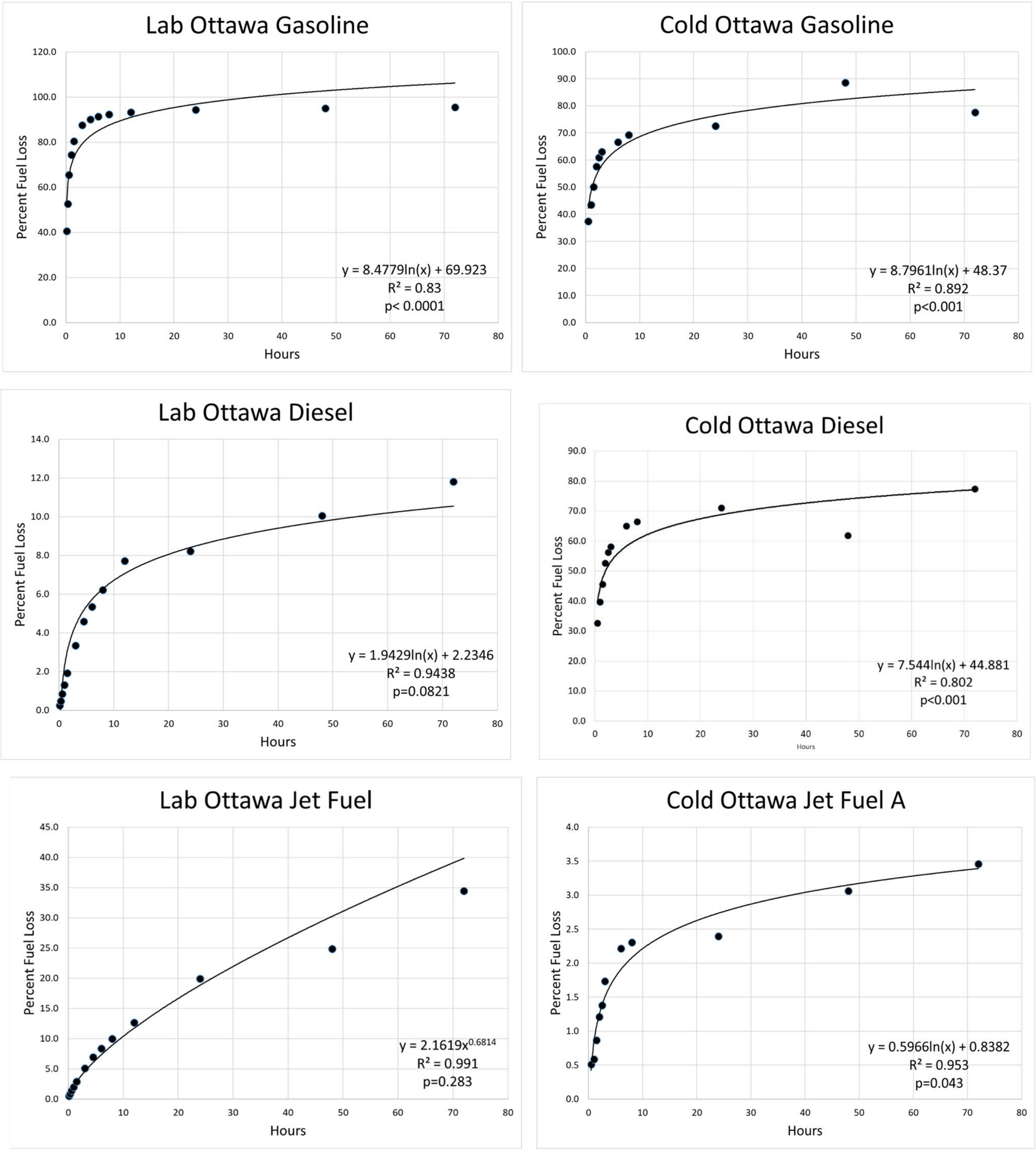

Fig. 7 Vaporization curves for Ottawa sands for both lab conditions and cold weather conditions. Lines and equations of best fit as well as p values are provided

after 20 h. This is attributed to changing of weather conditions. The irregularity of the curves of both lab conditions and cold weather conditions with both substrates suggests jet fuel A may have different chemisorption behavior than other fuels in this study. This assertion is supported by the different vaporization curve of jet fuel A under lab conditions as well.

Temperature does have a dramatic effect on the vaporization of gasoline and a lesser effect on the vaporization of heavier fuels. We note that diesel has a gel point on

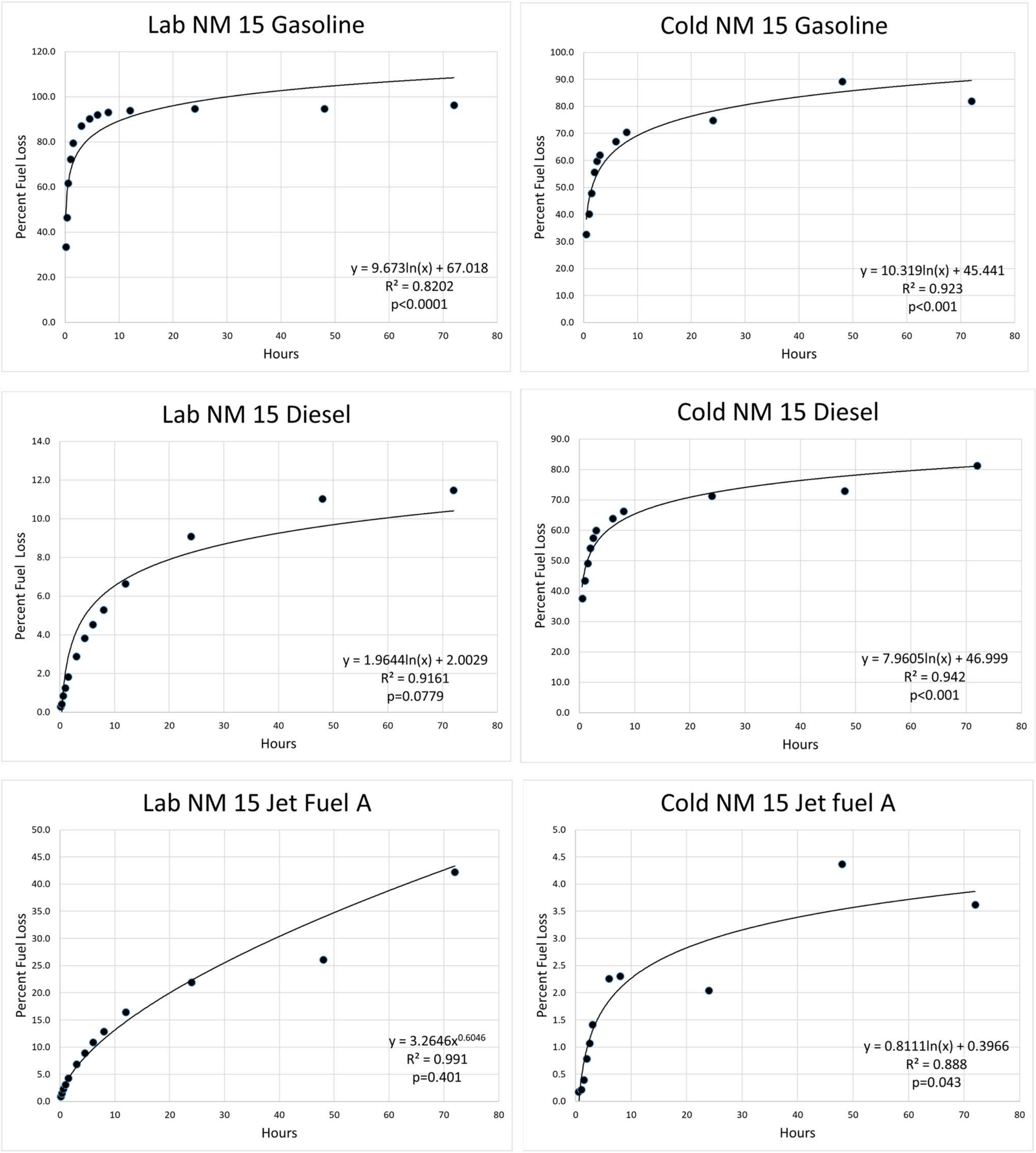

Fig. 8 Vaporization curves for NM 15 sands for both lab conditions and cold weather conditions. Lines and equations of best fit as well as p values are provided

average of − 8.1 °C (see Supplemental Table 1), and yet there was no visual change observed or behavioral change in the plots that relate to gel formation. Although hyperspectral remote sensing—UAV investigations are relevant for both warm and cold conditions the implications for this are that hyperspectral UAV investigation of spills in cold weather environments or conditions inherently provide larger time windows for imaging because of the presumably lower rates of vaporization and will likely capture the true extent of the spill, although this assertion is complicated by the diesel data.

Comments on hypotheses

With respect to the hypotheses evaluated in this investigation, fuel types can be easily discriminated from each other as liquids but do share similar features. These features are similar on substrates investigated, but can vary over time as indicated by lab experiments where features of diesel at ~ 2310 and 2350 nm were not observed on the Ottawa sand samples until the 5-week time point, features at ~ 2310 and ~ 2350 nm were not observed on the Ottawa sand with jet fuel A initially, but were detected 12 h after application. Such behaviors are attributed to loss of lighter components of the fuels. In proper context, the differences in the ramp topology in the visible may be useful if it is known what liquid is of concern and other constraints exist experimentally or if the system studied is simple.

The hypothesis that fuel types will behave variably on different substrate sands is only partially supported. Most vaporization curves are logarithmic, not linear or some other type. Jet fuel A, however, showed a power distribution for lab conditions. This indicates that not all fuel types evaporate in the same manner. Coefficients for lines of fit for logarithmic cases vary between the substrate types between approximately 0.02 and 1.6, arguing for some level of systematic behavior between the different sands.

The hypothesis that fuels types will evaporate demonstrable less at lower temperatures is only partially supported. Diesel fuel evaporated faster under cold conditions for both substrates and this is unexpected. Wind conditions were not monitored in the cold weather enclosure as it was built to restrict wind but allow for ambient temperature and the observed phenomenon may be an effect of low speed turbulent wind. Alternatively, there may be an unrecognized physicochemical behavior causing the phenomenon. The undetermined or unobserved effect occurring may involve moisture where water ponded or frosted grains, causing diesel fuel to "float" on the sample surface more, increasing exposure to air. Admittedly, this mechanism is speculation. Although there is not a clear explanation, this finding alone indicates the need for more experiments in cold weather environments with diesel and other substrates.

Additionally for diesel, features at ~ 2310 and 2350 nm were not observed on the Ottawa sand samples until the 5-week time point, while they were consistently observed on the NM 15 samples for all time points. For room temperature experiments, jet fuel A was detectable out to 5 weeks on Ottawa sand and the NM 15 samples. Similar to the diesel fuel, features at ~ 2310 and 2350 nm were not observed on the Ottawa sand with jet fuel A initially, but were detected 12 h after application, much sooner than the diesel fuel + Ottawa sand sample. This variation suggests that under some conditions, time plays a critical role in detection and is broadly consistent with changing spectral behaviors observed by Allen and Krekeler (2010).

Comments for future work

Our results indicate that detailed reflective spectroscopy investigations of a wider range of fuels and petroleum on a wider range of substrates is justified and would potentially enhance detection. Such data would be useful for investigations similar to those of Correa Pabón et al. (2019), Ahmed et al. (2018), Asadzadeh and de Souza (2017) and Del'Papa Moreira Scafutto and de Souza Filho (2016). Additionally, our work suggests that investigating reflective spectra variation on high production volume organic compounds is feasible and that investigation of liquids such as alcohols, aromatic solvents, ketones, chlorinated solvents as well as chemicals that are directly applied to broad areas such as glyphosate and atrazine on other sand substrates is warranted. A much expanded comprehensive database of organic liquids that have potential to be pollutants with appropriate substrates under a range of temperature conditions would be useful for environmental and emergency management across a broad spectrum. Such a detailed dataset would enable faster, more definitive identification and enable more accurate information to be provided to decision makers.

The results could have been far more random with no correlation in vaporization on spectral features. However, our results justify more detailed work on fuel vaporization on multiple types of sands and other substrates under a range of conditions, which requires significant effort. Field-based and lab-based experiments at different temperature, humidity and wind conditions would likely resolve the variability observed and would take a few years to execute if using field experiments. Through repeated experiments over a period of several seasons, a far more statistically robust dataset could be obtained and analyzed and a mathematical model or models could be developed. The current results suggest that such efforts are warranted and are likely to be met with some level of success.

Further detailed work using a wider range of well-characterized substrates such as sands (e.g., Oglesbee et al. 2020) and sediments that are common in large areas of the US and elsewhere such as glacial till (Barnes et al. 2020) would be beneficial for understanding variation in vaporization behavior and spectral properties. Additionally, well-characterized substrates such as urban road sediments and associated materials (e.g., Dietrich et al.2018, 2019; LeGalley et al. 2013; LeGalley and Krekeler, 2013) along with concrete and asphalt should be investigated in the future. Although these may prove challenging for detection and discrimination of fuels, they are important substrates owing to how commonly fuel spills occur on them. Furthermore, there are specific ores or wastes in mine settings where diesel spills should be easily identified such as well characterized quartzite (e.g., Lindeman et al. 2020) or settings where diesel is an inherent historic component of the mine waste itself such as phosphate tailings in Florida (Krekeler et al. 2008). There are other mine settings where detailed characteristics of waste and reflective spectra have been obtained as well (Krekeler et al. 2010). Broader study of very well characterized substrates should be done to address both pragmatic detection questions as well as a step towards understanding the many processes involved in vaporization.

Fuel spills are well recognized as being tied to both disasters such as hurricanes and violent crime such as arson and concealing human bodies. Burke et al. (2019) conducted a reflective spectroscopy study of clothing in the context of using hyperspectral imaging for search and rescue as well as criminal contexts. More recent preliminary work has been done on makeup in the context of violence against women (Vest et al. 2020). The data and interpretations provided on fuels in this study should also aid in developing hyperspectral remote sensing techniques and reflective spectroscopy as a search and rescue tool and a tool for forensic investigation.

Conclusions

Fuel—substrate reflective spectroscopy experiments can provide insight for detection and discrimination for hyperspectral studies. Not all fuels evaporate in the same manner in these experiments as it appears that diesel may evaporate unexpectedly fast under cold weather conditions. The mechanism for this is not clear. Results provide justification for the commitment of efforts to long-term experiments of fuels and related organic compounds.

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