DETECTING AND DISCRIMINATING PETROLEUM AND PETROLEUM PRODUCTS FROM WATER ON TERRESTRIAL BACKGROUNDS WITH HYPERSPECTRAL REMOTE SENSING

by

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**Figure 4-44:** MF/IS results for water, motor oil, and light crude on vegetation substrate, FLAASH atmospheric compensation with cross-track illumination correction, Image ID: 20050907_005_012. (Left) MF/IS values $\geq 0.010$ overlain on false color composite, RGB: 1600/1050/650 nm. (Center) 3-band composite of MF/IS results with water-vegetation (blue), motor oil-vegetation (green), and light crude-vegetation (red) loaded. Pixels with MF/IS values $\geq 0.010$ are highlighted. (Right) Library spectra and mean spectra...

**Figure 4-45:** MF/IS values overlain on false color composite, RGB: 1600/1050/650 nm for light crude (red), motor oil (green), and water (blue) on (left) Ottawa sand substrate, (center) quartzic beach sand (QBS) substrate, and (right) vegetation substrate. Top row includes MF/IS values $\geq 0.02$ for QUAC-compensated cubes. Center row includes MF/IS values $\geq 0.01$ for QUAC-compensated cubes. Bottom row includes MF/IS values $\geq 0.01$ for FLAASH-compensated cubes. Note that for all three substrates, the vast majority of pixels for the flooded petroleum tank areas are identified as water........

**Figure 4-46:** Results of SAM rule classifier for light crude, motor oil, and water on Ottawa sand substrate, image ID: 20050906_012_001. (Left) False color composite: R/G/B: 1600/1050/650 nm. The tank that was the source of the spill is circled in red. Filled polygons are regions of interest discussed in the text. (Center) SAM Rule Classifier (0.01-0.35 radians), non-water areas masked out, QUAC image: possible hydrocarbons=red, water=cyan, equal likelihood of both=white. (Right) SAM rule image (0.20-1.0 radians), non-water areas masked out, FLAASH image: possible hydrocarbons=red, water=cyan, equal likelihood of both=white. .................................

**Figure 4-47:** SAM rule values for light crude (red) and water (green) from four ROIs in Image 20050906_012_001. (Upper left) Values for the blue ROI covering the residential street closest to the refinery. (Upper right) Values for the green ROI covering the flooded berm of the compromised tank. (Lower left) Values for red ROI covering residential street four blocks from the refinery. (Lower right) Values for yellow ROI adjacent to the flooded berms and apparently partially protected by berms or booms. (Bottom) Mean SAM rule values (in radians) for each ROI.................................................................

**Figure 4-48:** Spectra for ROIs highlighted in Figure 7 above, along with library spectra. (Top) Spectra for the QUAC-compensated scene. (Middle) Library spectra for water-Ottawa sand (green), and light crude-Ottawa sand (red). (Bottom) Spectra for the FLAASH-corrected scene. In the QUAC scene, the red and yellow ROI's were dominated by water and/or motor oil and the blue and green ROIs by light crude. ......................................

**Figure 4-49:** Digitized field map of areas affected/unaffected by the Murphy Oil Refinery spill overlaid on image 20050906_012_001. (Left) False color composite: R/G/B: 1600/1050/650 nm. (Center) Digitized field map of oil-affected areas from Franklin (2006) (red=heavy, orange=moderate, green=light, blue=unaffected). (Right) Digitized field map overlain on SAM rule image. Note how well the cyan pixels in the rule image compare to blue pixels in the overlay and how well the red pixels correspond to the red overlay areas. In the residential areas, the moderate and lightly oiled areas (orange and green) have better results for water than for light crude. .....................................................

**Figure 4-50:** SAM rule values for non-masked pixels for each of the colored polygons in Image 20050906_012_001. (Top) Plot of SAM rule values for light crude (Material #1) and water (Material #2) for four ROIs based on a field-compiled map of the spill. (Bottom) Table summarizing each polygon's SAM rule statistics. The values in the "Oil Status" column are from Franklin (2006)...........................................................

**Figure 5-1:** Handheld photograph of crushed aggregate and asphalt lab samples (left) and the same samples illuminated by UV light (right). Fluorescing oil colors the substrates with a mustard yellow color in the right photograph. The oil produced the same color for all substrates and for a neat sample in a glass petri dish. ..........................
**LIST OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>AAPG</td>
<td>American Association of Petroleum Geologists</td>
</tr>
<tr>
<td>ACPA</td>
<td>American Concrete Pavement Association</td>
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<tr>
<td>AGL</td>
<td>Above Ground Level</td>
</tr>
<tr>
<td>AIS</td>
<td>Airborne Imaging Spectrometer</td>
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<tr>
<td>AISA</td>
<td>Airborne Imaging Spectrometer for Applications</td>
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<tr>
<td>AK DEC</td>
<td>Alaska Department of Environmental Conservation</td>
</tr>
<tr>
<td>ALOS</td>
<td>Advanced Land Observation Satellite</td>
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<tr>
<td>API</td>
<td>American Petroleum Institute</td>
</tr>
<tr>
<td>ASAS</td>
<td>Advanced Solid-state Array Spectroradiometer</td>
</tr>
<tr>
<td>ASD</td>
<td>no longer an acronym, used to be “Analytical Spectral Devices”</td>
</tr>
<tr>
<td>AST</td>
<td>Aboveground or Atmospheric Storage Tanks</td>
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<td>ASU</td>
<td>Arizona State University</td>
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<td>AVIRIS</td>
<td>Advanced Visible Infrared Imaging Spectrometer</td>
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<td>B</td>
<td>Blue</td>
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<tr>
<td>BBC</td>
<td>British Broadcasting Company</td>
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<tr>
<td>bbl/d</td>
<td>Barrels per day</td>
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<td>BGS</td>
<td>British Geological Survey</td>
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<tr>
<td>BOREAS</td>
<td>BORreal Ecosystem-Atmosphere Study</td>
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<td>BP</td>
<td>British/Beyond Petroleum</td>
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<tr>
<td>BRDF</td>
<td>Bidirectional Reflectance Distribution Function</td>
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<td>C</td>
<td>Celsius</td>
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<td>CASI</td>
<td>Compact Airborne Spectrographic Imager</td>
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<tr>
<td>CCD</td>
<td>Charge Coupled Device</td>
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<td>CFR</td>
<td>Code of Federal Regulations</td>
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<td>CH, C-H</td>
<td>Carbon-Hydrogen</td>
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<td>cm</td>
<td>centimeter</td>
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<td>CNN</td>
<td>Cable News Network</td>
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<td>COMPASS</td>
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<td>CSIRO</td>
<td>Commonwealth Scientific and Industrial Research Organisation</td>
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<td>E85</td>
<td>Ethanol fuel blend (~85%) with gasoline</td>
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<td>EDS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
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<td>Empirical Line Method</td>
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<td>ENvironment for Visualizing Images</td>
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<td>ETM+</td>
<td>Enhanced Thematic Mapper Plus</td>
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<td><em>Exxon Valdez</em> Oil Spill Trustee Council</td>
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<td>Fast Line-of-Sight Atmospheric Analysis of Spectral Hypercubes</td>
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<td>Field of View</td>
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<td>FWPCA</td>
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<tr>
<td>g</td>
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<td>G</td>
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<td>GSFC</td>
<td>Goddard Space Flight Center</td>
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<td>HATCH</td>
<td>High accuracy ATmospheric Correction for Hyperspectral data</td>
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<td>IFOV</td>
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<td>kph</td>
<td>kilometers per hour</td>
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<td>LIFI</td>
<td>Laser-Induced Fluorescence Imaging</td>
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<td>MNF</td>
<td>Minimum Noise Fraction</td>
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<td>Mixture Tuned Matched Filter</td>
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<td>National Oceanic and Atmospheric Administration</td>
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<td>Orbiting Carbon Observatory</td>
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<td>OPA</td>
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<td>OSPU</td>
<td><em>Oil Spill Program Update</em></td>
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<td>QBS</td>
<td>Quartzic Beach Sand</td>
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<td>QUAC</td>
<td>QUick Atmospheric Correction</td>
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<td>R</td>
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<td>RADAR</td>
<td>Radio Detection and Ranging</td>
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<td>R/G/B</td>
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<td>RH</td>
<td>Relative Humidity</td>
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<td>ROI</td>
<td>Region of Interest</td>
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<td>SAED</td>
<td>Selected Area Electron Diffraction</td>
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<td>SAM</td>
<td>Spectral Angle Mapper</td>
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<td>SAR</td>
<td>Synthetic Aperture RADAR</td>
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<tr>
<td>SASI</td>
<td>SWIR Airborne Spectrographic Imager</td>
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<td>Scanning Electron Microscope</td>
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<td>SMACC</td>
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<td>SNR</td>
<td>Signal to Noise Ratio</td>
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<td>SPCC</td>
<td>Spill Prevention, Control, and Countermeasure</td>
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<td>Specim</td>
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<td>SpecTIR</td>
<td>Spectral Technology and Innovative Research</td>
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<td>SPIE</td>
<td>The International Society for Optical Engineering</td>
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<td>SPOT</td>
<td>Satellite/Systeme Pour l’Observation de la Terre</td>
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<td>sr</td>
<td>steradian</td>
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<td>SRM</td>
<td>Standard Reference Materials</td>
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<td>SWIR</td>
<td>Shortwave Infrared (1300-2500 nm)</td>
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<td>TEM</td>
<td>Transmission Electron Microscope</td>
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<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>TM</td>
<td>Thematic Mapper</td>
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<td>Thompson Ramo Wooldridge</td>
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<td>μm</td>
<td>micrometer</td>
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<td>United States</td>
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<td>Ultraviolet</td>
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<td>VNIR/SWIR</td>
<td>Visible/Near Infrared/Shortwave Infrared (400-2500 nm)</td>
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<td>W</td>
<td>Watt</td>
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<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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ABSTRACT

DETECTING AND DISCRIMINATING PETROLEUM AND PETROLEUM PRODUCTS FROM WATER ON TERRESTRIAL BACKGROUNDS WITH HYPERSPECTRAL REMOTE SENSING

C. Scott Allen, Ph.D.

George Mason University, 2011

Dissertation Director: Dr. Barry N. Haack

Petroleum and petroleum product spills are frequent and as both Hurricane Katrina and the Deepwater Horizon accident demonstrated, they can be catastrophic. A prominent portion of the response is mapping the extent to which oil has reached both shoreline and inland areas. Yet, petroleum and water–when present on common substrates such as sand, concrete, and vegetation–are often difficult to distinguish in panchromatic and multispectral imagery. This research demonstrates how hyperspectral remote sensing, also known as imaging spectroscopy, provides petroleum detection and discrimination from water on terrestrial backgrounds. Utilizing spectral libraries, it also performs material identification and successfully discriminates some petroleum products from one another as a means of further classification and mapping spill extent.

To achieve these goals, this effort collected spectral signatures of four crude oils and five refined petroleum products on ten common terrestrial substrates and compared
them to water on the same backgrounds over a period of 1-90 days, depending on liquid volatility. The result is the first publicly available spectral library for petroleum and petroleum products on terrestrial substrates in the reflective portion of the electromagnetic spectrum (400-2500 nm) for use in petroleum spill detection and response. It also establishes a baseline for the use of imaging spectroscopy as a technique for confident, accurate petroleum detection in the terrestrial environment. Using common material identification algorithms, the spectra were successfully applied to airborne hyperspectral data from the Hurricane Katrina disaster in 2005 as a proof-of-concept for discriminating petroleum from water.
INTRODUCTION

Petroleum product spills are common events both in the U.S. and around the world. Each year, almost 14,000 oil spills are reported to the Environmental Protection Agency (EPA) and the U.S. Coast Guard National Response Center (USCG/NRC) reported >30,000 spill incidents each year from 2000 to 2007, thousands of which were related to petroleum products (EPA, 2008a; NRC, 2008). The sources for these spills commonly include equipment failure, storage tank rupture, and leaks or overfilling of aboveground, atmospheric and underground storage tanks (ASTs/USTs). Other common sources are leaks and spills from pumps, valves, pipelines, transformers, derailed rail cars, tanker trucks, and ocean-going tankers; and spills at transportation cross-over points such as rail, truck, tanker loading facilities, and gas stations (EPA OSPU, 2001-2007; CFR, 2003). Petroleum can be transferred up to 15 times between the source and its destination, with a chance for spillage at each transfer point (EC, 1994).

Petroleum and petroleum product spills are often high-profile events, both in the U.S. and abroad. In the spring of 2010, the Deepwater Horizon explosion and subsequent sinking created the largest oil spill in U.S. history, approximately 4.9 million barrels (206 million gallons/780 million liters) over 87 days. At its peak, the spill oiled more than 1000 miles (1600 km) of shoreline in the Gulf of Mexico and a year later, more than 500 miles (800 km) are impacted by tar balls and/or light oiling (NOAA, 2011). Until the
Deepwater Horizon, the Exxon Valdez spill in 1989 was perhaps the most famous spill in U.S. history, when approximately 257,000 barrels (11 million gallons/41.6 million liters) of crude oil spilled into Prince William Sound in Alaska, subsequently oiling approximately 1300 miles (2100 km) of shoreline (EVOSTC, 2011). As of 2008, ExxonMobil had paid $3.5 billion in compensation and restoration and more than 33,000 persons were still seeking compensation for the event (Arnold, 2008). In 2003, Colonial Pipeline settled a civil claim with the EPA and agreed to pay $34 million for seven spills during the late 1990s that collectively spilled 1.45 million gallons (5.5 million liters) of crude oil over a five state area. Colonial also agreed to spend $30 million to upgrade the pipeline as part of the settlement (EPA OSPU, 2003).

During March of 2006, a corroded feed into the Trans-Alaskan pipeline owned by British Petroleum (BP) ruptured, spilling at least 267,000 gallons (1 million liters) of oil (BBC, 2006). In the summer of 2006, an Israeli airstrike on a Lebanese power plant caused a fuel oil spill 3.3 - 4.4 million gallons (12.5-16.6 million liters) in size (NPR, 2006). In 2005, an explosion at a petrochemical facility in China spilled “an estimated 100 tons of benzene compounds into the Songhua River” (Lague, 2005). The resulting slick spanned 80 km when it reached Harbin, a city of 3.8 million, and shut down the water supply of the city for five days. The spill eventually flowed into the Amur River at the Chinese border with Russia and when it reached the city of Khabarovsk, it was 176 km long and had traveled approximately 1000 km (Lague, 2005; USA Today, 2005). Three months earlier, Hurricane Katrina damaged petroleum pipelines and storage tanks in Louisiana, causing more than 7 million gallons (26.5 million liters) of oil spills in that
In 2004, a pipeline rupture near the Suisun Marsh—the second largest marsh in California—resulted in a 40,000 gallon (151,000 liter) diesel fuel spill in an ecologically sensitive area (CNN, 2004).

In the U.S., acts of sabotage have resulted in the spillage of petroleum products as well. In 1997, a person intentionally dynamited a pipeline and four years later, in 2001, a hunter fired at least four bullets into the Trans-Alaskan pipeline. The latter event caused more than 275,000 gallons (1 million liters) of crude oil to spill forth from the ruptured pipeline (EPA *OSPU*, 2002). These events demonstrate how pipelines are excellent targets for terrorist activity because they are “soft” targets; they are easy to strike. Furthermore, disruption immediately impacts economic activity while providing an environmental disaster as well.

The petroleum infrastructure in the U.S. also needs persistent monitoring of both pipelines and facilities that store and use petroleum products. For example, there are currently over 200,000 miles (320,000 km) of pipeline in the U.S. alone, monitored by thousands of personnel via automated devices and manual spotting (EIA, 2003). From 1973-2000, inland pipelines were the source of 17.5% of the volume of total oil spilled in the U.S. (EPA *OSPU*, 2004).

Despite the persistent problem of petroleum product spills and leaks, current methods of spill detection and delineation are slow, inaccurate, and tedious despite federal mandates for spill prevention and contingency plans in the Clean Water Act and the Oil Pollution Act of 1990 (FWPCA, 1973; OPA, 1990). Spills are often only detected when someone stumbles upon them or discovers them by accident. According to the
1995 EPA Spill, Prevention, Control and Countermeasures (SPCC) survey, visual inspection is the most common method of leak detection (EPA, 1996b; EPA, 1996c). In the same survey, there were 2607 “oil-storing” facilities in the U.S., of which only 399 used any form of automated leak detection (15.3%) (EPA, 1996a). In 2002, the EPA documented instances where a security guard discovered a spill and one where an engineer in a passing train spotted a leak in a tanker car on a train headed in the opposite direction (EPA OSPU, 2002). More recently, in December of 2007, a 4000 gallon (15,000 liter) spill was detected only when pressure from the compromised pipeline eventually caused a whistling sound that was audible to people working nearby (AK DEC, 2007).

When spills are detected, it commonly takes days to set-up recovery, determine the extent of the spill, and to initiate clean-up efforts. In the case of the Lebanese power plant, workers were not on site for 34 days due to the hostilities (NPR, 2006). During these intervals, it is common practice to fly over the affected area using airplanes and remote sensors. The purpose is to gain a synoptic view of the event and to attempt to visually identify the extent of the spill. The imagery is usually panchromatic or natural color imagery, although SAR (synthetic aperture radar) and thermal infrared (IR) sources are increasingly being used (Hayes and Michel, 1992; Goodman, 1994; EC, 1994; EPA, 1999; Fingas and Brown, 2000; NOAA, 2007).

Figure 1-1 provides an example of the difficulty associated with delineating petroleum spills in littoral areas. This aerial photograph was taken shortly after a 98,000 gallon (371,000 liter) fuel oil spill in Buzzards Bay, MA, in April of 2003 (Buzzards Bay
Eventually, this spill impacted 93 miles (150 km) of coastline and clean-up lasted over four years (Buzzards Bay Project National Estuary Program, 2008). The red polygons in the photo are the interpreter’s estimates of oil extent in the water, although he/she is wise to caveat delineation in the caption of the photograph, which states: “Oil landing ashore in same area? (interpretation, not confirmed)” [emphasis added] (Buzzards Bay Project National Estuary Program, 2003). Blue arrows added by this author point to areas that are wet where it is unclear whether water or oil is the wetting agent. Note that the interpreter did not attempt to identify the wetting agent in these areas.

Figure 1-1: Aerial photograph of an oil spill in Buzzards Bay, MA. Red areas are interpreted as areas of the spill. Blue arrows added by the author point to areas that are wet where it is unclear whether water or oil is the wetting agent (Source: Buzzards Bay Project National Estuary Program, 2003).
As Figure 1-1 demonstrates, discriminating between water and petroleum is difficult to accomplish with human vision. Figure 1-2 shows three “natural color” images: sand wetted with diesel fuel (A), dry sand (B), and sand wetted with water (C). These images were captured in succession with a handheld digital camera from a nadir position approximately 1 m above the targets. While it is simple to distinguish the dry sand (B) from the two wet sands due to its brighter appearance, the two wet sands (A and C) are extremely difficult to confidently separate using human vision and as mentioned above, this is the most common method for identifying spills today.

![Figure 1-2: Photographs of three sand samples: sand wetted with diesel fuel (A), dry sand (B), and sand wetted with water (C). Photographs by the author.](image)

Figures 1-1 and 1-2 demonstrate how difficult it is to delineate oil and diesel fuel, respectively, from an airborne platform or even from a 1 m distance. One solution that should provide more accurate and quantitative information is replacing or supplementing
traditional photography with data from a hyperspectral sensor. When analyzed in conjunction with spectral libraries, airborne/spaceborne hyperspectral data can produce maps identifying the extent of these materials (Sabins, 1997; Richards and Jia, 1999).

1.1 Introduction to Hyperspectral Sensing

Over the last decade, the field of remote sensing has experienced a significant proliferation of high resolution sensors. Recent technological innovations are spurring continual advancement in not only the granularity of spatial resolution from space, which is commonly acknowledged and embodied by the successful launches of IKONOS (1999), EROS-A1 (2000), QuickBird-2 (2001), OrbView-3 (2003), Formosat (2004), IRS-P5 (CARTOSAT-1) (2005), ALOS (2006), Kompsat 2 (2006), WorldView-1 (2007), GeoEye-1 (2008), and WorldView-2 (2009), but also a revolution in the spectral resolution of airborne and spaceborne sensors.

Technological innovation has also spawned a whole generation of high spectral resolution imaging systems, normally referred to as “hyperspectral” sensors. While the prefix “hyper” normally refers to an excess of some quantity, in this case it refers to the large number of bands these sensors possess. While the number of bands is often large by conventional remote sensing standards—often in the 100’s—the fine sampling interval is vital to the underlying premise of much of remote sensing: All materials have a unique spectral signature that can be measured by the fashion in which the materials absorb, reflect, emit, and transmit electromagnetic radiation (Sabins, 1997; Richards and Jia,
1999; Ball, 2006; Campbell, 2007). In addition to the euphemistic term, “hyperspectral” sensing, the study of matter using radiation is also known as spectroscopy (Ball, 2006).

The spectral signature is a unique graph of reflectance, absorbance, transmittance, and/or emissivity of an object. In the visible/near infrared/shortwave infrared (VNIR/SWIR) portion of the electromagnetic spectrum (400-2500 nm wavelengths), reflectance is usually plotted along the y-axis, usually as a percentage, scaled from 0-1 or 0-10,000. Wavelength ($\lambda$) is plotted along the x-axis, usually in micrometers ($\mu$m) or nanometers (nm). An example is provided in Figure 1-3, which includes spectra of talc, healthy green vegetation, and a soil. Different objects reflect different percentages of incoming radiation (i.e., irradiance) throughout the spectrum. Theoretically, analysts can then identify the surface object based upon its unique spectral signature. Specifically, they identify materials by interpreting the reflectance amplitude, and/or the spectral location, shape, and intensity of absorption features that are specific to a material. For example, carbonate minerals such as calcite and aragonite all have absorption features around 2300 nm (Hunt, 1977; Clark et al., 2006). Increasingly, analysts are performing non-literal analysis by using material identification algorithms to interpret spectra and to match them to spectral library samples.
The crux of the hyperspectral sensing concept is its ability to measure a virtually continuous spectrum at very narrow, contiguous spectral ranges, returning a spectrum without sampling gaps and with very fine spectral resolution. Typical spectral resolution for hyperspectral sensors operating in the VNIR/SWIR portion of the electromagnetic spectrum are 5-20 nm (Rickard et al., 1993; Green et al., 1998; Simi et al., 2001). This fine sampling interval allows analysts to identify materials with high levels of confidence, despite similar chemical compositions. This tool is an extension of lab-based procedures and methodologies that make it much easier to compare the spectrum for each
pixel to specimens from a spectral library for classification, identification, and feature extraction purposes.

This is in contrast to traditional multispectral sensing limited to a few (e.g., 3-7), fairly wide spectral bands, typically 70-250 nm, that produce a spectrum with discrete spectral “snap shots.” In Figure 1-4 (left), the multispectral instrument (Landsat TM/ETM+) is scanning in six bands, represented by the six filled dots in the plot. Each band has a spectral range from 60 (Band 3) to 280 nm (Band 7). Note the relatively wide spectral range of each band compared to the hyperspectral image cube (Figure 1-4 (right)), which is 224 bands, each with a band width of 7-20 nm. As a result, the hyperspectral signature has much finer spatial resolution and is better suited for distinguishing subtle differences in materials.

![Figure 1-4: Spectral signatures of the same three materials taken by a 6-band multispectral sensor (left) and by a 224-band hyperspectral sensor (right). The blue spectrum is of talc. The green spectrum is of healthy, green vegetation. The black spectrum is of a soil. Talc spectra from the U.S. Geological Survey (USGS) Spectral Library (Clark et al., 1993). Vegetation and soil spectra are from C.D. Elvidge (unpublished) and included with the ENVI™ software package. Resampling and supplemental graphics by the author.](image)
As mentioned above, the much finer spectral resolution of the hyperspectral sensor provides analysts with the ability to perform material identification on a very sample-specific basis. For example, Figure 1-5 (left) demonstrates how hyperspectral sensing can distinguish one clay mineral (kaolinite, black trace) from a sulfate mineral (alunite, red trace). This is possible because alunite has a distinct absorption feature at 1764 nm and kaolinite has a uniquely shaped doublet (i.e., an absorption feature with two distinct reflectance minima) at 2165 and 2205 nm. Such distinctions would be quite difficult, if not impossible, with a multispectral sensor (Figure 1-5 (right)).

Figure 1-5: Spectral signatures of kaolinite (black) and alunite (red). It is possible to distinguish alunite from kaolinite in the hyperspectral image (left) whereas these distinctions are absent from the spectrally coarser multispectral image (right). Spectra from the U.S. Geological Survey (USGS) Spectral Library (Clark et al., 1993). Resampling by the author.

While airborne hyperspectral sensors have existed for decades, the last fifteen years have witnessed a proliferation of sensors and the first space-based hyperspectral sensors. The National Aeronautics and Space Administration/Johnson Space Center
(NASA/JSC) developed the first airborne hyperspectral sensor, Scanning Imaging Spectroradiometer (SIS), in the early 1970s. SIS had 32 bands and a spectral range of 430-800 nm (Irons, 1995). NASA/JSC and the Naval Ocean Systems Center used the optics from the SIS instrument for the next airborne sensor, Advanced Solid-state Array Spectroradiometer (ASAS), which had 62 bands, a spectral range of 404-1023 nm, and debuted in 1981 (Irons, 1995). That same year, Geophysical Environmental Research (GER) produced a non-imaging sensor, the Geophysical Environmental Research Spectroradiometer (GERS), which was a single-pixel instrument that measured spectra from 1960-2500 nm across 64 bands (Kruse et al., 1999). In 1983, NASA/Jet Propulsion Lab (JPL) fielded the next airborne hyperspectral sensor, Airborne Imaging Spectrometer (AIS), which had 128 bands and a spectral range of ~1200-2500 nm (Kruse et al., 1999). The first airborne hyperspectral sensor that covered the full reflective portion of the electromagnetic spectrum (400-2500 nm) was the Advanced Visible InfraRed Imaging Spectrometer (AVIRIS), which NASA/JPL first fielded in 1987 (Green et al., 1998). A partial listing of current airborne systems scanning in the reflective portion of the electromagnetic spectrum includes AVIRIS, Hyperspectral Digital Imagery Collection Experiment (HYDICE), Night Vision Imaging Spectrometer/Thompson Ramo Wooldridge Imaging Spectrometer (NVIS/TRWIS III), Hyperspectral Mapper (HyMap), COMpact Airborne Spectral Sensor (COMPASS), Airborne Imaging Spectrometer for Applications (AISA), Compact Airborne Spectrographic Imager/SWIR Airborne Spectrographic Imager (CASI/SASI), and Hyperspectral Spectral Technology and Innovative Research (HyperSpecTIR) (Green et al., 1998; Rickard et al., 1993; Simi et
al., 2000; Folkman et al., 1996; HyVista, 2007; Simi et al., 2001; Specim, 2007; ITRES, 2007; SpecTIR, 2008). In addition, NASA launched the first successful spaceborne hyperspectral sensor, Hyperion, aboard Earth Observing 1 (EO-1) in 2000 and the Air Force launched Sindri, another hyperspectral sensor, aboard MightySat II.1 the same year (Pearlman et al., 2003; USGS, 2008b; General Dynamics, 2005). The following year, the European Space Agency (ESA) launched a hyperspectral sensor, Compact High Resolution Imaging Spectrometer (CHRIS) (SSTL, 2008).

Hyperspectral sensing is still developing and the field of hyperspectral applications is understandably quite fertile for exploration. Perhaps the most conventional use of the data to-date has been for geological work (Hunt, 1977; Clark et al., 1993; Sabins, 1997; Richards and Jia, 1999; AVIRIS, 2008). Minerals have wide spectral diversity, often with strong spectral features that can be determined in a laboratory and thus, lend themselves well to spectral signature matching with hyperspectral data. Hyperspectral sensing also has potential for land cover mapping and identification of vegetation features and cultural surfaces (e.g., roads, roofs). Vegetation classification—especially for agricultural applications—water quality, and coral reef mapping have been well established for more than a decade (e.g., Landgrebe, 1995; Lelong et al., 1998; Neuenschwander et al., 1998; Holden and LeDrew, 1999). Hyperspectral sensing can also distinguish between impervious surface materials such as concrete and asphalt (Herold et al., 2004). Safe, non-invasive health care screening of potential tumors and land mine detection also hold potential (SPIE, 2004).
Like any remote sensing data, there are a number of limitations to the use of hyperspectral data. Data are relatively expensive and availability is limited when compared to panchromatic, multispectral, and radar imagery archives. For example, in early 2008 there were more than seven million images available from the Systeme Pour l’Observation de la Terre (SPOT) satellite series and more than four million images comprising the Landsat data archive whereas the Hyperion archive had <35,000 scenes (SPOT, 2007; USGS personal communication, 2008). In contrast to the Landsat archiving and collection plan, the USGS/NASA hyperspectral partnership does not attempt global land coverage. Hyperion acquisitions are instead driven by customer requirements for specific areas (USGS, 2008c).

While data are becoming more available through government (e.g., AVIRIS) and commercial airborne platforms there are also two spaceborne hyperspectral sensors on orbit with moderate spatial resolution (10-100 m): NASA’s Hyperion and ESA’s CHRIS, both launched a decade ago. Reflecting a shift in priorities towards the Moon and Mars and away from earth science, NASA launched a hyperspectral satellite mission to the Moon in 2008, the Moon Mineralogy Mapper (M3) (NASA-JPL, 2010). NASA anticipates revisiting moderate spatial resolution reflective hyperspectral imaging of the Earth later this decade with the launch of the Hyperspectral InfraRed Imager (HyspIRI) (NASA-JPL, 2011).

The limited availability of spectral libraries is another restriction on the use of hyperspectral data. Spectral libraries are collections of spectra for various materials that are supposed to be exemplary. Theoretically, they contain adequate metadata including
instrumentation, photo-documentation, measurement protocols, quality metrics, and environmental descriptions. They are usually collected in a lab environment under a controlled setting but are also collected in the field, if the conditions are appropriate (e.g., clear sky, photo-documentation provided). While there are robust repositories for some applications, such as geology spectral libraries provided by the USGS, NASA-JPL, Commonwealth Scientific and Industrial Research Organisation in Australia (CSIRO), Johns Hopkins University, and Arizona State University (Clark et al., 1993; Clark et al., 2006; Grove et al., 1992; CSIRO, 2007; Salisbury et al., 1991a; Salisbury et al., 1991b; Salisbury et al., 1994; Korb et al., 1996; ASU, 2008), there are very few libraries for remote sensing of solids and liquids in the VNIR/SWIR that are also easily accessible. While many of the aforementioned libraries contain some spectra for some non-geologic materials such as vegetation, snow, and man-made materials, they are quite limited. Currently, there are no publicly available spectra for liquid petroleum on terrestrial backgrounds with supporting metadata, something also noted by other authors (Clark et al., 2009).

Another limitation to hyperspectral sensing relates to the amount of electromagnetic radiation available to the sensor, usually expressed as radiance (commonly W/m²·sr·μm). When sensors constrain either their instantaneous field of view (IFOV) or spectral band width, they constrain the amount of energy that will ultimately reach the charge coupled device (CCD) onboard the scanner. While technology consistently improves these instruments’ sensitivity to incoming energy, they do have a minimum threshold for registering a valid response (Green et al., 1998).
Hyperspectral sensors usually parse energy into hundreds of bands instead of the typical 4-15 bands of multispectral systems so they severely constrain the amount of energy incident upon the detectors. For example, the Hyperion sensor has 34 bands, each with a 10.4-10.9 nm spectral width, in the same region as band 7 on Landsat Enhanced Thematic Mapper Plus (ETM+) (2090-2350 nm) (USGS, 2008b; NASA, 1998). If other major variables such as ground sample distance (GSD), radiometric resolution, quantum efficiency, etc. are equal and assuming that the spectral response functions of both systems are exactly the same over this region, each of these Hyperion bands receive approximately 3% of the energy that the detectors for band 7 on Landsat ETM+ receives.

The lower radiance values for Hyperion bands compared to Landsat bands are manifest in lower signal to noise ratios (SNR) for Hyperion. SNR in any given band—commonly measured as the mean radiance divided by the standard deviation—is higher for Landsat Thematic Mapper (TM)/ETM+ band 7 (2090-2350 nm) versus that of any single Hyperion band in the same portion of the electromagnetic spectrum. For example, Green et al. (2003a) and USGS (2008a) cite SNR values ranging from 25-40 in this region. Using a model from NASA/Goddard Space Flight Center (GSFC), Platt and Goetz (2004) produced an estimated SNR value of 67 for a Landsat ETM+ scene of the urban/rural fringe in Colorado.

The narrow spectral range in hyperspectral imagery is at once its strength and its weakness. The extreme sensitivity of the narrow spectral bands means that sensor spectral calibration is extremely important. It also means that compensating for atmospheric interference (e.g., scattering/path radiance, absorption, adjacency effect) and
normalizing the sensed spectrum to account for the shape of the solar spectrum are key procedures when using these data (Richards and Jia, 1999). Fortunately, there are numerous tools for performing these procedures, facilitating the use of hyperspectral sensing for material identification. This research will apply these concepts to detection and delineation of liquid hydrocarbons for the purpose of improving upon photo/manual identification of spills.

1.2 Applying Hyperspectral Remote Sensing to Petroleum Detection

Hyperspectral remote sensing provides highly accurate and potentially, product-specific information about materials based upon their spectral signatures (Sabins, 1997; Richards and Jia, 1999; Campbell, 2007). Where petroleum product spills and leaks occur, hyperspectral data sets can assist in spill detection, tank/pipeline leakage, and spill delineation not just along pipeline corridors, but also at accident sites, oil refineries, and petrochemical facilities. Petroleum detection maps can also be used to validate dozens of oil spill weathering and drift models (EPA, 2008b; NOAA, 2008a). In addition, preliminary investigations indicate that low levels (i.e., 0.01 g/cm²) of some petroleum products can be detected by a ground-based spectrometer (Allen and Satterwhite, 2006). The results can provide end-users such as oil spill responders with significantly higher confidence in the nature and the extent of spill events.

In addition to detecting and delineating spills, hyperspectral sensing can also be helpful at the remediation stage of a clean-up. Remediation never recovers 100% of the lost product. A survey of representative EPA publications provided values ranging from
20% (Ashland Oil Spill, Ohio, 1988) to greater than 91% (Colonial Pipeline Spill, Virginia, 1993). Despite the high percentage of oil recovery in the case of the Colonial Pipeline spill, over 34,000 gallons (129,000 liters) were still lost into the local ecosystems (EPA OSPU, 2002; EPA, 2008a). Hyperspectral sensing’s capability to detect even very small quantities of a hydrocarbon can provide information about the quality of the clean-up at the surface. It can also efficiently identify lingering amounts after an event such as the 500 miles (800 km) of shoreline still lightly oiled along the Gulf Coast a year after the Deepwater Horizon disaster.

Returning to the example of diesel fuel on sand, water on sand, and dry sand from Figure 1-2, Figure 1-6 depicts how this research can contribute to faster, more confident detection and discrimination of spill products in the context of potential confusers such as water. The spectral signatures of the three similar samples from Figure 1-2 are plotted in the reflective portion of the electromagnetic spectrum (400-2500 nm). Upon looking at the reflectance values of samples A and C, it is now clear that they are not the same material because of intensity differences (10-15%) in regions such as 1500-1600 nm and 2000-2100 nm. Furthermore, black arrows in the figure point to absorption features that when compared to a spectral signature library, indicate the presence of organic molecules (1200, 1700-1800, and >2300 nm) and hydroxyl ions (OH⁻) commonly found at the surface of many soil particles (2200 nm). The opacity of water in the SWIR masks the hydroxyl ion absorption feature in the water-wetted sand (Satterwhite and Allen, 2006). Casting the ease of this decision against the difficulty associated with discriminating
water from diesel fuel in Figure 1-2 and the uncertain wetting agent in Figure 1-1, it is clear that hyperspectral sensing can greatly assist spill response and delineation efforts.

Figure 1-6: Reflectance spectra of three samples similar to those in Figure 1-2. The sand in the photos has been replaced by a similar quartzic sand in the plot: sand wetted with diesel fuel (A), dry sand (B), and sand wetted with water (C). Distinguishing the two wet sands is difficult using human vision or even with traditional 4-band multispectral systems (Blue (B), Green (G), Red (R), Near Infrared (NIR)). Black arrows indicate absorption features that also help separate materials from one another.

Previous authors have demonstrated how hyperspectral data can help detect spills and seeps, delineate spills, and assist in post clean-up evaluations and inspections (Bianchi et al., 1996; van der Meer et al., 2000; Yang et al., 2000; Ellis et al., 2001; Hörig et al., 2001; McCoy et al., 2001; van der Meer et al., 2002; Kühn et al., 2004). Although
these previous spectral studies have directly or indirectly detected the surface presence of various hydrocarbons, they neglect a number of extremely important factors such as a thorough discussion and measurement of soil and hydrocarbon physical and chemical properties. They also neglect inherent soil optical depth properties (Satterwhite and Allen, 2005). Previous work does not establish minimum hydrocarbon detection thresholds on any substrates. These two factors provide minimum bounding parameters against which one might expect to successfully detect hydrocarbons on a wide range of appropriate backgrounds. See section 2. Literature Review for a more thorough discussion of previous research efforts in this area.

1.3 Research Rationale

Given the current state of hyperspectral remote sensing of petroleum and petroleum product spills, this investigation addresses three research questions:

1. Using hyperspectral data in the reflective portion of the electromagnetic spectrum (400-2500 nm), can petroleum and petroleum products be spectrally separated from water on a variety of commonly found substrates?

2. Can petroleum products be spectrally separated from one another when applied to a variety of substrates?

3. Can spectral signatures measured in support of questions #1 and 2 be successfully applied to airborne hyperspectral data with the goal of detecting petroleum or petroleum products?

Addressing these questions hinges upon the spectral signatures of petroleum and petroleum products and water on a variety of substrates. The spectral signatures for the vast majority of these liquid-substrate combinations are currently not available to the earth remote sensing community. The first step in addressing the research questions is
the measurement of these spectra. A systematic approach involving common petroleum products and well constrained substrate characteristics provides a suitable data set for revealing the causes of variability in spectral signatures.

As part of the library creation process, this effort measured and compared the spectral signatures of liquid-substrate combinations over time, in order to determine if changes in spectra provide a useful proxy for volatility and quantity on the surface. For volatiles, the liquid evaporates from the substrate, its influence gradually waning on the spectral signature of the liquid-substrate mixture. Over time, the mixture’s spectral signature gradually reverts to that of the “uncontaminated” substrate, before the liquid was applied. The statistical relationship between the fluid volatility, measured by its mass, and the spectra was also investigated. This process is especially helpful in cases where two petroleum products possess very similar spectral signatures that might otherwise be difficult to distinguish, as is the case of motor oil and diesel fuel. A baseline data set captured at one point in time can be compared to data captured at a later date. The liquids’ volatility, manifest in their spectral signatures, is indicative of one product or another.

A selected set of spectra from the signature library were then applied to airborne hyperspectral data with the goal of discriminating crude oil from water. One of the challenges of hyperspectral data analysis is the complexity associated with spectral manipulation and material identification. Further explanation is provided in section 3. Methodology.
2 LITERATURE REVIEW

As examples above indicate, petroleum spills occur in both aquatic and terrestrial environments. From 1973-2004, almost half (49.9%) of all polluting spills in the U.S. were in terrestrial environments (USCG, 2006). Yet, the use of hyperspectral data for hydrocarbon detection and characterization on terrestrial backgrounds is a neglected field of study despite considerable potential for improved detection and delineation. This is especially true considering the frequency of such events and the considerable attention paid to aquatic spills (EPA OSPU, 2001-2007; USCG, 2006; NOAA, 2008b).

Attempts to use electro-optical imagery to distinguish oil from water go back at least forty years (Vizy, 1974). Salisbury et al. (1993) used hyperspectral measurements in the thermal infrared, 8-14 μm, to discriminate oil slicks from water. Numerous authors have used multispectral and hyperspectral data to map oil spills in marine environments. Readers are directed to Wettle et al. (2009) for a bibliography extending back to 1990 and to Rogne et al. (1983) for an earlier effort. More recently, Clark et al. (2010)—responding to the Deepwater Horizon incident—used AVIRIS airborne hyperspectral data to identify and quantify oil floating on water in the Gulf of Mexico.

Detecting oil slicks and spills in open water is a well-established application for radar but using SAR for petroleum detection on terrestrial substrates is much less
common. Readers are directed to Fingas and Brown (2000) and Brekke and Solberg (2005) for summaries of these capabilities.

Previous authors have delineated numerous hydrocarbon absorption features in the reflective region of the electromagnetic spectrum (Hirschfeld and Hed, 1981; Cloutis, 1989; Gaffey et al., 1993; Clark et al., 2009). These features are caused by vibrational transitions at the molecular level. A major absorption feature at 1726 nm is a likely combination of symmetric and asymmetric CH$_2$ (carbon-hydrogen) and CH$_3$ stretches. These are second and third order overtones of the dominant C-H stretch at ~3450 nm. CH$_2$ stretching is also the most likely cause for a major absorption feature at 1760 nm. This doublet’s nonsymmetrical shape is consistent with multiple, overlapping C-H absorption bands. The features at 2260 nm and 2307 nm are indicative of CH$_2$ and CH$_3$ stretches and bends. Varying combinations of the C-H bonds contribute to the “hydrocarbon plateau” in the 2300-2450 nm spectral region (Cloutis, 1989; Gaffey et al., 1993).

Researchers have collected field spectra for various hydrocarbons applied to a soil substrate. Hörig et al. (2001) acquired ground level field spectra as well as airborne spectra for several sandy soils and “oil-contaminated soil.” Unfortunately, they do not elaborate on any of the physical or chemical properties of either the soil or the oil. For example, there is no information about the soil porosity, or even a description of the soil. Neither is there information about the oil. There are no measurements of properties such as density, age, or origin. The authors did detect the major hydrocarbon absorption features at ~1730 and ~2300 nm using a simple band ratio technique and a color
composite technique. Unfortunately, in their corresponding airborne data collection, they were unable to capture pure pixels of their reference targets, which severely limited their ability to extend their analysis to an airborne platform. Their follow-on article uses the same data to derive a “Hydrocarbon Index” which uses the strong hydrocarbon absorption feature at 1730 nm and contrasts it with nearby continuum bands at 1705 and 1741 nm, borrowing from the ubiquitous normalized difference vegetation index (NDVI) (Kühn et al., 2004). Their data set is still limited to one “oil-contaminated sand” and an “orange plastic” sample. They again neglect to characterize either the oil or the soil but this is an important first step in hydrocarbon detection heuristics. Bianchi et al. (1996) also detect “oil” but discuss neither the oil’s nor the soil’s properties.

Other field campaigns have successfully detected hydrocarbon micro-seepages in terrestrial environments (van der Meer et al., 2000; Yang et al., 2000; Ellis et al., 2001, McCoy et al., 2001; van der Meer et al., 2002). Yang (2000) and van der Meer (2000, 2002) employed indirect detection methods using red-edge shift as well as a direct detection method from mineral alteration. Ellis et al. (2001) found “oil-impacted soils” and other surfaces within industrial sites and brown-fields, relying exclusively on the minor absorption feature at ~2300 nm. However, they were unable to find pure pixels in the airborne imagery of these field sites, although they perform linear unmixing on their targets. Given that these authors also neglected to include any physical measurements or quantities of their samples, their casual use of “oil-impacted soil” and surfaces is unclear and poorly defined, especially when considering that these signatures are included in a
spectral library as exemplars for future work. Ellis does contribute a “Hydrocarbon Detection Spectral Ratio,” that is provided in Equation 2-1 below:

\[
R = \frac{(R_{2297\text{ nm}} + R_{2329\text{ nm}})}{(2 \times R_{2313\text{ nm}})}
\]  

(2-1)

where \(R_{xxxx\text{ nm}}\) is the reflectance value at the wavelength denoted in the subscript. Values of \(R>1\) “indicates potential hydrocarbons.” Ellis et al. (2001) have only tested their ratio on asphalt.

McCoy et al. (2001) successfully detected hydrocarbon micro-seepages on soils with a field spectrometer. Their focus was on two “fairly weak” absorptions at 1180 and 1380 nm, and two “broader, but much stronger” features at 1680-1720 and 2300-2450 nm. They used band ratio methods for detecting the hydrocarbons. Although McCoy et al. (2001) are a bit more explicit than previous work in discussing their samples, they only go so far as to name their contaminant, “Blackburn Field Crude Oil.” Like others, there is no quantification of either soil or oil properties.

Taylor (2000) found hydrocarbon contaminated soils using two different portions of the spectrum, the shortwave infrared (SWIR, 1300-2500 nm) and the longwave infrared (LWIR, 5-15 \(\mu\text{m}\)). In the SWIR, the author detected the major absorption features and used stressed vegetation as an indicator. In the LWIR, the author used color composites to detect hydrocarbons. Again, there is no discussion of either the soil or the hydrocarbons used in the study.

These authors demonstrate how hyperspectral data can help detect spill and leaks, delineate spills, and assist in post clean-up evaluations and inspections. Although these previous spectral studies have directly or indirectly detected the surface presence of
various hydrocarbons, they neglect a number of extremely important factors such as a discussion and measurement of soil and hydrocarbon physical properties, along with inherent soil optical depth properties. Soil optical depth is that depth in the soil profile beyond which an irradiance applied at the surface does not return to the surface via scattering, downward reflection, and absorption processes (Satterwhite and Allen, 2005). Previous authors also do not establish minimum hydrocarbon detection thresholds on any substrates. These two parameters provide minimum bounding parameters against which one might expect to successfully detect hydrocarbons on various backgrounds.
3 METHODOLOGY

This research addresses some of the deficiencies in hyperspectral detection and identification of liquid hydrocarbons in four ways: 1) measuring the spectral signatures of water and nine liquid petroleum and petroleum products on ten commonly found substrates, 2) comparing the wavelengths and persistence of petroleum and petroleum products on a variety of common substrates, 3) confirming previous estimates of minimum detection and identification thresholds for some volatile petroleum products while expanding the list of substrates, and 4) applying these spectra and standard hyperspectral image processing techniques with minor modifications to airborne hyperspectral data with the goal of discriminating petroleum from water in imagery.

3.1 Approach

Due to the lack of publicly available petroleum-substrate spectra, data first needed to be collected. In a controlled lab environment, a ground-based field spectrometer was used to measure the spectral signatures of water and nine petroleum and petroleum products on ten commonly found substrates in the reflective portion of the electromagnetic spectrum, 350-2500 nm. Time and temperature are the driving factors in petroleum evaporation (Fingas, 2004). This effort focused on time while controlling temperature. Sample spectra were collected at regular intervals at least until the samples
effectively ceased to change, defined here as a change of <1% when compared to previous spectra. For volatile products, measurement ranges were as short as three days and for more stable products, they lasted for >100 days.

3.2 Lab Measurements

Using a ground-based field spectroradiometer (ASD FieldSpec-Pro™ Far Range-2 (FR-2)), biconical reflectance spectra of petroleum products on a variety of common substrates were measured in the reflective portion of the electromagnetic spectrum (350-2500 nm) (Schaepman-Strub et al., 2006). A representative set of both crude and refined products, applied to a representative set of substrates, were evaluated.

3.3 Sample Preparation and Handling

Samples for this experiment were placed in either petri dishes or plastic tubs. Liquid-only samples were placed in glass petri dishes, 10.0 cm in diameter and 1.0 cm in depth (Figure 3-1). Liquid-substrate samples were placed in plastic petri dishes that were 8.5 cm in diameter and 1.5 cm in depth (Figure 3-2). The most commonly used plastic tubs were 9.0 cm in inside diameter at the top which then tapered to 7.5 cm at the base (Figure 3-3). These tubs were 5.5 cm deep. Occasionally, asphalt samples were too large for the standard tub and two slightly larger tubs were used. The first measured 11.4 cm in diameter at the top, tapering to 8.9 cm at the bottom and 7.6 cm in depth (Figure 3-4). The second was rectangular and measured 10.2 cm x 14.0 cm and was 7.0 cm in depth (Figure 3-5).

Each plastic petri dish and tub was painted with two coats of flat, black paint in order to minimize radiation scattering from the sides of the holder and spurious spectral
contributions from the container materials. The petri dishes were then filled with the 1.0-
1.5 cm of the appropriate substrates: bentonite, calcareous sand, gypsum, highly organic
soil, Ottawa sand, and a quartzic beach sand (QBS) (Figure 3-2). This depth was more
than enough to negate any reflectance effects from the black-painted bottom of the dish.
Satterwhite and Allen (2005) found that this value, the optical depth, is 5-8 particles deep
and less than 5 mm for even coarse-grained sand. The asphalt, concrete, calcite-dolomite
crushed aggregate, and vegetation samples were inserted in the small, plastic tubs
(Figures 3-3, 3-4, and 3-5).

Figure 3-1: Clear, glass petri dish used as a sample holder for liquid
measurements without substrates, 10.0 cm in diameter x 1.0 cm in depth.
This masking tape is the “target” for placing the petri dishes for
photographs and also provided for contrast purposes in this photograph
(100-4293.jpg). The Mini ColorChecker™ in all photos is 8.25 cm in width x
5.7 cm in height.
Figure 3-2: Ottawa sand sample in petri dish, 8.5 cm in diameter x 1.5 cm in depth, no liquid applied (102-3366.jpg).

Figure 3-3: Calcite-dolomite crushed aggregate sample in plastic tub, 9.0 cm in diameter tapering to 7.5 cm at base x 5.5 cm in depth, no liquid applied (100-3391.jpg).
Six samples of each refined product-substrate combination were prepared. Five samples were coated with the liquid while the sixth served as a control. After initial preparation, substrate samples were left to air-dry for approximately one day to minimize unbound water contribution to the samples. Due to limited quantities of each crude oil,
four samples of each substrate were prepared. Three served as liquid samples and one served as a control.

### 3.4 Liquids

A set of nine petroleum and petroleum products were chosen to gather a representative collection of both crude and refined products that spanned a wide range of volatilities. The liquids are listed in Table 3.1, along with a brief rationale for their inclusion.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Rationale for Inclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>Highly volatile, common industrial chemical</td>
</tr>
<tr>
<td>Gasoline</td>
<td>Common spill material, 10% ethanol</td>
</tr>
<tr>
<td>E85 fuel</td>
<td>85% ethanol, 15% gasoline, increasingly common spill material</td>
</tr>
<tr>
<td>Diesel fuel</td>
<td>Very common in Europe and in industrial equipment in the U.S.</td>
</tr>
<tr>
<td>Motor oil</td>
<td>Common spill material, difficult to spectrally distinguish from diesel fuel</td>
</tr>
<tr>
<td>Crude oil (light)</td>
<td>Representative range of crude oils, common spill materials</td>
</tr>
<tr>
<td>Crude oil (intermediate, sour)</td>
<td></td>
</tr>
<tr>
<td>Crude oil (intermediate, sweet)</td>
<td></td>
</tr>
<tr>
<td>Crude oil (heavy)</td>
<td>Included for comparison to petroleum and petroleum products</td>
</tr>
<tr>
<td>Water</td>
<td></td>
</tr>
</tbody>
</table>

Readily available refined products were purchased and stored in air tight containers to minimize any premature evaporation. Substrate samples were weighed and their
spectra collected. Liquid densities were calculated from their mass and volume as determined by a scale and a graduated cylinder. After application to the substrates, liquid mass was also calculated in accordance with procedures outlined in Allen and Satterwhite (2006). Representative photographs were taken as well using a black background and a Mini ColorChecker™ color standard.

Each low viscosity petroleum product was poured into a hand sprayer and then sprayed onto each substrate in even amounts. This included the acetone, gasoline, ethanol fuel blend (~85%) with gasoline (E85), diesel fuel, and water samples. A baster was used to drip liquids with high viscosity—motor oil and all four crude oils—onto the substrates. There were five samples of each refined product/substrate combination and due to limited quantities, three samples of each crude/substrate combination. There was also a control for each substrate that did not receive any hydrocarbon application. In order to avoid distortion by liquid pooling on the surface of each substrate, application ceased at the first visible signs of pooling. For permeable substrates, the surface saturation indicates that interstitial spaces between substrate particles are filled. For impervious substrates, smaller quantities were needed to achieve a pooling layer on the surface since there was little to no percolation into the substrate.

After each sample was sprayed, it was weighed and its spectra collected in accordance with the procedures outlined in section 3.6 Spectral Measurements below. Photographs were taken of each sample before liquid application and immediately after liquid application. Thereafter, photographs were only taken of Sample #1 at each time interval. Samples were then set aside until their next measurement where the process was
repeated. Losses in mass at subsequent intervals quantified product loss over time and to a lesser extent, changes in the substrates (e.g., water loss/gain to/from the atmosphere). Hand sprayers only contained one refined product, so that cross-product contamination did not occur.

During the first day, measurements were frequent enough that samples remained on a lab cart. After the first day, samples were stored in a chemical hood under room temperature conditions (20-23° C) and a steady 1.6 kph air flow from the hood fan to minimize meteorological contributions to evaporative loss.

3.5 Substrates

For this effort, water and petroleum were spilled on ten substrates, which are listed in Table 3.2, along with a brief rationale for their inclusion.
### Table 3-2: Substrates (n=10) used for measurements.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Rationale for Inclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt</td>
<td>Ubiquitous pavement surface, high bitumen content, spectrally dark substrate</td>
</tr>
<tr>
<td>Bentonite</td>
<td>Common secondary containment (berm) substrate, low permeability, high sorption capacity, clay texture</td>
</tr>
<tr>
<td>Calcite-Dolomite Crushed Aggregate</td>
<td>Common substrate at industrial facilities and on unpaved surfaces</td>
</tr>
<tr>
<td>Concrete</td>
<td>Common pavement surface, concrete dikes are common secondary containment (berm) substrates</td>
</tr>
<tr>
<td>Calcareous Sand</td>
<td>Found in some locales with petroleum deposits, absorption features overlap with hydrocarbons, offshore spills often come ashore and impact beach sands</td>
</tr>
<tr>
<td>Gypsum</td>
<td>Found in some locales with petroleum deposits, absorption features overlap with hydrocarbons</td>
</tr>
<tr>
<td>Highly Organic Soil</td>
<td>Organic matter absorptions will interfere with hydrocarbon absorptions, spectrally dark substrate</td>
</tr>
<tr>
<td>Ottawa Sand</td>
<td>“Ideal” quartzic sand with high physical/chemical homogeneity</td>
</tr>
<tr>
<td>Quartzic Beach Sand</td>
<td>Offshore spills commonly come ashore and impact beach sands</td>
</tr>
<tr>
<td>Vegetation</td>
<td>Common spill substrate, complicated by inclusion of turgid material, leaf litter, and underlying soil</td>
</tr>
</tbody>
</table>

Sections 3.5.1-3.5.10 discuss each material in turn.

#### 3.5.1 Asphalt

Asphalt is ubiquitous in populated areas; >90% of roads in the U.S. are paved with asphalt (NAPA, 2010). As a result, spills on impervious surfaces such as parking lots, roads, and other paved surfaces such as airport tarmacs commonly occur on this substrate.

Asphalt is composed of a variety of ingredients. It is approximately 95% gravel, stone, and sand which is dominated by quartz and dolomite-rich lithologies (NAPA,
The remaining 5% is composed of large, heavy hydrocarbon molecules—often referred to as the asphaltene fraction—that coat the other materials and cements them into an impervious mass (Gary and Handwerk, 1993; NAPA, 2010). The hydrocarbons vary in length from 50-1000 carbon atoms and consist of 80-87% carbon, 9-11% hydrogen, 2-8% oxygen, with the balance consisting of nitrogen, sulfur and trace metals (Herold and Roberts, 2005).

The asphalt used here consisted of surface sections of unknown vintage that were taken from a parking lot demolition site. Samples were 3.2-3.8 cm thick (1.25-1.50”) and collected in situ from mildly weathered locations on site. They were not damaged by wrecking equipment before collection. Sections were chiseled into smaller pieces to fit inside of collection vessels. Careful effort was made not to leave any chisel marks, which exposed the darker, high-gloss unweathered asphalt beneath the surface. In addition, no effort was made to sweep any accumulated dust from the surface to replicate in situ conditions. As the photographs in Figure 3-6 demonstrate, the asphalt is a weathered medium to dark gray color with a dull luster.
Since asphalt coats both the aggregate and cements it together, the spectral signature of asphalt pavement is initially dominated by the hydrocarbon components’ spectra. As a result, freshly paved asphalt surfaces are spectrally dark across the VNIR/SWIR region of the spectrum due to the strong absorption of the long hydrocarbon chains in this region. Asphalt surfaces do brighten spectrally with age as the asphalt erodes, lighter ends evaporate, dust accumulates on the surface, and the contribution of
the spectrally brighter, aggregate component increases (Herold et al., 2004; Herold and Roberts, 2005).

3.5.2 Bentonite

Bentonite is an umbrella term for common, impure clay mostly comprised of smectites. Smectites are highly absorptive of polar molecules such as water and hydrocarbons. When subjected to wetting by these liquids they can expand while maintaining their crystalline structure (Moore and Reynolds, 1997). Combined with low cost and ubiquity, bentonite’s high sorption capacity makes it an attractive material for both secondary containment dikes and external liners for ASTs (EPA, 1996b; EPA, 1996c). Secondary containment generally refers to mechanisms designed to contain spills and leaks that have escaped their primary containment vessel (e.g., an AST). “Impervious soil” liners are comprised of “silty clay and soil mixed with bentonite” (EPA, 1996c, p. 61).

Pulverized bentonite samples were procured from a commercial source (American Colloid VOLCLAY® SPV 200) for use as substrates. According to the manufacturer, the bentonite is dominated by montmorillonite ((Na, Ca)_{0.33}(Al_{1.67}Mg_{0.33})Si_{4}O_{10}(OH)_{2}\cdot nH_{2}O) but contains small quantities of feldspar, calcite, and quartz; ≥65% of the montmorillonite is <74 μm in size as well (American Colloid, 2001). Mineralogical analysis of 40 samples is included in Table 3-3. The mean SiO₂ and Al₂O₃ content are 61.34% and 26.54%, respectively. The remaining 12.12% is a mixture of magnesium, iron, sodium, calcium, and potassium oxides. Figure 3-7 includes two transmission electron microscopy (TEM) images and a selected area electron diffraction (SAED) pattern for the
bentonite sample material. The image on the left in Figure 3-7 shows numerous lamellar aggregates with smaller silica particles interspersed for the <2 μm size fraction. The image on the right in Figure 3-7 shows a single montmorillonite grain and the SAED pattern (inset), whose pattern of concentric rings indicates turbostratic stacking of 2:1 layers typical for this mineral. Moisture content is 7.9% and total organic content is 1.5%.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>61.34</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>26.54</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.81</td>
</tr>
<tr>
<td>MgO</td>
<td>5.27</td>
</tr>
<tr>
<td>CaO</td>
<td>1.23</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.74</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.06</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100.00</td>
</tr>
</tbody>
</table>
As the photographs in Figure 3-8 demonstrate, bentonite samples were uniform in appearance. They were poured into sample holders and gently shaken to level the surface but not tamped. They were then left to air dry for at least 12 hours to equilibrate with indoor humidity conditions.
3.5.3 Calcareous Sand

Three sands were included in the set of substrates: a calcareous sand, a quartzic beach sand, and Ottawa sand. The sands were included because oil spills on water often wash ashore onto sandy substrates, including the example in Figure 1-1. The calcareous sand has the distinction of possessing an absorption feature—the carbonate anion feature from ~2330-2350 nm—that overlaps with the hydrocarbon absorptions >2300 nm, which
may interfere with detection of the latter (Hunt, 1977; Gaffey et al., 1993). Furthermore, carbonate rocks are common and act as the reservoirs for approximately 50% of the world’s oil (Gaffey et al., 1993). Spectra of hydrocarbons on a carbonate substrate of any kind provide useful information about how they might appear on a rocky substrate.

The calcareous sand samples were collected from the vicinities of Akumal and Tulum, Mexico (20°24’N, 087°18’W). Eight samples were collected and measured. Samples consist of calcite, aragonite, and a magnesium-rich calcite with an average of 0.3% moisture content and 2.3% total organic content, based on loss on ignition. Quantities of each type vary greatly for each sample, ranging from 24-84% aragonite, 7-38% calcite, and 8-57% magnesium-rich calcite, as determined by Krekeler et al. (2009) using X-ray diffraction (XRD) (Figure 3-9). Scanning electron microscopy (SEM images in Figure 3-10) reveals representative sub-rounded grains from the sample sand (A) and a typical sub-rounded prismoidal-shaped grains (B).
Figure 3-9: X-ray diffraction pattern for calcareous sand sample (source: Krekeler et al., 2009).
Sieve separates for the calcareous sand are plotted in Figure 3-11. As the plot indicates, the samples are a medium to coarse sand, using the U.S. Department of Agriculture (USDA) soil classification system (Brady and Weil, 2002). Five of the sieves retained 79.0% of the samples: 0.710, 0.600, 0.500, 0.425, and 0.355 mm. The 0.50 mm sieve retained the largest percentage of the soil samples (26.0%). The
remaining four sieves accounted for 10.8%, 12.3%, 17.7%, and 12.3% of the samples, in descending order of size. Mean soil porosity is 43% (Krekeler et al., 2009).

![Sieve separates of calcareous sand sample.](image)

As the photographs in Figure 3-12 demonstrate, the sand is bright-colored, lighter than Munsell color Gley 1 8/N. Occasionally, 1-2 pebble-sized rocks (Figure 3-12, upper left) or small lignin fragments (Figure 3-12, lower left, lower right) interrupted the sand’s surface. Samples were poured into sample holders and gently shaken to level the surface.

45
but not tamped. They were then left to air dry for at least 12 hours to equilibrate with indoor humidity conditions.

Figure 3-12: Representative photographs of calcareous sand samples (101-6404.jpg (upper left), 100-4140.jpg (upper right), 100-5219.jpg (lower left), 101-5820.jpg (lower right)).
3.5.4 Calcite-Dolomite Crushed Aggregate

Gravel-sized crushed aggregate is another common material along transportation routes, both as the primary road surface and as a common material along the shoulders of paved roadways. It is also frequently found between buildings, under pipe galleries, and is a common surface for access roads at industrial facilities (EPA, 1996b).

Multiple bags of a gray-white crushed aggregate were procured from a local home improvement store. As the photographs in Figure 3-13 demonstrate, most stones are gravel-sized, 2-75 mm along their greatest diameter (Brady and Weil, 2002). The coating has a Munsell color of Gley 2 8/10B and the interior color is Gley 2 4/10B. Sample moisture is 0.05% with 0.09% total organic content. Individual stones were gently washed under tap water to remove fine dust—revealing the rock coating—and then left to air dry for at least 24 hours before pouring into sample containers for use in data collection. The random packing of stones often left cavities into which liquids could penetrate the sample and also created self-shadowing during spectral data acquisition.
3.5.5 Concrete

Like asphalt, concrete is a ubiquitous surface material in populated areas. It is used as a paving material, for parking garages, and is commonly used for airport tarmacs. Concrete pads are also common foundations for ASTs. According to an American Petroleum Institute (API) 1989 study, “approximately 88 percent of all ASTs with storage capacity of less than 42,000 gallons are set on concrete pads” (EPA, 1996b).
Additionally, concrete dikes are extremely common for secondary containment and as external liners for ASTs because they are inexpensive to construct and resistant to oil (EPA, 1996b; EPA, 1996c). Secondary containment generally refers to mechanisms designed to contain spills and leaks that have escaped their primary containment vessel (e.g., an AST). For these reasons, concrete is a common substrate for petroleum spills (EPA, 1996b; EPA 1996c).

Concrete is composed of two major components: aggregate and a cementitious paste. Aggregate includes crushed stone, gravel, and sand. It makes up approximately 60-75% of concrete by volume. The cementitious paste that binds the aggregates together can vary widely in the amount of each ingredient, depending on application and on the chemical composition of the materials: cement (7-15%), fly ash (≤19%), water (14-21%), and air (≤8%) (FHWA, 1999; ACPA, 2010).

Samples from a local parking lot demolition project were procured for use as substrates. Despite extended cutting with a concrete saw, they proved too difficult to cut into small enough pieces to fit the sample holders. As an alternative, a general purpose structural concrete with 4000 psi compressive strength (i.e., QUIKRETE™ Concrete Mix 1101) was hand mixed, poured, and forcefully tamped directly into painted sample holders to a depth of 3-4 cm. Samples usually had level surfaces but occasionally, uneven pouring resulted in slightly sloped surfaces. Samples were left to cure indoors for a minimum of 48 hours before use in the lab. Based on loss on ignition data, the concrete mix has 1.4% moisture content before hand-mixing. When mixed according to the
manufacturer’s specifications, the samples contain 7.3-10.5% water by mass (QUIKRETE™, 2007).

Figure 3-14 includes representative photographs of a number of the cured concrete samples before liquid application. The cementitious paste often dominated the surface presentation (Figure 3-14, upper left, lower left, lower right) but occasionally aggregate speckled the samples at the surface (Figure 3-14, upper right). Munsell colors for the samples vary from 7.5YR 7/1 to Gley 2 8/5PB.
Contrary to asphalt surfaces, concrete surfaces usually darken spectrally with age. Herold et al. (2004) cite increasing levels of iron-oxidation at the surface and dust/soil accumulation as the causes.
3.5.6 **Gypsum**

Gypsum is the most common sulfate mineral and is commonly found in association with carbonate rocks such as dolomite and limestone (Deer et al., 1992). It is also common in desert sand in many locales where petroleum is extracted, including the Middle East and Southwestern Asia. Iran was the world’s fourth leading gypsum producer in 2008 (Brady and Weil, 2002; BGS, 2010). Gypsum was also included because it has multiple absorption features that overlap with those of hydrocarbons. Molecular water causes absorptions at ~1200, 1750, and 2270 nm, all of which overlap with hydrocarbon absorptions at the same wavelengths (Hunt, 1977; Gaffey et al., 1993).

Gypsum (CaSO$_4$·2H$_2$O) samples were procured from a commercial source for use as substrates. Sieve separates are plotted in Figure 3-15. As the plot indicates, the samples are well sorted very fine to medium sand, using the USDA soil classification system (Brady and Weil, 2002). The very fine sieves retained 27.8% of the sample while the fine and medium sieves retained 26.9% and 22.1%, respectively. The balance is in the coarse (14.1%) and very coarse (6.1%) sieves, with negligible quantities (<2%) in the silt and gravel classes. Sample moisture is 0.04% and organic content is below detectable levels.
Figure 3-15: Sieve separates of gypsum sample.

The SEM images in Figure 3-16 show representative anhedral to euhedral-shaped grains.
Figure 3-16: SEM image of gypsum sample. Grains are anhedral to euhedral in shape with diameters ranging from 0.005-1 mm.

As the photographs in Figure 3-17 demonstrate, the gypsum is a very bright, white with Munsell color Gley 2 8/5BG. Occasionally, 1-2 pebble-sized clumps (Figure 3-17, upper right, lower left) occurred at the sample surface. Samples were poured into sample holders and gently shaken to level the surface but not tamped. They were then left to air dry for at least 12 hours to equilibrate with indoor humidity conditions.
3.5.7 Highly Organic Soil

None of the sands have substantial quantities of organic matter. Neither do the bentonite or gypsum samples. Furthermore, soil organic matter is obscured under the grass blades and leaf litter in the vegetation sample. For this reason, a soil with high (2.9%) organic matter content was also used as a substrate.
Aside from the total organic carbon content, SEM/EDS (energy dispersive X-ray spectroscopy) analysis of the sonicated silt/soil fraction revealed large quantities of pyroxene, feldspar, and plagioclase. The quantities of the most common inorganic elements are included in Table 3-4.

Table 3-4: SEM/EDS chemical analysis of inorganic elements in highly organic soil (water excluded).

<table>
<thead>
<tr>
<th>Element</th>
<th>Area 1</th>
<th>Area 2</th>
<th>Area 3</th>
<th>Area 4</th>
<th>Area 5</th>
<th>Area 6</th>
<th>Area 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>34.04%</td>
<td>49.45%</td>
<td>65.21%</td>
<td>54.90%</td>
<td>52.84%</td>
<td>58.79%</td>
<td>38.68%</td>
</tr>
<tr>
<td>Al</td>
<td>1.42%</td>
<td>0.33%</td>
<td>9.80%</td>
<td>0.73%</td>
<td>1.80%</td>
<td>12.43%</td>
<td>1.32%</td>
</tr>
<tr>
<td>Si</td>
<td>6.28%</td>
<td>0.66%</td>
<td>17.68%</td>
<td>20.87%</td>
<td>3.18%</td>
<td>19.54%</td>
<td>20.03%</td>
</tr>
<tr>
<td>Ca</td>
<td>4.84%</td>
<td>0.47%</td>
<td>3.91%</td>
<td>9.77%</td>
<td>0.16%</td>
<td>5.37%</td>
<td>19.22%</td>
</tr>
<tr>
<td>Fe</td>
<td>25.68%</td>
<td>26.24%</td>
<td>0.22%</td>
<td>5.78%</td>
<td>21.93%</td>
<td>0.40%</td>
<td>13.50%</td>
</tr>
<tr>
<td>Ti</td>
<td>26.45%</td>
<td>21.79%</td>
<td>-</td>
<td>18.70%</td>
<td>-</td>
<td>-</td>
<td>0.86%</td>
</tr>
<tr>
<td>Na</td>
<td>-</td>
<td>-</td>
<td>3.08%</td>
<td>-</td>
<td>3.47%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>1.29%</td>
<td>0.57%</td>
<td>-</td>
<td>0.63%</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mg</td>
<td>-</td>
<td>0.49%</td>
<td>-</td>
<td>7.96%</td>
<td>0.77%</td>
<td>-</td>
<td>5.89%</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.49%</td>
</tr>
<tr>
<td>K</td>
<td>-</td>
<td>-</td>
<td>0.12%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
</tr>
</tbody>
</table>

The soil was collected from a highly disturbed site without any vegetation and immediately sealed in a five gallon (19 liter) bucket to preserve moisture in the sample. As the photographs in Figure 3-18 demonstrate, the soil is a dark brown color and tends to clump together. Munsell color is 7.5 YR 4/4 before air drying. Loss on ignition determined that moisture content is 18.6%, averaged across three samples. Samples were poured into sample holders and gently shaken to level the surface but not tamped. The clumps produced modest amounts of self-shading when illuminated by the lamp. To
maintain procedural protocol, they were then left to air dry for at least 12 hours, even though a large portion of the moisture evaporated from the samples during that time period. The spectral effect of the evaporated water is discussed in section 4. Discussion below.

Figure 3-18: Representative photographs of highly organic soil samples (101-6518.jpg (upper left), 101-6937.jpg (upper right), 100-5597.jpg (lower left), 100-4796.jpg (lower right)).
3.5.8 Ottawa Sand

Ottawa sand is a coarse, quartzic sand from a series of deposits near Ottawa, Illinois. It is commonly used as an industry standard because of its lack of impurities and uniform particle size (Raveia et al., 2008). As a result, it forms an idealized substrate for hydrocarbon contamination. It has minor iron oxide absorption features (<2%) in the VNIR and a mild hydroxyl absorption at ~2200 nm.

Samples were procured from a commercial source (Fisher Scientific) for use as substrates. Mechanical sieve analysis of the sand confirmed particle size homogeneity, as indicated in Figure 3-19, where 76.1% of the sample was retained on the 0.710 mm sieve. Of the remaining 23.9%, 21.5% was retained on the 0.600 mm sieve with the balance falling on the 0.850 mm (1.6%) and 0.500 mm (0.8%) sieves. The entire sample was retained on the series of coarse grained sieves, using the USDA soil classification system (Brady and Weil, 2002).
Figure 3-19: Sieve separates of Ottawa sand sample.

The SEM image in Figure 3-20 demonstrates the particle homogeneity in the Ottawa sand. Grains are rounded to well-rounded in shape and most range in size from 0.6 mm along the minor axis to 1.0 mm along the major axis.
Figure 3-20: SEM images of Ottawa sand. Grains are rounded to well rounded in shape with diameters ranging from 0.6 mm along the minor axis to 1.0 mm along the major axis.

As the photographs in Figure 3-21 demonstrate, the Ottawa sand is a very bright, white, and nearly translucent color. Samples contain 0.02% moisture content and 0.26% total organic content. Munsell color is 2.5Y 8/1. Samples were poured into sample holders and gently shaken to level the surface but not tamped. They were then left to air dry for at least 12 hours to equilibrate with indoor humidity conditions.
3.5.9 Quartzic Beach Sand

Since many oil spills occur in littoral or maritime environments, beach sand is a common substrate against which petroleum detection will have to occur. A quartzic beach sand was collected from the foreshore area of a beach in Kitty Hawk, NC. The uppermost 2.5 cm of sand was collected from three, 0.3 x 0.3 m squares and immediately...
double-bagged to prevent evaporative loss. The sand contains 4.9% water and 0.13% total organic content, as measured by loss on ignition for three samples.

Mechanical sieve analysis of the sand in Figure 3-22 shows that the samples are a moderately well-sorted medium to coarse sand, using the USDA soil classification system. More than half of the samples, 52.9%, were retained on the medium-sized sieves: 0.425, 0.355, 0.300, and 0.250 mm. The coarse sieves retained 23.8% of the sample. The fine and very coarse sieves retained 13.4% and 7.5%, respectively. The remainder is in the gravel (1.8%) and very fine (0.5%) sieves.

Figure 3-22: Sieve separates of quartzic beach sand sample.
As the photographs in Figure 3-23 demonstrate, the beach sand is a light brown color frequently interrupted by small shell fragments ranging in color from white to black. Overall Munsell color is 10 YR 7/3. Samples were poured into sample holders and gently shaken to level the surface but not tamped. To maintain procedural protocol, they were then left to air dry for at least 12 hours, even though a large portion of the interstitial water evaporated from the samples during that time. The spectral effect of the evaporated water is discussed in section 4. Discussion below.
3.5.10 Vegetation

Vegetation, especially grasses, is also a common spill substrate along beaches, at industrial sites, and in wetlands. The vegetation substrate used here consists of a plug approximately the size of the sample container that was dug out of the ground and used for measurements within four hours of extraction. The samples are a combination of
three broad material classes: turgid green vegetation in the form of lawn grass and occasional wild strawberries, leaf litter from both the grass and surrounding oak trees, and the underlying soil, which is similar to the highly organic soil substrate.

The 10 substrates, combined with 3 or 5 sample replicates, quickly filled the chemical hood in the lab space. As a result, sample measurements were spread out over a 10-month period (June-March), during which vegetation undergoes normal seasonal patterns. Emergence had already occurred in June when measurements began, as indicated in the upper left photograph in Figure 3-24. In early December, the grass was still turgid but senescence was imminent—as evident in the upper right photograph. The lower left and right photographs are representative of vegetation samples from late December through late February and early March. The seasonal patterns in vegetation are also evident in the substrate spectra, which are discussed in section 4. Discussion below.
3.6 Spectral Measurements

Biconical reflectance spectra were collected using an ASD FieldSpec-Pro™ Far Range-2 spectroradiometer (FR-2) (Schaepman-Strub et al., 2006). The FR-2 spectral
sampling interval is 1.5 nm from 350-1050 nm and 10-12 nm from 1050-2500 nm. Spectra are then upsampled to 1 nm using the ViewSpecPro™ software provided by ASD (Hatchell, 1999). Resulting spectra contain 2152 samples from 350-2500 nm. Unfortunately, noise limits the spectral response in the 350-400 and 2400-2500 nm regions, resulting in a low signal-to-noise ratio. Data collected in this region were reviewed for quality and discarded since intra-sample standard deviations (1 σ) in these regions frequently exceeded 1%.

The ASD FR-2 instrument was equipped with a fore-optic attachment with an 8-degree field of view (FOV). Figure 3-25 and Equation 3-1 depict how the spot size is determined (Hatchell, 1999; D.J. Williams personal communication, 2008).

If the instrument is looking nadir:

\[ y = x \tan \alpha \]  

(3-1)

where

- \( y \) = radius of the spot size (m)
- \( x \) = distance from sensor to target (m)
- \( \alpha \) = Sensor FOV half-angle

The optical head was positioned 0.5 m above the samples with a nadir-viewing angle so that it only detected the reflectance from the sample and not from any surrounding backgrounds. The spot size in this configuration was 7.0 cm in diameter.
Lighting was provided by a 250 W Lowel Pro-light (Underwriters Laboratories (UL) Standard 1573) or 250 W ASD Pro-Lamp at a distance of 43 cm from the sample. In accordance with ASD’s recommendations, the lamp was positioned flanking the sample and angled approximately 30° off-nadir (Hatchell, 1999; ASD, 2001). The heat from the lamp added a small amount of energy to the samples, thereby artificially increasing the rate of liquid evaporation from the surface. Given that the heat contributed to greater evaporation, all samples were exposed to the light for approximately 30 seconds per measurement to create a standard treatment for this study.

Calibrating hyperspectral sensors is a vital component of the measurement process. For this study, sensor calibration was performed every 5-10 minutes, using a white reference standard. The standard was a Spectralon™ panel whose spectra were the mean of 50 or 60 co-adds. At the beginning of each session of measurements, the ASD
FR-2 system dark current was measured to minimize its additive influence on spectra. This value was also the mean of 50 or 60 co-adds. The dark current correction was reviewed periodically during the measurement process using the ASD ViewSpecPro™ software and re-measured if necessary.

During every session, spectra of a NIST traceable (Standard Reference Materials (SRM)-1920a) mylar® sheet were also collected to ensure that wavelength assignments were accurate and did not drift over the course of the observation period. The mylar® sheet wavelengths are accurate to +/-1 nm and wavelength assignments for the ASD spectra met this specification. The mylar® wavelengths are 1128.7, 1659.9, 1904.6, 1951.4, 2130.8, 2155.0, 2180.7, 2255.3, 2331.0, and 2444.5 nm.

The spectra for the gasoline, motor oil, and diesel fuel each consist of 30 co-adds. Due to an issue with instrument scanning speed, the spectra for water, E85, and all four crude oil samples each consist of 20 co-adds. Both the 20 and the 30 co-add spectra have intra-sample standard deviations <1% at all wavelengths from 400-2400 nm. Five spectra for each sample were collected and averaged. These spectra were then averaged with the spectra for each of the other samples (n=2 (crude oils) or n=4 (water, E85, gasoline, diesel fuel, motor oil)) to create representative spectra for each liquid-substrate combination.

3.7 Airborne remote sensing data analysis

3.7.1 Airborne Data Acquisition

The ultimate value of a hydrocarbon-substrate spectral library is its utility for data captured from airborne and spaceborne sensors. In September 2005—during the
Hurricane Katrina disaster—the Boeing Company commissioned SpecTIR, Inc. (SpecTIR, 2008) to collect airborne VNIR/SWIR hyperspectral data of a variety of locations in and around New Orleans, LA. Boeing provided these data sets to the Earth Systems and Geoinformation Sciences (ESGS) department at George Mason University. A number of these flightlines were used as an initial test of the ability of the library to segregate petroleum from floodwaters. Unfortunately, there is no ground truth information available for the data set and numerous searches have failed to produce credible information about the location of spills outside that at the Murphy Oil refinery (EPA, 2008c). For this reason, analysis will be largely limited to a data set that includes the Murphy Oil refinery.

The SpecTIR data set consists of hundreds of flightlines gathered using the HyperSpecTIR-3 (HST-3) instrument. The vendor acquired data from 6-10 September 2005. According to the “Data Information: Final Data Set Release” document that accompanies the data set, all data were acquired with a “high” sun angle, near solar noon and under “[p]artially” to “[m]oderately [c]loudy” conditions. Aerosol load was dominated by “[h]igh water vapor” with “[v]ery high” surface moisture content, as evidenced by a note that the MODerate resolution atmospheric TRANmission model (MODTRAN) derived atmospheric compensation “was not able to entirely polish out the 960 [sic] and 1116 [sic] nm liquid water absorption features” (SpecTIR, 2005). SpecTIR provided all data in radiance (mW/cm²·sr·nm) and some data sets in reflectance using a MODTRAN-based model.
3.7.2 Image Processing Methodology

The image processing methodology for the SpecTIR radiance cubes consists of four steps:

1) Image pre-processing (metadata collection, artifact mitigation)
2) Atmospheric compensation (FLAASH and QUAC)
3) “Bad bands” removal to eliminate bands attenuated by noise and atmospheric absorption
4) Material Identification (MTMF and SAM algorithms)

The first step in the image processing methodology includes both metadata collection and artifact detection/mitigation. Fortunately, the SpecTIR data set includes most of the information required for inputs to the rest of the analytical process, including image dates and times, airframe flying height, GSD, Global Positioning System (GPS) positions for scene centers, and scene geo-referencing/projection information in an ENvironment for Visualizing Images (ENVI®)-compatible geographic look-up table (*.glt) file (SpecTIR, 2005). The document does not contain the instrument’s FOV, but it can be derived based on the available metadata and Equation 3-2:

\[
\text{FOV (mrad)} = \frac{\text{GSD (m)}}{\text{Flying Height (km)}} \quad (3-2)
\]

Since most of the passes are at an altitude of 2 km above ground level (AGL) and the stated GSD in the metadata is 2 m, the HST-3 instrument FOV is 1 mrad.

While most of the basic metadata are included with the data set, there is no information or discussion of any image artifacts such as spectral smile.

A fundamental component of hyperspectral data analysis is atmospheric compensation of the data set. Atmospheric compensation transforms at-sensor radiance
data, usually expressed as $W/m^2\cdot sr\cdot \mu m$, into unitless reflectance values by removing the solar continuum and minimizing the attenuating effect of atmospheric scattering and absorption features. As Equation 3-3 demonstrates, reflectance ($\rho$) is the quantity of energy reflected ($\Phi_{\text{reflected}}$) by a target divided by the quantity of energy incident upon the target ($\Phi_{\text{incident}}$). Reflectance values are wavelength dependent, hence the lambda ($\lambda$) subscript in equation 3-3 (Wolfe, 1978):

$$\rho_{\lambda} = \frac{\Phi_{\text{reflected}}}{\Phi_{\text{incident}}} \quad (3-3)$$

Transforming radiance data into reflectance permits the comparison of hyperspectral image pixels to signatures in a spectral library.

Ideally, airborne campaigns are conducted under controlled conditions where calibration panels can be deployed for use with the empirical line method (ELM), which is conventionally the most accurate method of atmospheric compensation (Conel, 1990). The calibration panels are also a risk mitigation strategy because when utilized for ELM, they provide useful reflectance values for targets, even in the presence of sensor artifacts, calibration errors, and/or under partially cloudy acquisition conditions. Since the SpecTIR campaign was not conducted under controlled conditions, field-expedient calibration panels were not available and other methods must be employed.

In real world conditions such as the Hurricane Katrina disaster, it may not be possible or practical to deploy calibration targets for hyperspectral data collections. This also applies to other situations such as an oil spill response scenario where the location (e.g., remote expanses along the Trans-Alaskan pipeline) or the circumstances (e.g., southern Lebanon in the summer of 2006) may prevent the use of in situ calibration
sources. In these situations, techniques such as the Fast Line-of-sight Atmospheric Analysis of Spectral Hypercubes (FLAASH) (Felde et al., 2004) and QUick Atmospheric Correction (QUAC) (Bernstein et al., 2006) can provide atmospheric compensation. An alternative method–using in-scene materials for ELM calibration targets–has shown promise with VNIR and VNIR/SWIR multispectral sensors but was not attempted here (Moran et al., 2001; Karpouzli and Malthus, 2003; Baugh and Groeneveld, 2008).

FLAASH uses the MODTRAN radiative transfer code and atmospheric models to provide an alternative to ELM for radiance to reflectance transformation. While less accurate than ELM, it has an advantage of not requiring in situ targets of known reflectance values (Felde et al., 2004).

QUAC is a purely empirical method that exclusively uses in-scene information to perform a more approximate and faster atmospheric compensation than physics-based codes such as FLAASH. QUAC is similar to ELM in that it assumes that there is a linear relationship between radiance and reflectance, an assumption for which there is a growing body of evidence (Moran et al., 2001; Karpouzli and Malthus, 2003; Baugh and Groeneveld, 2008). It derives a gain and an offset from the data and then applies them to the radiance cube to convert from radiance to reflectance. QUAC requires neither radiometrically calibrated data nor the image metadata required by FLAASH. It does make three fundamental assumptions about the data set: 1) that there are ~10 or more “diverse materials” (Bernstein et al., 2005) in the scene that include a broad range of spectral brightness values (i.e., bright, dark, and intermediate endmembers), 2) that first and second order endmember statistics are largely independent of scene composition and
the endmember selection process and 3) that “sufficiently dark” (Bernstein et al., 2005) (i.e., reflectance ≈ 0) pixels are present in the scene to derive an offset for the whole scene (Bernstein et al., 2005; Bernstein et al., 2006). The algorithm uses the Sequential Maximum Angle Convex Cone (SMACC) algorithm to pick scene endmembers. It derives the gain by dividing the mean of the scene endmembers by the mean of representative endmembers from a spectral library that is included with the algorithm (Bernstein et al., 2006).

It bears mentioning that the second assumption above requires validation across a wide variety of environmental and land cover conditions. Bernstein et al. (2005) successfully tested it in predominantly rural and urban data sets. They found that limited land cover types in the rural data set mitigated its effectiveness there, although the results were still satisfactory. They also note that images that exclusively contain water are also problematic. Also, the algorithm has the potential to work when solar irradiation is unknown, such as occurs in high cloud cover conditions.

After performing atmospheric compensation, bands that are noisy and that are still significantly affected by atmospheric absorptions were manually removed from the data set. All of the bands in the following regions were masked at this stage before progressing to the material identification stage: <450, 900-1000, 1100-1200, 1300-1500, 1800-2060, and >2350 nm. Since each of the HST-3 data sets have different wavelengths, the actual bands vary slightly from scene to scene.

Once the data sets were converted from radiance to reflectance and bad/noisy bands were removed, standard hyperspectral material identification techniques were
employed to analyze data with the goal of discriminating oil from water in flooded areas of New Orleans in the days after Hurricane Katrina. These techniques include the Spectral Angle Mapper (SAM) and ratioing the matched filter (MF) score to the infeasibility score (IS) provided in the Mixture Tuned Matched Filter (MTMF) algorithm (ITT Visual Information Solutions, 2006).
4 DISCUSSION

4.1 Lab Measurements

4.1.1 Liquids

Figure 4-1 plots the spectra of thin films (0.9-1.6 mm) of each liquid from Table 3-1 in glass petri dishes on a Spectralon™ background. The liquid hydrocarbons have sharp, asymmetric absorption doublets (crudes (spectra #2-5), diesel fuel (#8), and motor oil (#9)), a triplet (gasoline (#7)), and a quadruplet (acetone (#10)) between 1675-1780 nm, broad overlapping absorptions from 2275-2400 nm, and a variety of other sharp absorptions throughout the NIR/SWIR. Water (spectrum #1) presents the broad absorptions at 975 and 1200 nm in the NIR, the latter portion of the strong absorption feature at 1450 and near opacity at wavelengths >1950 nm in a thin film that is 1.6 mm thick.

Liquids with shorter carbon chains (e.g., gasoline) have absorption maxima at shorter wavelengths than similar liquids with longer chains (e.g., diesel fuel, motor oil), a phenomenon also observed by Clark et al. (2009). This is apparent in Figure 4-1 in both the first and second overtone regions from 1700-1786 nm and 1150-1210 nm. In the first overtone region, gasoline’s absorption maximum is at 1701 nm whereas it is at 1726 nm for both diesel fuel and motor oil. In the second overtone region, the gasoline absorption maximum is at 1193 nm and at 1210 nm for diesel fuel and motor oil. The identical
locations of the absorption maxima for diesel fuel and motor oil—despite widely
differing nominal carbon chain ranges—is due to a significant drop in absorption maxima
diversity when alkanes, which constitute a significant plurality in these liquids, have ≥6
carbon atoms (Potter and Simmons, 1998; Clark, et al., 2009).

![Reflectance/Transmission spectra of ten thin, liquid films on Spectralon™ background. Water spectrum (#1) from Satterwhite and Allen (2006).](image)

**Figure 4-1:** Reflectance/Transmission spectra of ten thin, liquid films on Spectralon™ background. Water spectrum (#1) from Satterwhite and Allen (2006).

The crude oils are all nearly opaque at wavelengths <1000 nm (Figure 4-1).

Beyond 1000 nm, the light crude (spectrum #2) and the intermediate, sweet crude
(spectrum #4) become somewhat transparent, increasing in reflectance to peaks at ~1600 and ~2100 nm. The intermediate, sour crude (spectrum #3) and the heavy crude (spectrum #5) maintain near-opacity until after the first major water vapor absorption region, 1300-1500 nm. After that point their reflectance increases enough to reveal the hydrocarbon absorption features in the SWIR, peaking at approximately 2100 nm. The opacity of each crude in the visible spectrum is evident by the photographs in Figure 4-2.

In contrast to the crudes, both the refined products and water are highly transmissive in the visible spectrum (Figure 4-3), the NIR and some of the refined products remain so into the SWIR. All of the refined products and water remain >80% transmissive from 500-900 nm. The refined products remain >90% transmissive up to 1100 nm. Acetone, gasoline, diesel fuel, and motor oil remain >80% transmissive in the SWIR from 1500-1600 nm whereas the E85 and water are significantly more opaque (<45% transmissive) after the first major water vapor absorption region. The ~70% transmissivity in motor oil from 1950-2100 nm is likely due to the thinner film (0.9 mm) than those in all of the other liquids (1.3-1.6 mm). It would likely be more akin to the 50-65% values in acetone, gasoline, and diesel fuel if a thicker film were available.
Figure 4-2: Photographs of crude oil products. From L to R: light crude (100_5056.jpg), intermediate sweet crude (101-6856.jpg), intermediate sour crude (101-6538.jpg), and heavy crude (101-6202.jpg). The bright spot in the lower right hand corner of the heavy crude picture is specular reflection of the camera flash.

Figure 4-3: Photographs of refined products and water. From L to R (top row): acetone (100-3405.jpg), gasoline (100-4176.jpg), and E85 (100-5470.jpg), (bottom row): diesel fuel (100-4683.jpg), motor oil (100-3908.jpg), and water (101-5849.jpg).
While they never reach the transmission levels of the refined products or water, the crude oils all reach their maximum transmission levels in SWIR. The light and intermediate, sweet crudes are 30-40% transmissive between 1510-1650 and 1950-2100 nm. The intermediate, sour crude is >20% transmissive from 2060-2120 nm and the heavy crude is >10% transmissive at 2030-2140 nm.

All of the liquid samples in Figure 4-1 are 0.9-1.6 mm in depth. An additional set of measurements demonstrates how transmission and absorption change with the quantity applied to a substrate. Figure 4-4 plots quantities of the intermediate, sweet crude on a Spectralon™ background normalized to 100% reflectance. As increasing quantities of the crude oil are applied to the substrate, the liquid’s thickness increases from an initial value of 0.8 mm (spectrum #1) to 5.1 mm (spectrum #7). Declining reflectance is plotted against crude oil depth in Figure 4-5. Extrapolating from these data, the reflectance maxima at 1610 nm and 2080 nm will be effectively zero for liquid layers that are ~8.3 and ~7.4 mm thick, respectively. This indicates that <1 cm of oil absorbs 100% of radiation at reflective wavelengths and has both 0% transmission and reflection at this acquisition geometry.
Figure 4-4: Reflectance/Transmission spectra of intermediate, sweet crude on Spectralon™ background at varying depths.
Figure 4-5: Increasing intermediate, sweet crude depth causes decreases in reflectance at 1610 and 2080 nm reflectance maxima. Dashed lines plot exponential fits to the data.

The discontinuity at 975 nm in Figure 4-4, spectrum #1 (0.8 mm) is the junction between the first and second spectrometer in the ASD instrument. Discontinuities of this nature are common for two reasons. First, the fiber optics for each of the ASD’s three spectrometers are not uniformly spread out in the optical head and, as a result, each spectrometer looks at a slightly different portion of the target. Second, targets with high degrees of spatial heterogeneity present different sub-target characteristics, depending on their location within the sample. For example, the grass/leaf litter/soil substrate frequently has a high degree of spatial heterogeneity as can be seen in Figure 4-6. As the different fiber optics view different portions of the target, they will see differing quantities of healthy, green leaf blades, leaf litter, and the underlying soil. Varying
combinations of these three substrate constituents often lead to inter-spectrometer discontinuities.

Figure 4-6: Photograph of grass/leaf litter/soil substrate demonstrate high spatial heterogeneity (100-4651.jpg).

4.1.2 Substrates

Figure 4-7 plots the spectra of the ten substrates from Table 3-2 without any liquids. They include impervious surfaces (e.g., concrete, asphalt) but are dominated by permeable substrates (e.g., bentonite, calcareous sand, calcite-dolomite crushed aggregate, gypsum, a highly organic soil, Ottawa sand, quartzic beach sand, and vegetation). By design, they cover a broad range of reflectance values, ranging from uniformly dark asphalt to spectrally bright gypsum, calcareous, and Ottawa sands. Many
of the substrates have their own absorption features, especially in the SWIR, and which are discussed in turn below.

![Reflectance spectra of ten substrates](image)

**Figure 4-7**: Reflectance spectra of ten substrates, including permeable and impervious surfaces. No liquids applied.

4.1.2.1 Asphalt

The asphalt spectrum (Figure 4-7, #10) is a flat, dark (i.e., \( \rho < 0.17 \)) relatively featureless spectrum. There is a very small (1%) absorption feature from 2200-2400 nm indicative of dust which accumulated on the unswept surface in situ and which tended to
gather in pits on the surface, the gradual expression of the aggregate due to bitumen weathering, combined with bitumen absorption. The spectrum is very similar to the asphalt spectra from Herold and Roberts (2004). The flat, almost featureless spectrum, combined with the large size of parking lots demonstrates why asphalt is often an ideal dark endmember for in-scene calibration efforts.

4.1.2.2 Bentonite

Bentonite (Figure 4-7, spectrum #4) is comprised mostly of montmorillonite, which typically has high reflectance ($\rho > 0.5$) in the NIR and most of the SWIR after rising sharply from a low point at 400 nm through the visible spectrum. The bentonite samples also possess the strong (8-10%) hydroxyl absorption feature at 2205 nm typical of clays and the rapid decline in reflectance after 2270 nm. This spectrum is consistent with the montmorillonite samples in the USGS spectral library (Clark et al., 1993).

4.1.2.3 Calcareous Sand

As mentioned above, the calcareous sand samples included both calcite and aragonite. The spectrum (Figure 4-7, spectrum #1) possesses the typical carbonate anion absorption centered at 2334 nm. Whereas the exemplar mineral spectra from the USGS library have fairly flat, bright ($\rho > 0.80$) reflectance from approximately 800-2080 nm—interrupted only by atmospheric water features—the samples’ mean reflectance drops consistently as wavelength increases in the SWIR, from ~0.80 at 1300 nm to ~0.70 at 1620 nm to ~0.52 at 2170 nm. The convex shape of the spectrum from 1500-1800 nm and the interrupted convex shape from 1950-2170 nm, before descending into the
carbonate absorption, are indicative of the small quantity of water in the sample. The sample spectrum also does not have the subtle ~3% feature at 2165 nm present in the USGS library spectra (Clark et al., 1993), and which is also evident in Hunt (1977). Strong absorption by water and the organic content in the sample may be masking the feature in the spectrum.

4.1.2.4 Calcite-Dolomite Crushed Aggregate

Much like the asphalt, the calcite-dolomite crushed aggregate produced a flat, relatively featureless spectrum (Figure 4-7, spectrum #8) across the VNIR/SWIR, albeit a brighter one ($\rho=0.20-0.25$). The exception is the modest (3%) carbonate absorption feature centered at 2334 nm, indicative of the calcitic-dolomitic mineralogy of the gravel (Hunt, 1977; Clark et al., 1993). When compared to the gravel road measured by Herold and Roberts (2004), their reflectance amplitudes are commensurate but their absorption features are quite dissimilar. This is expected given some of the mineralogical differences between the samples (e.g., iron oxides versus calcite) and is a good example of the spectral diversity of various gravels used for residential, commercial, and industrial purposes.

4.1.2.5 Concrete

Concrete is the other impervious surface in the substrate set. As mentioned above, concrete spectra are highly variable due to their mineralogical composition, weathering, and their other ingredients which vary widely based on their purpose. For example, in the Johns Hopkins Library that is included with the ENVI® image processing
software package, there are five concrete samples. Two have carbonate features around 2335 nm, three do not. The concrete spectrum here (Figure 4-7, spectrum #6) gradually increases in brightness from the visible to the SWIR, peaking at 2140 nm before a minor (2.5%) absorption feature around 2210 nm and subsequently gradually darkening. The shape of the spectrum follows the shape and amplitude of the two “old” concrete sidewalk spectra in Herold and Roberts (2004). It is important to note that the concrete samples here were not weathered, which explains their higher average reflectance (5-10%) since concrete tends to darken with age (Herold and Roberts, 2004).

4.1.2.6 Gypsum

Like the calcareous sand, the gypsum spectrum (Figure 4-7, spectrum #2) is very bright (ρ>0.7) in the VNIR. The six delimited absorption maxima at 995, 1204, 1536, 1749, 2216, and 2266 nm are caused by molecular water (Hunt, 1977). The spectrum matches both those in Hunt (1977) and in the USGS library (Clark et al., 1993).

4.1.2.7 Highly Organic Soil

The spectrum for the highly organic soil (Figure 4-7, spectrum #7) has numerous absorption features arising from different sources. Ferric (Fe³⁺) and ferrous (Fe²⁺) iron absorptions interrupt steadily increasing reflectance from 400-800 nm with a shoulder at ~500 nm and a broad, but shallow (<1%) absorption from 600-800 nm. Both ferric and ferrous iron also induce the broad, shallow absorption centered at 950 nm (Hunt et al., 1971a; Hunt et al., 1972). The convex shape of the spectrum from 1500-1800 nm and the interrupted convex shape from 1950-2150 nm, before descending into the hydroxyl absorption, are indicative of the water in the sample. Water and/or hydroxyls in clay
particles in the sample, combined with organic matter, cause the minor absorptions at 2208 (2.5%) and >2300 nm (2%), respectively.

As mentioned in section 3. Methodology above, the moisture content of the highly organic soil is 18.6%, averaged across three samples. The samples were then left to air dry for at least 12 hours, even though a large portion of the sample water evaporated from the samples during that time period. The spectral effect of the evaporated water from the highly organic soil shown in Figure 4-8, where the red trace with lower reflectance is the soil spectrum freshly poured from the sealed container into the petri dishes before air drying (18.6% water). The black trace with high reflectance shows the absorptive impact of water, especially at wavelengths >1500 nm. In this case, the sample was left to air dry for 21 hours during which 7.1 g evaporated, leaving the sample with 8.9% water. Whereas reflectance is minimally impacted (<4%) due to water’s high transmissivity in the visible spectrum, the loss of water in the NIR/SWIR where water is highly absorptive increases reflectance by 4.7-5.6% in the NIR and 5.3-7.9% in the SWIR. Water’s opacity in the SWIR masks the soil’s subtle (<1%) hydroxyl absorption at 2205 nm. The substrate’s iron oxide features in the VNIR are present in both spectra, preserved by the small quantity of water’s relatively high transparency at these wavelengths.

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Figure 4-8: Reflectance spectra of highly organic soil freshly deposited in petri dish (red trace with lower reflectance) and after 24 hours of air drying in climate controlled lab conditions (black trace with higher reflectance) (Temperature: 20-23° C and relative humidity (RH): ~60%).

4.1.2.8 Ottawa Sand

Ottawa sand is commonly used as an industry standard because of its lack of impurities and uniform particle size (Raveia et al., 2008). As a result, it has a spectrum (Figure 4-7, spectrum #3) that strongly resembles the unremarkable quartz spectrum in the VNIR/SWIR in both Hunt (1977) and the Ottawa sand spectrum in the USGS library (Clark et al., 1993). It has minor iron oxide absorption features (<2%) in the VNIR and a subtle (2.7%) hydroxyl feature at 2207 nm, probably caused by clinging fines commonly attached to the quartz grains (Aronson and Emslie, 1973).
4.1.2.9 Quartzic Beach Sand

Like the highly organic soil, the quartzic beach sand (Figure 4-7, spectrum #5) possesses a number of both ferrous and ferric iron oxide absorption features that create broad (>100 nm) absorptions in the VNIR (Hunt et al., 1971a; Hunt et al., 1972). The absorptions in the visible portion of the spectrum impart a brown color to the substrate. The hydroxyl feature with absorption maximum at 2208 nm is also similar in intensity (2.5%) to that in the highly organic soil.

As for all previous sample preparations, the quartzic beach sand samples were left to air dry for at least 12 hours, even though a large portion of the interstitial water evaporated from the samples during that time period. The spectral effect of the evaporated water is shown in Figure 4-9, where the red, darker trace is the sand spectrum freshly poured from the sealed container into the petri dishes before air drying (4.9% water). The black, brighter trace shows the absorptive impact of water, especially at wavelengths >1500 nm. In this case, the sample was left to air dry for 19 hours, during which 2.9 g evaporated, leaving the sample with 1.3% water. Whereas reflectance is minimally impacted in the VNIR (≤5%), the loss of absorptive water in the SWIR increases reflectance by 9-16%. Water’s opacity in the SWIR masks the sand’s subtle (<1%) hydroxyl absorption at 2208 nm. The substrate’s iron oxide features in the VNIR are present in both spectra, preserved by the small quantity of water’s relatively high transparency at these wavelengths.
Figure 4-9: Reflectance spectra of quartzic beach sand freshly deposited in petri dish (red trace with lower reflectance) and after 19 hours of air drying in climate controlled lab conditions (Temperature: 20-23° C and RH: ~60%) (black trace with higher reflectance).

4.1.2.10 Vegetation

The vegetation spectrum (Figure 4-7, spectrum #9) is a combination of turgid grass blades, leaf litter, and underlying soil. Figure 3-24 demonstrates the heterogeneous mix presented to both the camera and the spectroradiometer. While the grass blades are the tallest component, they are the least likely to present a surface orthogonal to the spectroradiometer’s field of view. The soil, and to a lesser extent the leaf litter, do present larger surface areas where the grass blades are not present. The result is a mixed spectrum that retains the shape of healthy green vegetation beginning the senescence process, hence the roughly equal absorption in the visible green (500-600 nm) and visible
red (600-700 nm), but whose overall reflectance is suppressed by the less-than-orthogonal blade orientation combined with the spectrally darker underlying soil.

Space limitations in the chemical hood forced the lab measurements to span multiple seasons. As a result, seasonality patterns are also evident in the vegetation spectra gathered over the course of these experiments, plotted in Figure 4-10. The spectra are the average of all sample substrates (n=3 for crudes, n=5 for refined products) before the application of any liquids. Samples gathered in June (spectrum #1) and August (spectrum #2) have typical healthy green vegetation spectra: strong absorption in visible blue (400-500 nm) and red (600-700 nm) regions due to photosynthesis, pronounced liquid water absorptions near 940 and 1135 nm, and convex shapes in the SWIR region (1500-1800 nm and 1950-2400 nm) with successively lower reflectances than the NIR region. Samples in late January (spectrum #6) and late February (spectrum #7) largely retain the spectral shape of vegetation but have more senescent material and hence, are missing the visible red absorption (when compared to visible green), have weaker liquid water absorptions, and have developed lignin absorptions between 2000-2100 nm that are usually masked by liquid water in turgid samples. The remaining samples, gathered in late November to late December (spectra #3-5), are mix of these two extremes. All three spectra have liquid water absorptions at 1135 nm that are nearly as pronounced as those in the turgid samples but more like the senescent samples at 940 nm. Spectra #3 and #5 do not have the visible red absorption but spectrum #4 does retain the absorption. This variation is likely a function of the samples themselves, where the
samples in spectrum #4 have more turgid material in them than those in spectra #3 and #5. Additionally, spectrum #3 is beginning to develop a lignin absorption.

Figure 4-10: Reflectance spectra of vegetation substrates spanning June to February. Note that June and August spectra are typical of healthy green vegetation whereas other spectra have less pronounced photosynthetic absorptions in visible red and in NIR liquid water bands. The January and February spectra also have pronounced lignin absorptions in the SWIR.

4.1.3 **Refined Petroleum Products on Selected Substrates**

A selected set of liquid-substrate spectra are presented in sections 4.1.3-4.1.6. Each liquid and each substrate in the test data set are included at least once in order to
provide a sample of their spectra. The spectra for all remaining liquid-substrate combinations are included in the Appendix.

4.1.3.1 E85 Fuel

A commercial E85 fuel (nominally 85% ethanol, 15% gasoline) was procured from a local gas station. It was highly transmissive in visible wavelengths, as indicated in Figure 4-1, spectrum #6. The 1.4 mm film of ethanol presents a major (>25%) asymmetric triplet at 1697, 1732, and 1762 nm, presumably caused by CH₂ and CH₃ stretches and bends in the first overtone region of the fundamental C-H stretches between 3300-3500 nm (Gaffey et al., 1993). The triplet’s asymmetric shape is consistent with multiple, overlapping C-H absorption bands. Various combinations of C-H absorption bands overlap to create a hydrocarbon plateau in the 2270-2400 nm region, where the slope of the reflectance spectrum is close to zero. Periodic absorption features can interrupt this otherwise smooth reflectance region, as is shown at 2308 and 2349 nm in spectrum #9, motor oil. The E85 also produces possible hydroxyl-induced absorption features at 2076 nm (~10%), 1017 nm (<1%), and 2173 nm (<1%) (Hunt et al., 1971a; Hunt et al., 1971b). Additionally, there is an unidentified minor feature at 1583 nm (2%). This thin film also produces more subtle absorptions in the second overtone region, manifest in an absorption feature at 1187 nm with shoulders at 1152 and 1207 nm. A minor feature (2-3%) at 908 nm is also present in the third overtone region (Gaffey et al., 1993).

Figure 4-11 plots E85 fuel applied to ten substrates (spectra #1-10) and free standing in two different depths in glass petri dishes on a Spectralon™ background.
spectra A and B). Spectrum A (4.2 mm) is sufficiently deep to be opaque (0-1%) from 2050-2400 nm and in the hydrocarbon absorption region from 1700-1740 nm. From 1740-1800 nm, its reflectance rises from 1.4% at the local minima of 1762 nm to 6.5% at 1800 nm. The second overtone at 1152, 1187, and 1207 nm is >50% absorptive at this layer thickness. The hydroxyl absorption at 1017 nm is present but the absorptions at 2076 and 2173 nm are masked by the liquid’s opacity at this depth. The third C-H overtone at 908 nm produces a 9% absorption in this sample. As indicated by the similar reflectance values in both spectra A and B, E85 is highly transmissive (>95%) in most of the visible spectrum, from 410-700 nm. It remains highly transmissive in the NIR until it begins to roll into the third C-H overtone feature.

Like spectrum A, spectrum B is also E85 fuel on a Spectralon™ background, though in sufficient quantity to only produce a 0.5 mm standing pool. The smaller quantity is sufficiently transmissive to detect all of the absorption features in the SWIR including the symmetric absorption triplet at 1697, 1732, and 1762 nm and the punctuated absorption features from 2270-2400 nm at 2273, 2307, and 2352 nm. The second C-H overtone is still detectable, although it is much weaker in the 0.5 mm sample (7%) than in the 4.2 mm sample discussed above. Additionally, the absorption at 1583 nm and the hydroxyl feature at 2076 nm are present (9%), although the hydroxyl features at 2173 and 1017 nm are not. The smaller quantity is also insufficient to present the third C-H overtone region.
Figure 4-11: (top) Reflectance spectra of E85 fuel in petri dishes and on ten substrates. (bottom) Wavelengths of maximum absorption for spectra.

Figure 4-12 plots the drying sequence of E85 applied to Ottawa sand. Spectrum E1 is the mean of all samples before E85 application. The only absorption feature is a minor (<2%) hydroxyl feature at 2207 nm, probably caused by small quantities of...
clinging fines on the sand particles. Spectra E2-E21 plot the drying sequence of 99.94% of the E85 on the sand samples from saturation at initial application (0.221 g/cm²) through 16 days (0.0001 g/cm²). Initially, E85 volatilized from the liquid layer on the Ottawa sand surface and exposed interstitial spaces between grains. Losses then occurred from E85-filled spaces deeper within the sample, which required liquid movement to the surface by capillarity or vapor movement through the sample pore space. To characterize the sample’s changing spectra relative to the evaporative E85 loss, frequent measurements were made during the first twelve hours after sample saturation and periodically thereafter. As the E85 evaporated, the spectra gradually reverted to their original state.
As mentioned above, each sample was weighed before its spectra were collected. Liquid loss, measured by mass, was plotted as a function of time. Multiple fits were used to test which best expressed loss over time (Figure 4-13). Fingas (1997, 1999) found that...
evaporation of petroleum products with 3-7 major components, such as diesel fuel, is best expressed by square root equations as a function of time. In this case, where E85 is evaporating from a sand substrate, a linear fit (dash-dots in Figure 4-13) over the first four hours (88% evaporated) provides the best $R^2$ value (0.99) whereas an exponential fit (dashed) provides the highest $R^2$ value (0.93) over the first 12 hours (99.8% evaporated). A linear fit to the neat sample over the first four hours also produced a strong $R^2$ value (0.98) but after 14 hours, is slightly better represented by an exponential ($R^2=0.87$) fit than a linear one ($R^2=0.83$) (not shown).

![Figure 4-13: Evaporation of E85 on Ottawa sand substrate over time. The process is best described by a linear function (dash-dots) ($R^2=0.99$) over the first 4 hours, when 88% of the liquid evaporated. Over the first 12 hours and 99.8% evaporation, the process is better described ($R^2=0.93$) by an exponential function (dashed).](image-url)
The initial E85 application produced all of the hydrocarbon absorptions seen in the liquid-Spectralon™ spectrum, although the minor feature at 2173 nm only becomes apparent (>0.5%) after 3 hours. The major absorptions from 2270-2400 nm persist the longest and are still detectable, if subtle (spectrum E21, <1%), 16.4 days after E85 application when 0.0001 g/cm² are present in the sample. This persistence and the sensitivity in this portion of the spectrum confirm previous findings for other petroleum products (Allen and Satterwhite, 2006). The major absorption from 1650-1800 nm persists for the first five hours, with only 4.5% of the E85 remaining on the sample (spectrum E13, 0.010 g/cm²). Between spectra E13 and E14 (355 minutes, 0.002 g/cm²), the absorption triplet from 1650-1800 degrades from 2.5% to 1%, making it difficult to detect in the latter spectrum. As a result, the minimum identifiable quantity for the E85 on Ottawa sand is 0.010 g/cm². The absorption at 2307 nm persists (>3%) until 414 minutes (spectrum E15, 0.0009 g/cm²) but is <2.5% by the measurement at 698 minutes (spectrum E16). As a result, the former is the minimum detectable quantity, as defined above. The minor features at 908 and 1014 nm are initially present but subtle (1% and <1%) and indistinguishable after 177 minutes (spectrum E10, 0.066 g/cm²). The major absorptions at 1187, 1583, and 2083 nm persist longer, lasting until 235 minutes (spectrum E12, 0.027 g/cm²) but are effectively missing from the E13 spectrum. The sand’s hydroxyl absorption feature is masked by ethanol’s opacity in the SWIR until 235 minutes (spectrum E12).
4.1.3.2 Gasoline

A commercial gasoline with 10% ethanol was procured from a local gas station during summer months. It was highly transmissive in visible wavelengths, as indicated in Figure 4-1, spectrum #7. The 1.4 mm film of gasoline shows the major (>75%) asymmetric triplet at 1702, 1720, and 1760 nm caused by CH$_2$ and CH$_3$ stretches and bends in the first overtone region (Gaffey et al., 1993). This feature also produces a minor shoulder at 1642 nm. The triplet’s asymmetric shape is consistent with multiple, overlapping C-H absorption bands. Various combinations of C-H absorption bands overlap to create a hydrocarbon plateau in the 2270-2400 nm region, where the slope of the reflectance spectrum is close to zero. The gasoline also produces absorption features commonly associated with hydroxyls at 1018 nm (3%), 2017 (5%), and a large one (40%) at 2171 nm (Hunt et al., 1971a; Hunt et al., 1971b). It is unclear whether or not oxygenates in the gasoline, such as ethanol, are the source for these absorptions. This thin film also produces more subtle absorptions in the second overtone region, manifest in a major (30%) absorption doublet at 1154 and 1192 nm and a minor feature (5%) at 913 nm in the third overtone region (Gaffey et al., 1993). The gasoline features are consistent with those previously found by Allen and Satterwhite (2006).

Figure 4-14 plots the drying sequence of gasoline applied to a gypsum substrate. Spectrum G1 is the mean of all samples before gasoline application. Spectra G2-G23 plot the drying sequence of gasoline on the samples from saturation at initial application (0.154 g/cm$^2$) through 87 days (0.0075 g/cm$^2$). Gasoline evaporates when exposed to most prevailing atmospheric conditions. Initially, it volatilized from the liquid layer on the gypsum surface and exposed interstitial spaces between grains. Losses then occurred
from gasoline-filled spaces deeper within the sample, which required liquid movement to the surface by capillarity or vapor movement through the sample pore space. To characterize the sample’s changing spectra relative to the evaporative gasoline loss, frequent measurements were made during the first nine hours after sample saturation and periodically thereafter. The spectra and fuel weight are determined for time intervals starting with the gasoline saturated sand (spectrum G2). As the gasoline evaporated, the spectra gradually reverted to their original state. Over the observation period of 87 days, 95.1% of the gasoline volatilized from the saturated sample. An exponential function fit to the gasoline losses over the first 9 hours, when 82.1% of the liquid evaporated, demonstrates a strong correlation ($R^2=0.95$) (Figure 4-15). A power fit provides the best fit to the data over the entire 87.1 day observation period ($R^2=0.88$), when 95.1% of the gasoline evaporated (Figure 4-16).
The initial gasoline application produced the hydrocarbon absorptions at 913 (<2%), 1192 (20%), and from 2270-2400 nm (Figure 4-14). Gasoline absorption from 1700-1800 nm is also present, indicated by the absorption at 1707 nm in spectra G2-G9, from initial application to 151 minutes after application. This absorption maximum is
shifted to slightly longer wavelengths than in the liquid-Spectralon™ (Figure 4-1). The other parts of the gasoline absorption triplet from 1700-1800 nm are masked by gypsum’s water absorption features at 1747 and 1764 nm. The gasoline is sufficiently transparent in the VNIR and shorter portion of the SWIR that gypsum’s 995, 1204, and 1536 nm water absorptions are all also present from the initial gasoline application onward (Hunt, 1977). Gypsum’s absorption at 2216 nm is masked in early spectra by gasoline’s increasing opacity at longer wavelengths. In this case, the feature re-emerges after just 34 minutes, as evident in spectrum G4 (0.121 g/cm²). The gypsum absorption at 2266 nm is initially masked by the hydrocarbon plateau but it too re-emerges after 34 minutes in spectrum G4. The gasoline features present in the liquid-Spectralon™ sample at 1018, 1642, 2017, and 2171 nm are not apparent in any spectra.
Figure 4-15: Evaporation of gasoline on gypsum substrate over time. The process is best described by an exponential function (dashed) over the first 9 hours, when 82.1% of the liquid evaporated.

Figure 4-16: Evaporation of gasoline on gypsum substrate over time (log scale). The process is best described by a power function (dashed) over the entire observation period (87.1 days), when 95.1% of the liquid evaporated.
Despite the persistence of a small portion of the gasoline sample, most of the gasoline’s spectral features disappeared in the first few hours and all of them disappeared by the end of the first day. As expected, the more subtle gasoline-induced absorption features disappear from the gypsum-gasoline spectra before the intense features. For example, the 913 nm feature’s absorption is <1% 34 minutes after application (spectrum G4, 0.121 g/cm²) whereas the shoulder at 1707 nm persists for 151 minutes (spectrum G9, 0.070 g/cm²). As Allen and Satterwhite (2006) discuss, hydrocarbon absorption in the VNIR/SWIR region is most sensitive and most persistent from 2300-2400 nm. It is therefore not surprising that the 2310 nm absorption is the last gasoline-induced feature to disappear from the spectra, sometime between 538 minutes (spectrum G16, 0.028 g/cm²) and the next sample at 836 minutes (spectrum G17, 0.021 g/cm²). Despite the persistence of the 2310 nm absorption, it is small, <1%, and after the shoulder at 1707 nm fades, the remaining absorptions are <0.5%. As a result, the minimum detectable quantity for gasoline on the gypsum substrate is 0.070 g/cm² (spectrum G9).

Judging by this analysis and by comparison to other substrates, gypsum is a more difficult substrate for gasoline detection than other, spectrally “bright” sands such as Ottawa, the quartzic beach, and calcareous sands used in this study. On each of those substrates, gasoline was detectable for ten hours or longer with similar application quantities. In addition, similar quantities applied to another quartzic sand in a similar meteorological environment persisted for more than seven hours and with a smaller remaining quantity (<10%) than the gasoline-spectra samples here (45.4%) (Allen and Satterwhite, 2006).
Detection of the gasoline on gypsum is complicated both by gasoline’s partial transmissivity and the gypsum absorption features. For example, gasoline transmission permits the gypsum absorption features at 995, 1536, and 2216 nm to be detectable, if subtle, from the initial gasoline application onward. The gypsum shoulder at 1225 nm is highly attenuated by the initial gasoline application, though, and only gradually re-appears as the liquid evaporates. The gypsum absorption at 2266 nm, while present, could easily be mistaken for the beginning of the hydrocarbon plateau from 2270-2400 nm. Additionally, the gasoline liquid absorption maxima from 1700-1800 nm are 1702, 1720, and 1760 nm. When applied to the gypsum, these values are 1707, 1747, and 1764 nm. Furthermore, as the gasoline evaporated, the 1747 and 1764 nm absorptions gradually migrated over three hours back toward the gypsum substrate’s absorption maxima at 1749 and 1768 nm (spectrum G10).

These phenomena highlight the complexity of liquid-substrate spectra, resulting in measurements that consist of substrate absorptions partially or completely attenuated by the liquid combined and modified by those imparted by the liquid. A spectral library with just gasoline liquid spectra or a variety of gasoline-substrate spectra is unlikely to encompass the absorptions associated with spectrum G2 above that includes: 1) gypsum absorptions at 995, 1536, 2216, and 2266 nm; 2) gasoline features at 913, 1192, and 2310 nm; while missing 3) gypsum features at 1204 and 1225 nm; 4) a gasoline feature at 1154 nm; and producing 5) gypsum/gasoline absorptions with modified absorption maxima at 1707, 1747, and 1764 nm.
4.1.4 Crude Oils on Selected Substrates

4.1.4.1 Light Crude

The light crude oil (42.2° API) is dark brown in color with <5% reflectance in the visible portion of the spectrum (Figures 4-2 and 4-1). A 1.6 mm film was nearly opaque until 950 nm where it became somewhat transmissive as evidenced by the rise in reflectance from 950 nm to peaks of 38% and 40% at 1615 and 2106 nm, respectively. The light crude produced major absorption features at 1728 and 1761 nm and the broad, overlapping absorptions from 2270-2400 nm. Additionally, it produced minor (<1%) asymmetric absorption features at 1206, 2007, and 2173 nm. There were no features detected at wavelengths <950 nm due to the crude oil’s effective opacity at these wavelengths.

Figure 4-17 plots the drying sequence of the light crude applied to a calcareous sand substrate. Spectrum H1 is the mean of all sand samples before crude application. The absorption at 2334 nm is typical for carbonates (Hunt, 1977; Clark et al., 2006). Spectra H2-H14 plot the drying sequence of crude on the samples from saturation at initial application (0.196 g/cm²) through 108 days (0.111 g/cm²). During this time period, 43.6% of the crude evaporated from the sample. The crude initially produced hydrocarbon absorptions at 1207 nm (<2%), a major (>15%) asymmetric doublet at 1726 and 1761 nm, a minor (<2%) feature at 2175 nm, and punctuated absorptions of the hydrocarbon plateau at 2309 (>3%) and 2346 nm (>1%). It also masked the sand’s carbonate absorption feature and continued to do so for the duration of the observation period. In the major hydrocarbon absorption regions at 1200, 1700-1800, and >2270 nm, the absorption maxima gradually shifted to longer wavelengths as time elapsed (Table 4-
1). This finding needs additional investigation but may be a promising method for distinguishing light crudes from heavier ones or for coarsely dating the vintage of spills.

![Reflectance spectra of light crude on a calcareous sand substrate.](image)

**Figure 4-17:** Reflectance spectra of light crude on a calcareous sand substrate.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Time Elapsed</th>
<th>Mass (g/cm²)</th>
<th>% Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1 samples (mean)</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>H2 0.5 minutes</td>
<td>0.196</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>H3 15 minutes</td>
<td>0.195</td>
<td>99.5</td>
<td></td>
</tr>
<tr>
<td>H4 1 hour</td>
<td>0.193</td>
<td>98.4</td>
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</tr>
<tr>
<td>H5 6 hours</td>
<td>0.187</td>
<td>95.5</td>
<td></td>
</tr>
<tr>
<td>H6 1.2 days</td>
<td>0.177</td>
<td>90.0</td>
<td></td>
</tr>
<tr>
<td>H7 5.3 days</td>
<td>0.155</td>
<td>79.0</td>
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</tr>
<tr>
<td>H8 11.4 days</td>
<td>0.142</td>
<td>72.6</td>
<td></td>
</tr>
<tr>
<td>H9 21.3 days</td>
<td>0.133</td>
<td>67.6</td>
<td></td>
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<tr>
<td>H10 40.3 days</td>
<td>0.124</td>
<td>63.1</td>
<td></td>
</tr>
<tr>
<td>H11 54.4 days</td>
<td>0.119</td>
<td>61.0</td>
<td></td>
</tr>
<tr>
<td>H12 69.8 days</td>
<td>0.117</td>
<td>59.5</td>
<td></td>
</tr>
<tr>
<td>H13 90.5 days</td>
<td>0.113</td>
<td>57.6</td>
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<tr>
<td>H14 108.4 days</td>
<td>0.111</td>
<td>56.4</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Time Elapsed</th>
<th>Mass (g/cm²)</th>
<th>% Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2 0.5 minutes</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>H3 0.5 minutes</td>
<td>0.196</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>H4 1 minute</td>
<td>0.195</td>
<td>99.5</td>
<td></td>
</tr>
<tr>
<td>H5 1 minute</td>
<td>0.193</td>
<td>98.4</td>
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</tr>
<tr>
<td>H6 1 minute</td>
<td>0.187</td>
<td>95.5</td>
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<tr>
<td>H7 5.3 days</td>
<td>0.177</td>
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<tr>
<td>H8 11.4 days</td>
<td>0.155</td>
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<tr>
<td>H9 21.3 days</td>
<td>0.142</td>
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<tr>
<td>H10 40.3 days</td>
<td>0.133</td>
<td>67.6</td>
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<tr>
<td>H11 54.4 days</td>
<td>0.124</td>
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<tr>
<td>H12 69.8 days</td>
<td>0.120</td>
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<tr>
<td>H13 90.5 days</td>
<td>0.117</td>
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<tr>
<td>H14 108.4 days</td>
<td>0.113</td>
<td>57.6</td>
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</tr>
</tbody>
</table>

**Table 4-1:** Migration of light crude oil absorption maxima over time, calcareous sand substrate.
Spectrum H2 has slightly stronger absorptions than the rest of the spectra. Yet the difference in crude oil mass is quite small, 0.001 g/cm² (0.5%), between these two data points. When the H2 spectrum was collected after the crude oil application, there was some crude oil on the top of the substrate that had not yet percolated into the sample. After 15 minutes (spectrum H3), the crude had percolated into the sample.

### 4.1.4.2 Heavy Crude

The heavy crude oil (19.6° API) is very dark brown colored with <1% reflectance in the VNIR portion of the spectrum (Figures 4-2 and 4-1). A 1.4 mm film was nearly opaque until 1300 nm where it became slightly transmissive, as evidenced by the rise in reflectance from 1300 nm to peaks of 3% and 12% at 1655 and 2110 nm, respectively. The heavy crude produced major absorption features at 1726 and 1758 nm and the broad, overlapping absorptions from 2270-2400 nm. Additionally, it produced a minor (3%) asymmetric absorption feature at 2174 nm. There were no features detected at wavelengths <1300 nm due to the crude oil’s effective opacity at these wavelengths.

Figure 4-18 plots the drying sequence of the heavy crude applied to the calcite-dolomite crushed aggregate. Spectrum Y1 is the mean of all aggregate samples before crude application. The absorption at 2334 nm is typical for carbonates but is masked in all of the crude oil samples (Hunt, 1977; Clark et al., 2006). Spectra Y2-Y16 plot the drying sequence of crude on the samples from saturation at initial application (0.315 g/cm²) through 109 days (0.275 g/cm²). During this time, 12.7% of the crude evaporated from the sample. The crude-aggregate combination produced a flat, dark (<3%) spectrum from 400-800 nm that then gently sloped upward until 2100 nm, interrupted only by the
hydrocarbon absorptions from 1700-1800 nm. The opacity of the heavy crude muted the major absorption features, which were <1% at 1725 and 1755 nm and 3-4% from 2275-2350 nm, including a shoulder at 2275 nm and absorptions at 2310 and 2340 nm.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Time Elapsed</th>
<th>Mass (g/cm²)</th>
<th>% Residual</th>
</tr>
</thead>
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<tr>
<td>Y1</td>
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<td>100.0</td>
</tr>
<tr>
<td>Y2</td>
<td>1.0 hour</td>
<td>0.313</td>
<td>99.5</td>
</tr>
<tr>
<td>Y3</td>
<td>3.0 hours</td>
<td>0.312</td>
<td>99.1</td>
</tr>
<tr>
<td>Y4</td>
<td>5.5 hours</td>
<td>0.311</td>
<td>98.8</td>
</tr>
<tr>
<td>Y5</td>
<td>11 days</td>
<td>0.306</td>
<td>97.1</td>
</tr>
<tr>
<td>Y6</td>
<td>5.5 days</td>
<td>0.294</td>
<td>93.3</td>
</tr>
<tr>
<td>Y7</td>
<td>12.4 days</td>
<td>0.287</td>
<td>91.2</td>
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<tr>
<td>Y8</td>
<td>20.5 days</td>
<td>0.284</td>
<td>90.3</td>
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<td>Y9</td>
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<td>0.289</td>
<td>89.0</td>
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<tr>
<td>Y10</td>
<td>47.5 days</td>
<td>0.279</td>
<td>88.6</td>
</tr>
<tr>
<td>Y11</td>
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<td>88.3</td>
</tr>
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<td>Y15</td>
<td>109.4 days</td>
<td>0.2746</td>
<td>87.3</td>
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</table>

Figure 4-18: Reflectance spectra of heavy crude on a calcite-dolomite crushed aggregate substrate.

4.1.4.3 Intermediate Sour Crude

The intermediate, sour crude oil (30.3° API) is very dark brown colored with <1% reflectance in the VNIR portion of the spectrum until 1200 nm (Figures 4-2 and 4-1). A 1.6 mm film was nearly opaque until 1200 nm where it became slightly transmissive as
evidenced by the rise in reflectance from 1200 nm to peaks of 12% and 21% at 1623 and 2102 nm, respectively. The intermediate, sour crude produced major absorption features at 1726 and 1759 nm and the broad, overlapping absorptions from 2270-2400 nm. Additionally, it produced an asymmetric absorption feature (9%) at 2172 nm. There were no features detected at wavelengths <1200 nm due to the crude oil’s effective opacity at these wavelengths.

Figure 4-19 plots the drying sequence of the intermediate, sour crude applied to a concrete substrate. Spectrum R1 is the mean of all concrete samples before crude application. The spectrum slopes upward quickly in the visible and then gradually until it peaks at 2137 nm. There is an absorption at 2206 nm as well. Spectra R2-R16 plot the drying sequence of the crude on the concrete samples from saturation at initial application (0.123 g/cm²) through 109 days (0.0894 g/cm²). During this time, 27.4% of the crude evaporated from the sample. The crude initially produced an asymmetric doublet at 1726 and 1759 nm (<5%), a minor (<3%) absorption at 2173 nm, and punctuated absorptions of the hydrocarbon plateau at 2309 (<2%) and 2347 nm (<1%) with a shoulder at 2282 nm. Like the light crude oil, the absorption maxima in the hydrocarbon absorption regions at 1700-1800 and >2270 nm shifted to longer wavelengths as time elapsed, although the effect was more mild and did not occur for all features (Table 4-2).
Most of the changes in reflectance intensity also occurred during the first day of observation. In the SWIR region, reflectance increased 10-15% from initial application (spectrum R2) through the end of the first day (spectrum R8). Thereafter, for the
remaining 108 days of observation, reflectance increased 2-5% in the SWIR. All of the absorption features persisted for the duration. While the doublet at 1726 and 1759 nm grew less intense over time (4% vs 1%), absorptions >2270 nm grew more intense (10% vs 15-20%) due to the rise in reflectance in the continuum spectrum at shorter wavelengths.

4.1.5 Spectral Discrimination of Hydrocarbons from Water

Figure 4-20 plots an intermediate, sweet crude and water on the same quartzic beach sand. The crude oil is nearly opaque throughout the 70-day observation period but does present the typical hydrocarbon absorption features at 1726, 1760, and from 2270-2400 nm (Figure 4-20,(top)). During that time period, 29.8% of the crude oil evaporated from the sand substrate. The starting quantity, 0.440 g/cm², was sufficient to minimize spectral changes over the observation period whereas a smaller initial quantity, such as the one for the similar intermediate, sour crude, 0.123 g/cm², was not sufficient to perform this function.

Water has absorption features in the NIR centered at 966 and 1180 nm and broad absorptions centered at 1450 and 1920 nm with a local reflectance maximum around 1695 nm (Figure 4-20,(bottom)). All of the water evaporated from the sand substrate by the end of the first day (spectrum W10). Its reflectance is brighter than the original sample spectrum (W1) since it is drier than the beach sand samples at the time of application. Negative values in the “Mass (g/cm²)” and “% Residual” columns of the table embedded in Figure 4-20 (bottom) indicate that water evaporating from the substrate during this time was present in the sample at the time of application. The
samples continued to dry between the second and third day (spectrum W11) and hence have a higher reflectance as water continues to evaporate from the substrate. Spectrally discriminating crude oil from water is possible given the different locations and shapes of their respective spectral signatures. If observations over time are possible, water’s greater volatility and complete evaporation from the substrate provide additional measures of separation from more stable materials such as crude oils and refined products, including diesel fuel and motor oil.

Table 4-3 plots the spectral separability of petroleum and petroleum products from water on all of the substrates. For substrates with reflectances $\geq 0.3$ in portions of the SWIR with hydrocarbon absorptions, both the crude oil and the refined products are all spectrally separable from water due to the strong ($\geq 5\%$) absorption in the first overtone region from 1700-1800 nm and/or the hydrocarbon plateau from 2270-2400 nm. These substrates include bentonite, calcareous sand, concrete, gypsum, Ottawa sand, and the quartzic beach sand. While the hydrocarbon absorptions are present in the liquid-asphalt samples, they were $<3\%$ in all cases except for light crude, where they were marginally detected (3-5%). While absorption features with these intensities are readily apparent in lab spectra, they are far from certain when using atmospherically compensated reflectance cubes gathered from airborne/spaceborne platforms.
Figure 4-20: Reflectance spectra of (top) intermediate, sweet crude and (bottom) water on a quartzic beach sand substrate.
Table 4-3: Spectral separability of petroleum and petroleum products from water using hydrocarbon absorption features and overall reflectance.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Acetone</th>
<th>Gasoline</th>
<th>E85</th>
<th>Diesel Fuel</th>
<th>Motor Oil</th>
<th>Light Crude</th>
<th>Intermediate Sour Crude</th>
<th>Intermediate Sweet Crude</th>
<th>Heavy Crude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Marginal</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Bentonite</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Calcareous Sand</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Calcite-Dolomite Crushed Aggregate</td>
<td>No</td>
<td>No</td>
<td>Marginal</td>
<td>Yes</td>
<td>Marginal</td>
<td>Yes</td>
<td>Yes</td>
<td>Marginal</td>
<td>Marginal</td>
</tr>
<tr>
<td>Concrete</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Gypsum</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Highly Organic Soil</td>
<td>Marginal</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Ottawa Sand</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Quartzic Beach Sand</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Vegetation</td>
<td>Marginal</td>
<td>No</td>
<td>Marginal</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

While most of the substrates’ utility—or lack thereof—is clear, the vegetation, highly organic soil, and calcite-dolomite crushed aggregate substrates are more complicated. The hydrocarbon absorptions are visible in all of the refined product-vegetation spectra but in the cases of acetone and E85, they were 3-5% in intensity, which is marginal for detection. For gasoline, the amount applied to the substrate was insufficient to achieve 3% intensity. Applying larger quantities would likely produce stronger features. The crude oils all produced strong absorption features in the 2270-2400 nm region, combined with sufficient opacity in the visible spectrum to mask the green peak and greatly attenuate the red edge in the NIR. Water’s high transmission in the visible spectrum preserves vegetation’s spectral shape, even into the NIR where it is increasingly opaque.

The same crude oil opacity in the VNIR also greatly assisted petroleum-water discrimination on the highly organic soil. In this case, it masked the broad iron oxide absorption features in the VNIR while significantly suppressing reflectance to straight, gradually increasing values up to ~0.10. While internal reflections from water produced
lower reflectances than for an unwetted sample, water’s transmissivity preserved the VNIR iron oxide features in the substrate. Overall reflectance was also higher than for oil, averaging ~0.15 in the NIR. The hydrocarbon absorptions from 1700-1800 nm and >2300 nm were also indicative of petroleum. These latter features permitted petroleum to be discriminated from water on some of the refined products that are also highly transmissive in the visible region (e.g., diesel fuel, motor oil). Given the subtle presence of the hydrocarbon features in the acetone, gasoline, and E85 spectra, larger quantities would have likely made them more easily distinguished from water.

Like the vegetation and highly organic soil substrates, the hydrocarbon absorptions are visible, if subtle, in all of the calcite-dolomite crushed aggregate spectra with liquids. In these cases, the carbonate absorption at ~2335 nm becomes a doublet with the first absorption maxima at ~2300-2320 nm due to the sensitive hydrocarbon feature in this region. Additional quantities of any of the liquids with subtle features would likely make absorption from 2300-2320 nm strong enough to be more readily detectable and spectrally separable from water.

4.1.6 Spectral Discrimination of Hydrocarbons from One Another

The diesel fuel and motor oil samples produced very similar absorption features, especially when limiting discussion to the major hydrocarbon features at 1700-1800 and >2300 nm (Figure 4-1). The common asymmetric doublet for both samples produced absorption maxima at 1725-1726 and 1758-1760 nm along with an asymmetric triplet at 2284-2285, 2308-2309, and 2348-2349 nm. There were larger differences in the more subtle hydrocarbon-induced absorptions at shorter wavelengths. For example, diesel fuel
had subtle absorption maxima at 916, 1033, and an asymmetric doublet at 1152 and 1198 nm whereas the motor oil features were at 929, 1038, 1155, and 1210 nm, respectively. As demonstrated in Figure 4-1, these NIR features are either not present (915-930, 1030-1040, 1150-1155 nm) or quite subtle, <2%, (1195-1210 nm) when applied in the quantities used here. As a result, it would be difficult to discriminate these liquids from one another based upon a single data acquisition. Clark et al. (2009) noted this similarity in alkanes with \( \geq 6 \) carbon atoms.

While it is difficult to initially spectrally discriminate diesel fuel from motor oil, in some conditions it is possible to do so by observing them over time. Figure 4-21 (top) shows the spectra for both diesel fuel and motor oil on the bentonite substrate over approximately 90 days of observation. Spectra O1 and D1 are the samples before motor oil and diesel fuel were applied, respectively. The spectral signatures are similar, including the bentonite’s hydroxyl absorption at 2205 nm, but the diesel fuel samples before application have a mean reflectance that is 4.6% higher across the spectrum (n=1653 spectra, \( 1 \sigma = 2.7\% \)). Likewise, the spectra for motor oil-bentonite and diesel fuel-bentonite during the first day—represented here by measurements at 3 hours (O2, D2) and 6-7 hours (O3, D3)—are also similar with absorption features at 1725-1726, 1758-1760, 2308-2309, and 2348-2349 nm. The bentonite’s hydroxyl absorption at 2205 nm is also apparent in these spectra. The 1190-1210 nm feature is present at different wavelengths for these samples: 1194-1195 for diesel fuel and 1208-1209 nm for motor oil—but this feature is subtle (\( \leq 1\% \)).
Figure 4-21: Reflectance spectra of diesel fuel and motor oil on (top) bentonite and (bottom) highly organic soil substrates.
While the initial motor oil-bentonite and diesel fuel-bentonite spectra are quite similar, diesel fuel’s greater volatility causes them to separate as time elapses. By the third day of observations (O4 and D4, Figure 4-21 (top)), the diesel fuel spectrum mildly darkens (<1%) in the VNIR up to ~800 nm but brightens from ~800 – 2400 nm. Initially, the brightening is <2% between 6 hours (D3) and 3.9 days (D4) but persists and is 12.5% at 9.4 days (D6), 16.0% at 23.4 days (D7), and 23.2% (D9) at 90.9 days. In addition to brightening, the spectra also present additional absorption features over the 90-day observation period. The features at 2308-2309 and 2348-2349 nm emerge from the overlapping C-H absorptions in the 2300-2400 nm hydrocarbon plateau. In the visible region, the diesel fuel-bentonite spectra also produce two additional absorption features, an extremely subtle one (<0.5%) at 538 nm and another feature at 620 nm (1.0% at 23.4 days, 1.3% at 90.9 days). While the diesel fuel-bentonite spectra are changing significantly over the 90-day observation period, the motor oil-bentonite spectra remain quite stable, evidenced by the superposition of spectra O2-O9 in Figure 4-21 (top). These spectra do gradually darken by a maximum of <1.5% but their stability, due to motor oil’s low volatility, contrasts sharply with changes in the diesel fuel spectra. It was possible to make similar diesel fuel-motor oil distinctions on the concrete, quartzic beach sand, gypsum, Ottawa sand, calcareous sand, and vegetation substrates, due to similar changes in spectral brightness over time (see Appendix). None of these substrates demonstrated the additional absorption features in the visible region as seen in the bentonite sample, though.
While an extended observation period provides the ability to spectrally distinguish diesel fuel and motor oil on a bentonite substrate, other substrates do not provide sufficient spectral contrast to make these distinctions. Figure 4-21 (bottom) illustrates the diesel fuel-highly organic soil and motor oil-highly organic soil spectra over the same 90-day observation period as for the bentonite example. Spectra O1 and D1 are the samples before motor oil and diesel fuel were applied, respectively. The mean spectra for both the diesel fuel-substrate (D2-D9) and the motor oil-substrate (O2-O9) spectra change <1% over the entire observation period. The diesel fuel spectra show a small amount of spectral brightening in the SWIR at the last two measurement intervals displayed, 50.4 days (D8) and 89.0 days (D9), but these values are quite small, 1.1% and 1.8%, respectively. The asphalt and the calcite-dolomite crushed aggregate substrates also provided insufficient spectral contrast for distinguishing diesel fuel from motor oil (see Appendix).

4.2 Airborne Hyperspectral Data Analysis

Ideally, both lab and field-based spectral signatures can be used to identify materials in remotely sensed data from airborne and spaceborne platforms. A representative set of the lab-measured spectra were applied to a series of airborne SpecTIR HST-3 hyperspectral data sets gathered in the aftermath of the Hurricane Katrina disaster in and around New Orleans in September, 2005. The image processing methodology is discussed above.
4.2.1 Image Pre-Processing

The first step in the image processing methodology included image metadata collection and image artifact detection. Fortunately, as discussed above, the data set included sufficient documentation for most of the necessary image metadata. The images did contain sufficient spectral smile to merit correction.

Spectral smile is a change in a sort of spectral mis-registration or drift across the columns (or samples) on the two-dimensional focal plane array at the heart of pushbroom imaging spectrometers. This artifact means that each pixel in a row of data will incorporate spectral information from slightly different wavelengths than those that should comprise the row if such mis-registration was not present. As Figure 4-22 demonstrates, the variation across a focal plane usually forms a curve that slopes upward (i.e., “smile”) or more commonly, downward (i.e., “frown”), at the edges of the imaging array (Mouroulis et al., 2000; Green et al., 2003b; Jupp et al., 2003).
Figure 4-22: Idealized spectral smile, or in this case, spectral “frown” across an imaging array. For a given wavelength (e.g., 450.0 nm), the actual value of the wavelength centers will be at shorter wavelengths near the edges of the image and at longer wavelengths in the middle of the image. Graphic from Green et al., 2003b. Annotations by the author.

Pre- and post-launch analysis of the Hyperion instrument indicated a spectral smile of 3-4 nm across the VNIR focal plane (Barry, 2001; Green et al., 2003b; Jupp et al., 2003). Green et al. (2003b) found that while the magnitude across the Hyperion VNIR focal plane remained roughly the same over time, the wavelength values migrated redward by 1-1.5 nm over the first few months of the mission. Unfortunately, there is little in the literature discussing spectral smile for the HST instruments. Taranik et al. (2007) lament the existence of spectral smile in the HST-3 instrument but do not quantify the extent of the artifact.
The effects of spectral smile are depicted in Figure 4-23. The image on the left in the figure is band 1 of a minimum noise fraction (MNF) transform applied to image 20050907_005_012. The disparate tones ranging from dark on the left to bright on the right of the image are a classic manifestation of spectral smile common in pushbroom instruments. The effect contributes to spurious results at the atmospheric compensation stage of processing, as indicated by the negative (black) values in the first 70-90 columns of the FLAASH water column vapor product (Figure 4-23, (center)) and water retrieval errors (magenta and red pixels) in the FLAASH cloud mask product (Figure 4-23, (right)).
Comparing pixel spectra from seven column locations across the image confirms the existence of significant spectral smile in the image. Figure 4-24 shows the sample locations highlighted by yellow circles. Spectrally bright targets such as petroleum tanks, gravel, and a trailer rooftop were chosen to provide strong contrast for the four well known atmospheric absorption features used to test for spectral smile. The features include two oxygen absorptions and two carbon dioxide absorptions that span the spectral range of the instrument and which are centered at the following wavelengths: 763 (O₂), 1265 (O₂), 1606 (CO₂), and 2058 nm (CO₂) (Wolfe, 1978; NASA-OCO, 2010). To minimize noise and potentially spurious single column/pixel results, region(s) of interest
(ROI(s)) that spanned 4-10 columns were collected for evaluation and depended largely on the size of the target. The number of pixels in each ROI varied from 14 to 105, and was dependent on target size. For example, petroleum tanks are large anthropogenic targets and in this image are ~30 m in diameter, enabling ROIs of >80 pixels in size. Meanwhile, the road target is comparatively thin, 2 pixels (4 m) wide. Gathering a 7-column wide ROI resulted in a 14-pixel ROI.

Figure 4-24: False color composite image (ID: 20090907_005_012) with ROIs used for spectral smile determination highlighted by dashed yellow circles.
Figure 4-25 shows the ROI spectra for each of the seven locations, labeled by their column location from left to right in the image. The upper plot shows the ROI spectra for 700-1300 nm, including both oxygen features. Note that all locations have a local minimum at the band centered at 766.4 nm. In an ideal scene, all locations across the scene conform to the same local minimum at all atmospheric absorption wavelengths. In this example, note that for the 1265 nm feature, the locations at columns 2-6 and 33-36 have local minima at a longer wavelength (1274.7 nm). The large drop in reflectance at 900 nm is a function of spectrometer crossover in the HST instrument. The lower plot shows the ROI spectra for 1500-2100 nm, including both carbon dioxide features. Note that the first three locations, columns 2-6, 33-36, and 57-62 have local minima at 1612.0 nm whereas the locations in the center (columns 89-98 and 140-150) and right (columns 205-213 and 240-247) part of the scene have local minima at 1603.7 nm. All locations except columns 240-247 have local minima that are two bands-wide for the 2058 nm carbon dioxide feature (2049.54 and 2057.83 nm). Spectra are not offset along the y-axis in this plot for ease of visualizing the differences between local minima.
Figure 4-25: ROI spectra for seven locations used to check for spectral smile in image 20050907_005_012. (top) ROI spectra for 700-1300 nm. While all locations have a local minimum at the 766.49 nm band, all locations do not share the local minima at 1265.66 nm. (bottom) ROI spectra for 1500-2100 nm. Three locations (columns 2-6, 33-36, and 57-62) have local minima at 1612.01 nm whereas the remaining locations have local minima at 1603.74 nm. All locations except columns 240-247 have local minima two bands-wide for the 2058 nm carbon dioxide feature.
Ideally, standard pre-processing or atmospheric compensation tools would correct for spectral smile but according to Jupp et al. (2003), the High accuracy ATmospheric Correction for Hyperspectral data (HATCH) algorithm (Qu et al., 2003) is the only atmospheric compensation technique that can compensate for spectral smile. Since HATCH was not available for this effort, a cross-track illumination correction was applied to the scene to mitigate the spectral smile. First, second, and third order polynomials were iteratively applied, processed through the FLAASH algorithm, and evaluated. All three solutions improved results but the second and third order polynomials provided a superior correction than that of the first order polynomial for the first 70 columns when compared to a 70 column ROI minimally affected by the smile (37% (1\textsuperscript{st} order), 3% (2\textsuperscript{nd} order), and 3% (3\textsuperscript{rd} order)). Results are included in Table 4-4.

Table 4-4: Results of cross-track illumination correction for Image 20070907_005_012 using water vapor as the figure of merit.

<table>
<thead>
<tr>
<th></th>
<th>Water Vapor (std atm-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>uncorrected image</td>
</tr>
<tr>
<td>Columns 1-70 (mean)</td>
<td>-4718</td>
</tr>
<tr>
<td>(vignetting region)</td>
<td></td>
</tr>
<tr>
<td>Columns 140-210 (mean)</td>
<td>4677</td>
</tr>
<tr>
<td>difference between ROIs</td>
<td>-9395</td>
</tr>
<tr>
<td>spurious pixels (#)</td>
<td>34,659</td>
</tr>
<tr>
<td>% spurious</td>
<td>32.1%</td>
</tr>
<tr>
<td>spurious pixels over land</td>
<td>&gt;29,000</td>
</tr>
</tbody>
</table>

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Since both the second and third order polynomials provided similar ability to match water vapor results from a portion of the image minimally affected by spectral smile, a decision about which correction method to use for atmospheric compensation requires additional discrimination criteria. Although the third order polynomial had many fewer spurious (i.e., negative) pixels over land in the corrected image (Table 4-4), many of the spurious pixels in the second order polynomial image were on pixels where standing water was trapped inside the petroleum tank berms. Since higher order polynomials make successively greater spectral and spatial changes to the imagery data, it is prudent to minimize this impact on the data while minimizing the impact of spectral smile (Jupp et al., 2003). Additionally, qualitative comparison of vegetation spectra from each image’s affected area supports this position. When compared to the vegetation spectra in the USGS spectral library, the second order polynomial image better preserved the subtle absorption feature at 1200 nm.

Furthermore, the second order polynomial significantly improved the spectral conformity in the image, as indicated in Figure 4-26. Like Figure 4-25 above, the ROI spectra at seven locations across the image are plotted and labeled by their column location from left to right in the image. The upper plot shows the ROI spectra for 700-1300 nm, including both oxygen features. Note that all locations still have a local minimum at the band centered at 766.49 nm but unlike the pre-correction image, all locations also share a local minimum at 1265.66 nm, mitigating the spectral smile. The large drop in reflectance at 900 nm is a function of spectrometer crossover in the HST instrument. The lower plot shows the ROI spectra for 1500-2100 nm, including both
carbon dioxide features. Local minima for columns 2-6 and 33-36 have been modified and spread out over both bands that encompass the carbon dioxide feature centered at 1606 nm (i.e., 1603.74, 1612.01). Likewise, the local minimum for columns 240-247 now spans the two bands for the 2058 nm carbon dioxide feature (2049.54 and 2057.83 nm), similar to the spectral shape for the other six locations. Spectra are not offset along the y-axis in this plot for ease of visualizing the differences between local minima. The third order polynomial correction did not improve upon these results. For these reasons, the second order polynomial correction was used as input for the next step: atmospheric compensation.
Figure 4-26: ROI spectra after cross-track illumination correction for seven locations used to check for spectral smile in image 20050907_005_012. (top) ROI spectra for 700-1300 nm. Note that all locations have the same local minima for both the 766.49 nm and 1265.66 nm bands. (bottom) ROI spectra for 1500-2100 nm. Local minima for columns 2-6 and 33-36 are spread out over both bands that encompass the carbon dioxide feature centered at 1606 nm. Likewise, the local minimum for columns 240-247 is also two bands-wide for the 2058 nm carbon dioxide feature.
The cross-track illumination correction largely eliminated the artifacts revealed in the MNF band 1 and subsequent processing products such as the column water vapor image and cloud mask from FLAASH. The corrected image’s MNF band 1, its column water vapor image, and cloud mask are included in Figure 4-27. The stark tonal variation in the MNF band 1 of the original image has been greatly mitigated in the corrected image. As mentioned above, most the of remaining spurious pixels in both the water vapor image (black) and the cloud mask image (red) are over standing water trapped inside petroleum tanks berms and over the river, which is common.

Figure 4-27: Results of cross-track illumination correction, Image ID: 20050907_005_012. (left) MNF band 1 of the image after correction. (center) FLAASH water column vapor image. Most of the remaining spurious pixels are over water. (right) FLAASH cloud mask image. Note the greatly reduced number of water retrieval errors (red pixels) when compared to Figure 4-23 above.
4.2.2 Atmospheric Compensation

The next step in the image processing chain is atmospheric compensation. As mentioned above, the radiance image was processed using both QUAC and FLAASH, creating two different reflectance cubes for the material identification stage. QUAC does not require any inputs beyond picking out a sensor from a drop down list and the results are displayed in Figure 4-28. FLAASH, on the other hand, is metadata-intensive. Scene latitude/longitude, sensor altitude, pixel size, flight date, and flight time were all included with the data set. Ground elevation was determined from the respective USGS 1:24,000 topographic maps for the area(s) of interest. The Atmospheric Model was set to tropical, in accordance with recommendations included in the FLAASH help files (Table 2-2, ENVI® v4.7) and based upon the scene latitude and flight date. Water vapor retrieval was performed using the 820 nm absorption feature and initial visibility was set to 20 km to account for the high water vapor content and poor visibility indicated in the data set’s metadata. Spectral polishing was disabled. Initially, wavelength recalibration was also disabled. For the remaining data fields in the primary FLAASH input screen, the default values were accepted (i.e., aerosol model=rural, aerosol retrieval=2-Band (K-T)).
The results for the initial FLAASH run are shown in Figure 4-29. Mean spectra from the seven ROIs used in the spectral smile evaluation are plotted and the four reference atmospheric absorption features are highlighted in the plot. Perhaps the most striking portion of the plot are the wildly varying spectra from 1970-2080 nm. All of the ROIs show reflectance intensity changes of 30-50% (0.3-0.5) over very short wavelength ranges (25-30 nm). Results such as these, manifest in ROIs representing a variety of material types, are often an indication of poor wavelength assignments in this portion of the spectrum. Unexpected absorptions also occur at 766 nm and there is a spurious spike in many of the spectra at the oxygen feature at 1265 nm. Despite minor intensity, the
carbon dioxide feature in the HST-3 1604 nm band is also present in most of the ROI spectra as a spike.

**Figure 4-29:** Results of initial FLAASH run for Image ID: 20050907_005_012. Wavelength Recalibration was disabled, resulting in poor results near many of the reference atmospheric absorption features, especially the carbon dioxide feature at 2058 nm.

Due to these poor results, FLAASH was run a second time with the wavelength recalibration option enabled. The default spectrograph definition file in FLAASH was modified to match the HST-3 sensor’s two spectrometers and used for this run. The results are shown in Figure 4-30. Changing this parameter greatly improved the spectra near the carbon dioxide feature at 2058 nm and produced modest improvement in the

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spurious absorptions for the 766 nm oxygen feature. Unfortunately, the process also induced a spurious spike for all ROIs in the 1265 nm feature. The process produced ambiguous results for the 1606 nm carbon dioxide feature. Spectra for bright features became slightly smoother, indicating better results, but became rougher for ROIs with darker spectra.

Figure 4-30: Results of the second FLAASH run for Image ID: 20050907_005_012. Wavelength Recalibration was enabled, resulting in better results near the 2058 nm carbon dioxide feature but exacerbating a spurious spike for the 1265 nm feature.

To improve the spurious feature at 1265 nm, a new spectrograph definition file was created and used for a third FLAASH iteration. A typical spectrograph definition
file has one line for each spectrometer in the instrument (e.g., AVIRIS=4, COMPASS=1). The HST-3 instrument has two spectrometers, one for wavelengths ≤900 nm (bands 1-39) and one for >900 nm (bands 40-227). The new spectrograph definition file artificially moved bands 40-93 (908-1341 nm) from the second spectrometer to the first. Band 93 was chosen as the last wavelength to move since it is located well inside the strong water vapor absorption feature from 1300-1500 nm. The choice of this exact band was somewhat arbitrary; any band in this atmospheric absorption region would be acceptable. The results from this FLAASH iteration are shown in Figure 4-31. The change in the spectrograph definition file largely removed the spurious spike at 1265 nm, although a small (0.5-2.0%) artifact remains in the spectra for 6 out of 7 ROIs. The ROI in columns 33-36, a probable dilapidated concrete pad, retains an artifact with an intensity of ~3.5%.
Wavelength recalibration was enabled with a modified spectrograph definition file, preserving improvements near the 2058 nm carbon dioxide feature while minimizing a spurious spike for the 1265 nm feature.

4.2.3 “Bad Bands” Removal

After atmospheric compensation, bad/noisy bands are removed from the data set. Bad bands are in wavelength regions where atmospheric constituents—mostly water vapor and carbon dioxide—greatly attenuate the signal received at the sensor, introducing spurious and abrupt changes in reflectance. The areas of fair to strong atmospheric absorption are noise-dominated and easy to discern from areas with high atmospheric transmission. These regions are bounded by bands in the following ranges: 900-1000, 1100-1200, 1300-1500, and 1800-1950 nm. Additionally, residual atmospheric absorption features not in these ranges such as the oxygen feature at 766 nm or the carbon dioxide features from 1950-2070 nm can cause exclusion of these bands. Lastly, low
SNR caused by decreased instrument sensitivity common at wavelengths >2350 nm and <400 nm in many airborne sensors creates more bad bands.

Figure 4-32 shows the QUAC reflectance cube before and after the removal of bad bands. The bad bands for this cube largely conform to the regions listed above save the residual oxygen feature and the carbon dioxide region where only those bands from 1950-1980 nm needed to be masked out of the reflectance cube. The final cube has 144 bands.
Figure 4-32: The QUAC reflectance cube for Image ID: 20050907_005_012, before (top) and after (bottom) bad bands removal from the image. Note the areas with high noise content evidenced by abrupt and extreme changes in reflectance intensity from 900-1000, 1100-1200, 1300-1500, 1800-2000, and >2350 nm.
It is important to note that, depending on atmospheric conditions at the time of data acquisition, the bands that need to be removed from the data set can expand further from the initial list above. For example, the FLAASH reflectance cube before and after bad bands removal is shown in Figure 4-33. In the top plot, the residual carbon dioxide features are present, along with bands from 850-900 nm and 1760-1800 nm that still need to be purged from the data set since spectra from all ROIs are clearly impacted by either the spectrometer crossover or the slightly broadened water vapor absorption at these wavelengths. The bottom plot in Figure 4-33 shows the results of the bad bands removal process, leaving 125 bands for the ROI spectra.
Figure 4-33: The FLAASH reflectance cube for Image ID: 20050907_005_012, before (top) and after (bottom) bad bands removal from the image. Note the areas with high noise content evidenced by abrupt and extreme changes in reflectance intensity from 850-1000, 1100-1200, 1300-1500, 1760-2070, and >2350 nm.
As the spectra for the ROIs in Figure 4-34 indicate, there is a residual “red-edge” in many, but not all, of the FLAASH-corrected pixels. In this image, the high water vapor content may have produced strong adjacency effects across the image, despite FLAASH’s attempts to remove this artifact from the data.

![Figure 4-34: ROIs spectra from the FLAASH-corrected image for the flooded berms. Note the residual red-edge in many, but not all, of the spectra, presumably of water. In this image, the high water vapor content may have produced strong adjacency effects across the image, despite FLAASH’s attempts to remove this artifact from the data. Y-axis scaled 4-15% reflectance. Bands used in image display (left): R/G/B: 1577/1037/649 nm.](image)

As the spectra for the ROIs in Figure 4-35 indicate, there is a residual “red-edge” in many of the QUAC-corrected pixels as well. This artifact is especially evident in dark
spectra, such as these, and is common in QUAC-corrected reflectance cubes (Bernstein, personal communication, 2008).

Figure 4-35: ROIs spectra from the QUAC-corrected image for the flooded POL berms. Note the residual red-edge in all of the spectra, presumably of water. Y-axis scaled 0-18% reflectance. Bands used in image display (left): R/G/B: 1579/1037/649 nm.

After the bad bands are removed from the reflectance cube, material identification is the last step in the image processing methodology.

4.2.4 Material Identification (MTMF and SAM algorithms)
Ultimately, the value of any spectral library is the ability to apply it to data collected from another time and place, and preferably, from an efficient method of data collection such as an airborne or spaceborne platform. A selected set of spectral
signatures gathered in the lab were utilized with two airborne hyperspectral data sets from the Hurricane Katrina disaster with the goal of detecting and delineating petroleum and petroleum product spills.

The following algorithms were used for the material identification stage: MTMF and SAM. These algorithms are discussed in detail elsewhere and widely used in the hyperspectral community. Readers are directed to Kruse et al. (1993), Turin (1960), and Boardman (1998) for SAM, the original matched filter, and MTMF (a matched filter variant), respectively. Additional information on MTMF is also provided by Williams and Hunt (2002).

4.2.4.1 Image 20050907_005_012

The first image analyzed, 20050907_005_012, includes a petroleum tank farm with eight tanks, all of which are surrounded by earthen berms. Figure 4-36 is a false color composite of the area (RGB: 1600/1050/650 nm). Pooled liquid is clearly standing in five berms while the other three appear to have wetter soil around them than better drained upland areas outside the berms. Without taking advantage of bidirectional reflectance distribution function (BRDF) conditions and phenomenology such as the Brewster angle, it is difficult to discriminate between standing hydrocarbons and water since increasing depths increase incoming photon absorption, preventing many from reflecting off the substrate, traversing the standing liquid a second time, and being detected by a sensor. Along the edges of these standing pools, though, the liquid depth should become more shallow, allowing a greater number of photons to penetrate the liquid in its transmissive wavelengths, reflect off the underlying substrate, re-emerge
from the liquid, and be detected by a remote sensor in a vertical-mixing scenario. Likewise, pixel-phasing will also produce a large number of pixels that appear to be mixed in a more classical fashion, horizontally, between standing liquid and non-submerged substrate.

Figure 4-36: Underlying berm materials. (left) False color composite for Image ID: 20050907_005_012, QUAC-corrected cube. RGB: 1600/1050/650 nm. (right) Mean spectra for primary land cover inside of the berms. Spectrum #1 is healthy green vegetation; spectrum #2 is a bare soil with significant iron oxides present.

According to the Natural Resources Conservation Service (NRCS), the primary soil types in this scene are the Cancienne silt and silty clay loam (NRCS, 2011). The primary, un-submerged land covers inside the earthen berms are healthy green vegetation and bare soil with significant iron oxides present (Figure 4-36). The bare soil spectrum is
also a good match to Baumgardner et al.’s (1985) “iron affected” silty clay loam. While there are no silty clay loams available in the petroleum-substrate library discussed above, the quartzic beach sand, the Ottawa sand, and the grass/litter/soil are used as substitute substrates in the material identification process.

For this image, the MTMF algorithm was used to attempt to discriminate petroleum from water. The pooled liquid did not occupy a large portion of the scene so it was presumed that the matched filter could successfully isolate their spectra without a large influence on the covariance matrix which serves to characterize the scene background. This approach is more expedient than having to identify each endmember in the scene before moving on to material identification, which may be important if these data are being analyzed during an emergency scenario. To simplify the process and the number of spectra processed while maintaining the ability to discriminate between petroleum and water, light crude and motor oil were selected as exemplars of the four crudes (1 light, 2 intermediate, and 1 heavy) and the four refined petroleum products (motor oil, diesel fuel, gasoline, E85 fuel) in the spectral library.

Instead of using the 2-D scatterplot to visualize results, the Matched Filter (MF) score was divided by the Infeasibility Score (IS) using the ENVI® Band Math function. This technique accelerates the discrimination step but does run the risk of an artificially high MF/IS score due to a low MF paired with a low IS. In first phase analysis such as an operational response to an active oil spill, analysts are likely to be willing to tolerate a few false positives for these shortened analytical time lines. Furthermore, they are unlikely to trust stray pixels. During second phase analysis, analysts can optimize
processing to minimize false positives by using the 2-D scatterplot, clumping and sieving, and/or combining results with other algorithms such as SAM.

The next four figures (4-37 to 4-40) show the results of the MF/IS ratio for a light crude-Ottawa sand, motor oil-Ottawa sand, and water-Ottawa sand library signatures applied to this scene. The three permutations, in order, are: 1) QUAC-compensated with cross-track illumination correction (Figure 4-37), 2) FLAASH-compensated with cross-track illumination correction at two thresholds (Figure 4-38 and 4-39), and 3) QUAC-compensated without cross-track illumination correction (Figure 4-40). The FLAASH-compensated cube without cross-track illumination correction performed the poorest and is not included. In each figure, the image on the left is a color composite of the MF/IS detection planes where red=light crude-Ottawa sand, green=motor oil-Ottawa sand, and blue=water-Ottawa sand. Pixels with MF/IS values <0 have been masked out, which eliminates some false positives with low MF scores paired with low IS scores. Pixels where the MF/IS ratio is $\geq 0.01$ (QUAC cubes) or $\geq 0.007$ (FLAASH cubes) are highlighted using the same legend as described above. In the center of each figure is a false color composite (RGB: 1600/1050/650 nm) with the highlighted pixels from the MF/IS ratio (values $\geq 0.01$ (QUAC) or $\geq 0.007$ (FLAASH)) overlaid for context. The tanks are also numbered arbitrarily from #1-6. On the right of each figure is a spectral plot including the library spectra and the mean spectra for all highlighted pixels of each type (light crude, motor oil, water) in the image. In the QUAC-compensated cubes (Figures 4-37 and 4-40), there is a red-edge artifact in the mean spectra for the crude-, motor oil-, and water-sand spectra. This is especially apparent when comparing these
spectra to those from the FLAASH cube (Figure 4-38). Gaps in the spectra are atmospheric absorption regions that were removed during the bad bands process. The library spectra were collected in laboratory conditions and do not need these regions removed, although they are removed during the spectral library resampling for the subsequent material discrimination process.

Figure 4-37 depicts the MF/IS results from the QUAC-compensated image with cross-track illumination correction. There are 612 water-Ottawa sand pixels; most cluster along the edges of the liquid in the berms, especially tanks #2-4. They do not score well in the centers of the pools, presumably due to the standing liquid absorbing most of the photons, preventing the substrate from contributing to the pixel spectrum. Note that there are very few motor oil-Ottawa (n=30) and light crude-Ottawa pixels (n=1). Additionally, most of the motor oil pixels are in two bad image columns. Although the number of pixels along the edge of tank #5 is scant, the convergence of pixels along the edges of the pools strongly indicates that the liquid in the berms is water that washed over the berms during recent flooding or during rain provided by the hurricane. As is typical for matched filters there are a large number of false positives, in this case for water-Ottawa along the unpaved roadway and along the edge of tank #6. Many of these pixels are mixed between a bare soil land cover and some other material such as unpaved roadway material (e.g., crushed aggregate) or petroleum tank paint, the latter of which often has organic binders or plasticizers that can produce hydrocarbon absorption features.
Figure 4-37: MF/IS results for water, motor oil, and light crude on Ottawa sand substrate, QUAC atmospheric compensation with cross-track illumination correction, Image ID: 20050907_005_012. (left) 3-band composite of MF/IS results with water-Ottawa (blue), motor oil-Ottawa (green), and light crude-Ottawa (red) loaded. Pixels with MF/IS values ≥ 0.01 are highlighted. (center) MF/IS values ≥ 0.01 overlain on false color composite, RGB: 1600/1050/650 nm. (right) Library spectra and mean spectra for all classified pixels.

Figure 4-38 provides the results for the FLAASH-compensated image with cross-track illumination correction. Very few pixels meet the same 0.01 threshold established for the QUAC cube: 82 (water-Ottawa), 7 (motor oil-Ottawa), and 1 (light crude-Ottawa). Almost half (n=40) of the water pixels are located on the edges of the standing liquid around tanks #3 and 4. Unlike the QUAC method, the FLAASH algorithm successfully mitigates the adjacency effect in the classified spectra, especially for motor oil (spectrum #5) and light crude (spectrum #6), as seen in the spectral plot in Figure 4-38. In these spectra, the residual “red edge” from 670-800 nm is largely removed. The library spectrum for water-Ottawa (#1) shows a similar but much more gradual increase.
in reflectance over the same wavelength range, which may have partially contributed to
the lingering “red edge” in the water-Ottawa spectrum (#4). A more likely source for this
edge is the contribution of the substrate to the spectra; in many cases the pixels are
located in berms where the nearest, dry pixels largely consist of vegetation.

Figure 4-38: MF/IS results for water, motor oil, and light crude on Ottawa sand
substrate, FLAASH atmospheric compensation with cross-track illumination correction,
Image ID: 20050907_005_012. (left) MF/IS values ≥ 0.010 overlain on false color
composite, RGB: 1600/1050/650 nm. (center) 3-band composite of MF/IS results with
water-Ottawa (blue), motor oil-Ottawa (green), and light crude-Ottawa (red) loaded.
Pixels with MF/IS values ≥ 0.010 are highlighted. (right) Library spectra and mean
spectra for all classified pixels.

To get a comparable number of pixels to those in the QUAC cube, the MF/IS
threshold was lowered from 0.01 to 0.007 (Figure 4-39). In this case, there are 531
water-Ottawa pixels, 107 motor oil-Ottawa pixels, and 4 light crude-Ottawa pixels. As
seen with the higher threshold, the vast majority of water-Ottawa pixels are congregated along the presumably shallow edges of the standing liquids inside the berms and spatially mixed pixels comprised of standing liquid and non-submerged substrate, especially tanks #2-4. The pixels along the edges of tanks #1 and 6 are more likely mixed pixels consisting of bare soil or vegetation, combined with the tank paint, a spectral confuser for petroleum. While in this image there are some motor oil-Ottawa pixels inside the liquid pools, they are vastly outnumbered by the water pixels, except in the case of tank #5, which is inconclusive (5 “pure” pixels classified as motor oil, 11 “pure” pixels classified as water). Most of the remainder are in two bad columns or are false positives on objects along the extreme right hand side of the image. Three of the four light crude pixels are false positives on an object in the same area while the fourth is a mixed pixel of tank paint and shadow cast by tank #5. Using the larger number of presumed motor oil and light crude false positives as a figure of merit, the slightly poorer results for this cube, when compared to the QUAC-compensated cube, may be a byproduct of FLAASH’s assumption of full solar illumination and clear skies. Field notes from the data acquisition state that the data were acquired under “[p]artially” to “[m]oderately [c]loudy” conditions.
The QUAC-compensated scene without illumination correction provides comparable results to the one with the correction (Figure 4-40). Again, the pixels cluster around the edges of the standing pools and in horizontally mixed liquid/substrate pixels, especially tanks #2-4. There are 524 water-Ottawa pixels, compared to 20 motor oil-Ottawa and one light crude-Ottawa pixel. Between the motor oil and the light crude, only one motor oil-Ottawa pixel falls in/on standing liquid. Numerous water-Ottawa false positives are again evident as mixed pixels along the unpaved road and along portions of the petroleum tanks. The red-edge artifact in all three in-scene ROI spectral means is again apparent.

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**LEGEND for Spectral Plot**

| 1 = Water-Ottawa (blue) (library) | 2 = Motor Oil-Ottawa (green) (library) |
| 3 = Light Crude-Ottawa (red) (library) | 4 = Water-Ottawa (blue) (MF/IS) |
| 5 = Motor Oil-Ottawa (green) (MF/IS) | 6 = Light Crude-Ottawa (red) (MF/IS) |

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**Figure 4-39**: MF/IS results for water, motor oil, and light crude on Ottawa sand substrate, FLAASH atmospheric compensation with cross-track illumination correction, Image ID: 20050907_005_012. (left) MF/IS values ≥ 0.007 overlain on false color composite, RGB: 1600/1050/650 nm. (center) 3-band composite of MF/IS results with water-Ottawa (blue), motor oil-Ottawa (green), and light crude-Ottawa (red) loaded. Pixels with MF/IS values ≥ 0.007 are highlighted. (right) Library spectra and mean spectra for all classified pixels.
Figure 4-40: MF/IS results for water, motor oil, and light crude on Ottawa Sand substrate, QUAC atmospheric compensation without cross-track illumination correction, Image ID: 20050907_005_012. (left) 3-band composite of MF/IS results with water-Ottawa (blue), motor oil-Ottawa (green), and light crude-Ottawa (red) loaded. Pixels with MF/IS values $\geq 0.01$ are highlighted. (center) MF/IS values $\geq 0.01$ overlain on false color composite, RGB: 1600/1050/650 nm. (right) Library spectra and mean spectra for all classified pixels.

Figures 4-41 – 4-44 show the material identification results substituting the quartzic beach sand and vegetation substrates in the cross-track corrected QUAC and FLAASH cubes. Since these substrates are more spectrally similar to those from unsubmerged pixels inside the petroleum tank berms, higher thresholds were used in the material identification process.

Figures 4-41 and 4-42 show the results using the QBS substrate for the QUAC and the FLAASH compensated cubes, respectively. The QUAC cube threshold is 0.02 while the FLAASH cube threshold is 0.01. In the QUAC cube, there are 51 water-QBS pixels. None of the pixels met the 0.02 threshold for either the motor oil-QBS or light...
crude-QBS spectra. Most of the positive identifications are false positives similar to those described above whereas approximately 18 pixels are located in areas with standing liquid, especially around tank #6 and to a lesser extent, around tank #3.

Using the lower threshold, the FLAASH cube has 787 water-QBS pixels, one motor oil-QBS, and nine light crude-QBS pixels. Fifty of the water-QBS pixels are located in a bad column in the middle of the image which crosses through the flooded berms for tanks #2 and 4. Potentially legitimate identifications are located around all six tanks, with considerable false positives (>100) located along the unpaved road, in petroleum tank shadows, and in mixed pixels consisting of the petroleum tank and the adjacent floating liquid. Whereas the strong resemblance of the mean water-QBS spectrum (Figures 4-41 and 4-42, spectral plot #4) to vegetation may be attributed to uncompensated adjacency effect in the QUAC cube, its presence in the FLAASH cube indicates that many of these pixels are more likely on a vegetated substrate than a purely sandy one.
Figure 4-41: MF/IS results for water, motor oil, and light crude on quartzic beach sand (QBS) substrate, QUAC atmospheric compensation with cross-track illumination correction, Image ID: 20050907_005_012. (left) 3-band composite of MF/IS results with water-QBS (blue), motor oil-QBS (green), and light crude-QBS (red) loaded. Pixels with MF/IS values $\geq 0.02$ are highlighted. (center) MF/IS values $\geq 0.02$ overlain on false color composite, RGB: 1600/1050/650 nm. (right) Library spectra and mean spectra for all classified pixels. No pixels met the 0.02 threshold for the light crude or motor oil.
Figure 4-42: MF/IS results for water, motor oil, and light crude on QBS substrate, FLAASH atmospheric compensation with cross-track illumination correction, Image ID: 20050907_005_012. (left) MF/IS values $\geq 0.010$ overlain on false color composite, RGB: 1600/1050/650 nm. (center) 3-band composite of MF/IS results with water-QBS (blue), motor oil-QBS (green), and light crude-QBS (red) loaded. Pixels with MF/IS values $\geq 0.010$ are highlighted. (right) Library spectra and mean spectra for all classified pixels.

Figures 4-43 and 4-44 show the results using the vegetation substrate for the QUAC and the FLAASH compensated cubes, respectively. Like the QBS substrate examples, the QUAC cube threshold is 0.02 while the FLAASH cube threshold is 0.01. In contrast to the relative paucity of identified pixels in the QUAC-compensated QBS cube ($n=51$), when the substrate is changed to vegetation, there are 534 water-vegetation pixels identified, along with one light crude-vegetation pixel and no motor oil-vegetation pixels. The order of magnitude increase in the number of identified pixels is likely an artifact caused by the uncompensated adjacency effect and the subsequent appearance of the distinctive vegetative red-edge in all the pixel spectra for this scene (see Figures 4-41
above and Figure 4-43 below). This argument is further buttressed by the fact that the number of pixels that meet the threshold for the FLAASH-compensated cube is commensurate between the QBS substrate (n=787) and the vegetation substrate (n=514) (see Figure 4-44 below), especially when compared to the order of magnitude difference between the QUAC-compensated QBS and vegetation substrates (n=51 vs 534).

In addition to the 514 water-vegetation pixels in the FLAASH-compensated cube, there were two motor oil-vegetation pixels and nine light crude-vegetation pixels. Of the 514 water-vegetation pixels, 58 were clearly in two bad columns spanning the flooded berms for tanks #2 and #4, along with the top of tank #4.
Figure 4-43: MF/IS results for water, motor oil, and light crude on vegetation substrate, QUAC atmospheric compensation with cross-track illumination correction, Image ID: 20050907_005_012. (left) 3-band composite of MF/IS results with water-vegetation (blue), motor oil-vegetation (green), and light crude-vegetation (red) loaded. Pixels with MF/IS values $\geq 0.02$ are highlighted. (center) MF/IS values $\geq 0.02$ overlain on false color composite, RGB: 1600/1050/650 nm. (right) Library spectra and mean spectra for all classified pixels. Note that no pixels met the 0.02 threshold for the motor oil-signature.
In summary, while the number of individual pixels identified varied across the three substrates (i.e., Ottawa sand, quartzic beach sand (QBS), and vegetation) and two atmospheric compensation strategies (i.e., FLAASH and QUAC), water was much more commonly identified than either motor oil or a light crude as the liquid(s) (reported as unidentified by emergency response teams) inside the flooded berms at this tank farm during the days in the wake of Hurricane Katrina. The results of each of these permutations are summarized in a set of small multiples (Tuft, 1990) in Figure 4-45. The uncompensated adjacency effect is especially evident in the QUAC cube with the 0.01 threshold where there is a disproportionately large increase in the number of
supposed detections when compared to the other substrates. The relatively large number of other false positives, while disconcerting, is not a significant concern since the analytical goal is not a land cover classification but instead a simple determination of the material type—hydrocarbon or water—inside the flooded berms.

Based on these results, water is a more likely candidate for the standing liquid in this scene than either a refined product such as motor oil or a light crude oil. Without ground truth information, these results are not definitive but they are encouraging. This conclusion is buttressed by the lack of any spill reports in the USCG NRC database for this area around the dates of Hurricane Katrina (NRC, 2011).
Figure 4-45: MF/IS values overlain on false color composite, RGB: 1600/1050/650 nm for light crude (red), motor oil (green), and water (blue) on (left) Ottawa sand substrate, (center) quartzic beach sand (QBS) substrate, and (right) vegetation substrate. Top row includes MF/IS values $\geq 0.02$ for QUAC-compensated cubes. Center row includes MF/IS values $\geq 0.01$ for QUAC-compensated cubes. Bottom row includes MF/IS values $\geq 0.01$ for FLAASH-compensated cubes. Note that for all three substrates, the vast majority of pixels for the flooded petroleum tank areas are identified as water.
Hurricane Katrina came ashore at New Orleans, LA, on 29 August 2005. By the next day, floodwater topped the dikes near the Murphy Oil Refinery in nearby Chalmette and Meraux, LA, submerging its petroleum tank farm. Four days later, on 3 September, a refinery worker and local residents discovered oil in the neighborhood adjacent to the refinery. Floodwaters that had spilled over the berms displaced one of the refinery’s tanks, spilling 25,110 barrels (1,054,620 gallons/3,991,737 liters) of a light crude oil (38° API). Ultimately, >1 mi² of neighborhoods, canals, and the refinery were affected (Franklin, 2006). Image 20050906_012_001 covers a portion of the refinery, including the compromised tank and significant portions of the adjacent community, and was captured three days after oil was discovered.

Due to the probable liquid depth throughout this scene, it is unlikely that a sufficient number of photons successfully exited the pooled water/oil to identify the underlying substrate. As a result, identification of the substrate is unlikely. A more realistic goal in this scenario is discrimination of areas in the scene where water or crude oil dominates the surface.

In this image, pooled liquid is one of the two most significant land cover types dominating the scene (Figure 4-46 (left)). As a result, attempting to isolate the liquid spectra from a covariance matrix, as a matched filter does, would prove difficult. Instead, for this image, the SAM algorithm was used to attempt to discriminate floating petroleum from water. In this case, the SAM rule image was more useful than the pre-thresholded SAM classified image because it is possible to interactively set thresholds based on spectral angle during data analysis. To minimize spurious returns from non-submerged...
areas in this scene, most of these areas were masked out after the atmospheric compensation step but before the material detection/identification step.

Figure 4-46: Results of SAM rule classifier for light crude, motor oil, and water on Ottawa sand substrate, Image ID: 20050906_012_001. (left) False color composite: R/G/B: 1600/1050/650 nm. The tank that was the source of the spill is circled in red. Filled polygons are regions of interest discussed in the text. (center) SAM Rule Classifier (0.01-0.35 radians), non-water areas masked out, QUAC image: possible hydrocarbons=red, water=cyan, equal likelihood of both=white. (right) SAM rule image (0.20-1.0 radians), non-water areas masked out, FLAASH image: possible hydrocarbons=red, water=cyan, equal likelihood of both=white.
The material detection/identification results are displayed in Figure 4-46. The image on the left is a false color composite (RGB: 1600/1050/650 nm). The compromised tank is circled in red. Floodwaters and/or oil occur throughout the scene, filling all areas at or around ground level including all of the petroleum tank berms, each road in the neighborhood adjacent to the refinery and the canal running next to the refinery in the lower right portion of the scene. The center and right images are color composites where a SAM rule image is displayed in each of the three display channels. In both images, the SAM rule image for water-Ottawa sand is displayed in red and light crude-Ottawa is displayed in both green and blue. In the QUAC scene, all three detection planes are scaled to the same range (0.01-0.35 radians) to minimize how histogram stretching might artificially enhance contrast. In the FLAASH scene, the colors are limited to 0.01-0.75 radians.

Contrary to matched filters, in SAM rule images the lower values are the better matches. As a result, a red pixel is indicative of a high SAM rule value for water-Ottawa in the red with simultaneous low green and blue values for light crude-Ottawa and hence, a poor match for water and a strong match for light crude. Likewise, a cyan pixel is a low value in the red for water with simultaneous high values for light crude-Ottawa in the green and blue. This is a poor match for light crude-Ottawa and a strong match for water-Ottawa. White pixels have relatively high values for both library spectra, and hence are inconclusively segmented. Black pixels are areas that are not underwater/under-oil and have been masked out. The center image is the result using the QUAC-compensated scene. The image on the right uses the FLAASH-compensated
scene. The lowest rule value for any material in any of the ROIs in the FLAASH scene was 0.54, well outside the standard SAM classification threshold of 0.10 radians. Like the previous image, probable cloud cover during image acquisition may have compromised FLAASH’s performance, which is only briefly discussed below. In all three scenes, there are four ROIs highlighted in red (169 pixels), blue (153 pixels), green (212 pixels), and yellow (250 pixels), from top to bottom.

As mentioned above, the red color in the QUAC-compensated image of Figure 4-46 (center) indicates that the area is largely covered in crude oil. At the refinery, the petroleum tank berms and the area just outside the right-most tanks have much stronger (i.e., lower) crude oil response than those for water. For the green ROI inside the ruptured tank berm, the mean and standard deviation values for light crude-Ottawa is 0.12 +/-0.03 whereas it is 0.23 +/-0.03 for water-Ottawa (1 σ, 212 pixels). The yellow ROI is in an area just outside the petroleum tank berms and is predominantly cyan indicating that it is water. The mean and standard deviation for this ROI is 0.09 +/-0.04 for water-Ottawa and 0.31 +/-0.05 for light crude-Ottawa (1 σ, 250 pixels). Moving away from the refinery into the adjacent neighborhood, the three blocks closest to the refinery along the road perpendicular to the tanks are also dominated by crude. Along the side streets, the closest street on the right and the two closest streets on the left have the strongest returns. The blue ROI along one of these streets returned values of 0.09 +/-0.04 for light crude-Ottawa and 0.31 +/-0.04 for water-Ottawa (1 σ, 153 pixels). Moving three blocks farther away from the refinery, the values for the red ROI are 0.05 +/- 0.02 for water-Ottawa and 0.34 +/- 0.03 for light crude-Ottawa (1 σ, 169 pixels).
Figure 4-47 shows the SAM rule image histograms for each of the ROIs. In each case, the red histogram displays the SAM rule value for light crude-Ottawa for all pixels inside the respective ROI whereas the green histogram displays the results for water-Ottawa. The top two plots are for the blue and green ROIs, respectively. Both show a strong preference for light crude (red) versus water (green). The middle two plots are for the red and yellow ROIs and demonstrate the opposite conclusion, a strong preference, indicated by lower SAM rule values, for water-Ottawa. The bottom plot in Figure 4-47 summarizes these histograms by plotting the mean for each ROI for both light crude (i.e., Material #1) on the left hand side of the x-axis and water (i.e., Material #2) on the right hand side of the x-axis. As the plot indicates, both the blue and green ROIs have much lower mean values for light crude-Ottawa than for water-Ottawa whereas both the yellow and red ROIs have much lower mean values for water-Ottawa than for light crude-Ottawa.
Figure 4-47: SAM rule values for light crude (red) and water (green) from four ROIs in Image 20050906_012_001. (upper left) Values for the blue ROI covering the residential street closest to the refinery. (upper right) Values for the green ROI covering the flooded berm of the compromised tank. (lower left) Values for red ROI covering residential street four blocks from the refinery. (lower right) Values for yellow ROI adjacent to the flooded berms and apparently partially protected by berms or booms. (bottom) Mean SAM rule values (in radians) for each ROI.
Spectra for each ROI are displayed in Figure 4-48. Note that the y-axes for the plots are scaled differently. Most notable is the dissimilarity between the image-derived ROI spectra from the QUAC-compensated cube (top) and the FLAASH-compensated cube (bottom) when compared to those from the spectral library (middle). The QUAC-derived spectra display the red-edge artifact also seen in image 20050907_005_012 above while all of the FLAASH-derived spectra have reflectance values <0 at wavelengths <500 nm. The blue and green ROIs have reflectance values <0 up to 800 nm. Despite these differences, both atmospheric compensation techniques show higher reflectances in the VNIR out to approximately 800 nm for the ROIs classified as water (i.e., red, yellow), presumably due to water’s transmissivity in this region of the spectrum. In the longer NIR wavelengths and in the SWIR, the four ROIs essentially have convergent spectra, due to the virtual opacity of both crude oil and water in these regions. While this ambiguity is disappointing, it is not surprising given the assumed depth of the floodwaters/oil combined with the poor spectral contrast commonly observed in pixels with low overall reflectance values. Additionally, the spectral library was designed for scenarios where the substrate is detectable beneath a thin liquid overlay. As a result, the library spectra (Figure 4-48, (middle)) are not very representative of those in the image (Figure 4-48, (top), (bottom)). FLAASH’s difficulty with the scene environmental conditions, specifically molecular scattering mitigation, are manifest in negative values for three of the four ROIs at wavelengths <800 nm. Like the previous image, probable cloud cover during image acquisition may have compromised FLAASH’s performance.
Figure 4-48: Spectra for ROIs highlighted in Figure 7 above, along with library spectra. (top) Spectra for the QUAC-compensated scene. (middle) Library spectra for water-Ottawa sand (green, and light crude-Ottawa sand (red). (bottom) Spectra for the FLAASH-corrected scene. In the QUAC scene, the red and yellow ROI’s were dominated by water and/or motor oil and the blue and green ROIs by light crude.

Given the lack of ground truth information for this data collection, the accuracy assessment of the classification results is restricted to the qualitative, manually digitized map from Franklin (2006). This map was compiled by field observations but there is understandably little metadata about the methods used to estimate the extent and intensity of oiling other than qualitative measures in the map legend of “heaviest,” “moderate,” and “light” oiling, combined with an area where oil lines were visually spotted on
structures. Figure 4-49 shows the false color composite of the scene (left), the false color composite with a manually digitized version of the field-compiled map overlain (center), and the SAM rule image for the QUAC-compensated cube with the digitized field-compiled map overlain (right). According to the field-compiled map, the blue and green ROIs are located in areas that were the most heavily oiled (Franklin, 2006). The yellow ROI is in an area that is marked as unaffected by the oil spill (blue dash-dots) whereas the red ROI is in the “heaviest” oiling area (red dash dots) but is very close to the edge of the “light” area (green dash-dots). In fact, >40% of the red ROI is <15 m from the edge of the “light” area. As mentioned above, the map has little geolocational accuracy metadata associated with it. While the potential mis-classification of the red ROI is disappointing, it is somewhat questionable given the proximity of the “light” oiled area and the strong preference for water versus light crude in the SAM rule image for the ROI (0.05 +/- 0.02 for water-Ottawa, 0.34 +/- 0.03 for light crude-Ottawa (1 σ, 169 pixels)).
Figure 4-49: Digitized field map of areas affected/unaffected by the Murphy Oil Refinery spill overlaid on image 20050906_012_001. (left) False color composite: R/G/B: 1600/1050/650 nm. (center) Digitized field map of oil-affected areas from Franklin (2006) (red=heavy, orange=moderate, green=light, blue=unaffected). (right) Digitized field map overlain on SAM Rule image. Note how well the cyan pixels in the rule image compare to blue pixels in the overlay and how well the red pixels correspond to the red overlay areas. In the residential areas, the moderate and lightly oiled areas (orange and green) have better results for water than for light crude.

Figure 4-50 summarizes the SAM rule scores for each of the hand-digitized polygons in Figure 4-49 (center). As noted above, the red-hatched area is listed in the field-compiled map as the area affected by the “heaviest” oiling; the orange-hatched area with “moderate” oiling; the green-hatched area with “light” oiling; and the blue-hatched
area as unaffected. The red-hatched area (i.e., areas of heaviest oiling) (39,548 non-masked pixels) average SAM rule value for light crude-Ottawa was 0.15 +/- 0.07 (1 σ) whereas it was 0.20 +/- 0.07 for water. For the blue-hatched polygon (i.e., unaffected by oiling) (27,549 pixels), the water-Ottawa value was 0.17 +/- 0.09 whereas it was 0.23 +/- 0.11 for light crude-Ottawa. Whereas the results for the red and blue polygons are encouraging, the results for the orange-hatched and green-hatched polygons are ambiguous: 0.17 and 0.16 for both light crude-Ottawa and water-Ottawa, respectively.

The large standard deviations for both the red and blue ROIs are expected given the complex nature of crude oil spills mixing with water both horizontally and vertically. The visual manifestations of this complexity are evident in the right image from Figure 4-49, where red pixels (oil) can be seen in the blue ROI (water) and cyan pixels (water) are visible in the red ROI (oil). Nonetheless, using the SAM rule image to segregate light crude from water successfully discriminates the heaviest oiled area from the area unaffected by the spill but still underwater. The presumably lighter concentrations of oil in the “moderate” and “light” affected areas produced results that are nearly identical to those for water, resulting in ambiguous segregation in these areas.
Figure 4-50: SAM rule values for non-masked pixels for each of the colored polygons in Image 20050906_012_001. (top) Plot of SAM rule values for light crude (Material #1) and water (Material #2) for four ROIs based on a field-compiled map of the spill. (bottom) Table summarizing each polygon’s SAM rule statistics. The values in the “Oil Status” column are from Franklin (2006).

<table>
<thead>
<tr>
<th>Oil Status</th>
<th>Polygon color</th>
<th>Number of unmasked pixels</th>
<th>Mean Light Crude-Ottawa</th>
<th>Standard Deviation (1 σ)</th>
<th>Mean Water-Ottawa</th>
<th>Standard Deviation (1 σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Heaviest&quot;</td>
<td>Red</td>
<td>39,548</td>
<td>0.15</td>
<td>0.07</td>
<td>0.20</td>
<td>0.07</td>
</tr>
<tr>
<td>&quot;Moderate&quot;</td>
<td>Orange</td>
<td>6366</td>
<td>0.17</td>
<td>0.06</td>
<td>0.16</td>
<td>0.05</td>
</tr>
<tr>
<td>&quot;Light&quot;</td>
<td>Green</td>
<td>5034</td>
<td>0.17</td>
<td>0.06</td>
<td>0.16</td>
<td>0.06</td>
</tr>
<tr>
<td>Unaffected</td>
<td>Blue</td>
<td>27,549</td>
<td>0.23</td>
<td>0.11</td>
<td>0.17</td>
<td>0.09</td>
</tr>
</tbody>
</table>
5 CONCLUSIONS AND FURTHER RESEARCH

5.1 Conclusions

World demand for oil continues to increase annually, in recent years by 1.5-2.0 million barrels per day (bbl/d). The Energy Information Administration estimates that world consumption will reach 90.0 million bbl/d in 2012 (EIA, 2011b). The U.S. imports approximately one-half of its oil—9.4 million bbl/d in 2010—with Canada (25%), Saudi Arabia (12%), Nigeria (11%), Venezuela (10%), and Mexico (9%) providing approximately two-thirds of the total (EIA, 2011a). These quantities are shipped by sea and through 200,000 miles (320,000 km) of pipeline in the U.S. and can be transferred up to 15 times from source to destination (EC, 1994; EIA, 2003). Petroleum’s ubiquity means that oil and refined petroleum product spills are, and will continue to be, a significant concern for the foreseeable future.

The Deepwater Horizon catastrophe is the most recent example of the collateral environmental damage from petroleum spills. Approximately 4.9 million barrels (206 million gallons/780 million liters) of crude leaked from the Macondo well for 87 days (NYT, 2010). At its peak, the spill oiled 1050 miles (1700 km) of coastline in the Gulf of Mexico, >500 miles (>800 km) of which still contained oil as of April, 2011, one year after the original spill. Despite the huge geographic area touched by the spill, the most common method of detecting oil reaching and persisting on shore was (and still is) by
visual spotting from aircraft or by in situ discovery by persons on site (NOAA, 2007; NOAA, 2011).

During environmental disasters such as the Deepwater Horizon, it is common practice to fly over affected areas and to use satellite-based resources to capture remote sensing data. While the purpose is to gain a synoptic view of the event and to visually identify impacted areas, this is often difficult to accomplish using panchromatic or natural color imagery over littoral or flooded areas where petroleum and petroleum products are often confused with water. Additionally, inland spills at industrial facilities can be mistaken for water pooling in secondary containment areas (i.e., behind berms) and vice versa. The goal of this research is to facilitate petroleum and petroleum product detection in these scenarios. It was accomplished using a twofold approach. First, lab spectra measured a representative set of petroleum, petroleum products, and water on common terrestrial substrates to populate a spectral library that can be employed during future natural disasters and industrial accidents. Second, the utility of these spectra were demonstrated when discriminating water from petroleum using remotely sensed hyperspectral data.

Petroleum product detection and identification rely on the availability of spectral signature libraries of target materials. Yet to-date, there are no publicly available spectral signature libraries for petroleum products. This research begins to fill this gap by measuring the spectral signatures in the VNIR/SWIR of four crude oils and five refined products on ten common terrestrial substrates and Spectralon™, creating 90 different liquid-substrate combinations and ten neat spectra for reference purposes. Spectra of
water on the same ten spectra substrates were also collected, resulting in a total of 110 liquid-substrate spectra in the library. These measurements were conducted over an extended period of time so that petroleum volatility, manifested in the spectra, can be an additional variable employed to discriminate these products from one another. Documented measurement protocols ensure that the results are reproducible. Selected analysis also began to establish minimum detection thresholds for some products on various substrates. This portion of the research quantified the significance of a substrate’s contribution to the spectrum of a liquid-substrate mixture.

This effort also demonstrates how hyperspectral sensors operating in the VNIR/SWIR portion of the electromagnetic spectrum can detect petroleum and differentiate it from water with both high confidence and high sensitivity when they are present on spectrally bright substrates such as most sands. Substrates with their own absorption features which overlap hydrocarbon features (e.g., gypsum) complicate but do not preclude detection provided a sufficient quantity of the hydrocarbon is present.

Ultimately, the value of any spectral library is the ability to apply it to data collected from another time and place, and preferably, from an efficient method of data collection such as an airborne or spaceborne platform. The spectral signatures generated here were used against airborne hyperspectral from the Hurricane Katrina disaster with the goal of detecting and delineating petroleum and petroleum product spills. Using the MTMF algorithm, analysis of a flooded petroleum tank farm indicated that standing liquid inside the secondary containment areas was likely to be water, not oil or a refined petroleum product. In the case of the Murphy Refinery oil spill, the target materials—oil
and water—are omnipresent in the scene, greatly obstructing a useful statistical representation of the background. As a result, the SAM algorithm was used instead of a matched filter to discriminate oil from water. A field-compiled map of the spill largely agreed with the analysis of the airborne hyperspectral data from the HST-3 sensor.

5.2 Further Research

As the hyperspectral imagery analysis demonstrates, considerable progress still needs to be made to accurately detect and hopefully, identify crude oil and refined petroleum products on terrestrial substrates.

In the absence of time to perform standard hyperspectral-based material identification, detection heuristics might be a suitable “first-phase” product. Normalized difference indices (NDIs) are well suited to this purpose and previous efforts have already put forth multiple indices for detecting hydrocarbons on terrestrial surfaces (Taylor, 2000; Kühn et al., 2004; Allen and Satterwhite, 2006). Future work should test these indices in a controlled environment to deduce which may best contribute to detecting both large and small quantities on a variety of substrates that range from the nearly ideal (e.g., Ottawa sand) to the vexing (e.g., gypsum, asphalt). These NDIs should also be able to discriminate petroleum from water, which is often difficult to do with the naked eye, the most common method in-use today.

In addition to detection heuristics, there are additional fruitful avenues of future research. Once a hydrocarbon is detected, additional metrics might be employed that can determine the depth of a standing liquid on a substrate. With that, combined with a reasonable assumption of the permeability of the substrate, a volume estimate of the spill
could be ascertained. Clark et al. (2010) have recently demonstrated these possibilities for oil on water as part of the *Deepwater Horizon* incident response effort.

As Fingas (1997, 1998) has noted, the rates of evaporation change with temperature. All of the lab measurements in this effort were conducted within a narrow, <5° C, range of temperatures. Instead of effectively controlling for temperature, additional efforts might measure how spectra change under a range of temperature regimes, with volatiles and semi-volatiles accelerating as the temperature rises. These efforts might assist incident responders or imagery analysts in deciding the identity of an unknown hydrocarbon based upon its rate of evaporation under various temperature regimes.

In addition to advancing the state of hyperspectral imagery analysis of hydrocarbons, future work might also employ other imaging modalities. As the photo in Figure 5-1 demonstrates, crude oil fluoresces when illuminated by ultraviolet (UV) light, an effect noted by multiple researchers over the last four decades (see e.g., Alaruri et al., 1995, for a summary). While airborne laser-induced fluorescence imaging (LIFI) sensors have existed for at least three decades, there is very little in the literature regarding fluorescence libraries. Additional research might build upon preliminary efforts such as Balick et al. (1996) to begin creating these libraries so that when airborne sensors become more common, they can leverage the time consuming work of creating a reference library of fluorescence spectra.
Figure 5-1: Handheld photograph of crushed aggregate and asphalt lab samples (left) and the same samples illuminated by UV light (right). Fluorescing oil colors the substrates with a mustard yellow color in the right photograph. The oil produced the same color for all substrates and for a neat sample in a glass petri dish.
APPENDIX

This Appendix includes plots for all liquids on all substrates not specifically discussed in the text above. They are organized in the following order: acetone, gasoline, E85, diesel fuel, motor oil, light crude, intermediate sour crude, intermediate sweet crude, heavy crude, and water. Within each liquid, the substrates are arranged alphabetically. Hence, acetone on asphalt is first and water on vegetation is last. There are 2 plots per page.

In the plots, the liquid and the substrate are listed at the top. Any inter-spectrometer offsets at 976 and 1801 nm are not mitigated in these spectra. The vertical gray boxes from 1300-1500 and 1800-2000 nm are meant to indicate regions where airborne/spaceborne instruments would be largely unable to image due to atmospheric absorption; these bands would thus have limited utility for most remote sensing applications.
Acetone on Highly Organic Soil

Acetone on Ottawa Sand

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Gasoline on Asphalt

Gasoline on Bentonite
Gasoline on Calcareous Sand

Gasoline on Calcite-Dolomite Crushed Aggregate
### Gasoline on Vegetation

- **Wavelength (nm):** 400-2400
- **Reflectance:** 0.0-0.8

- **Samples:**
  - Control - baseline
  - Samples - 0 mins
  - Samples - 13 mins
  - Samples - 28 mins
  - Samples - 42 mins
  - Samples - 59 mins
  - Samples - 91 mins
  - Samples - 127 mins
  - Samples - 149 mins
  - Samples - 181 mins
  - Samples - 211 mins
  - Samples - 241 mins
  - Samples - 273 mins
  - Samples - 308 mins
  - Samples - 361 mins
  - Samples - 422 mins
  - Samples - 491 mins
  - Samples - 545 mins
  - Samples - 607 mins
  - Samples - 905 mins
  - Samples - 1.0 days
  - Samples - 1.3 days
  - Samples - 1.7 days
  - Samples - 2.1 days
  - Samples - 3.1 days
  - Samples - 6.3 days
  - Samples - 6.7 days
  - Samples - 10.7 days
  - Samples - 36.6 days

### E85 on Asphalt

- **Wavelength (nm):** 400-2400
- **Reflectance:** 0.0-0.8

- **Samples:**
  - Control - baseline
  - Samples - 0 mins
  - Samples - 15 mins
  - Samples - 30 mins
  - Samples - 60 mins
  - Samples - 86 mins
  - Samples - 125 mins
  - Samples - 154 mins
  - Samples - 208 mins
  - Samples - 269 mins
  - Samples - 338 mins
  - Samples - 649 mins
  - Samples - 1.1 days
  - Samples - 1.5 days
  - Samples - 3.3 days
  - Samples - 7.2 days
Diesel Fuel on Calcareous Sand

Reflectance vs. Wavelength (nm)

Control - baseline
- Samples - 0 mins
- Samples - 16 mins
- Samples - 31 mins
- Samples - 48 mins
- Samples - 61 mins
- Samples - 90 mins
- Samples - 125 mins
- Samples - 148 mins
- Samples - 179 mins
- Samples - 241 mins
- Samples - 302 mins
- Samples - 368 mins
- Samples - 486 mins
- Samples - 1.0 days
- Samples - 2.0 days
- Samples - 3.5 days
- Samples - 5.5 days
- Samples - 7.5 days
- Samples - 9.5 days
- Samples - 13.3 days
- Samples - 15.6 days
- Samples - 18.3 days
- Samples - 21.6 days
- Samples - 25.2 days
- Samples - 31.4 days
- Samples - 36.8 days
- Samples - 46.0 days
- Samples - 59.5 days
- Samples - 64.6 days
- Samples - 80.0 days
- Samples - 89.0 days

Diesel Fuel on Calcite-Dolomite Crushed Aggregate

Reflectance vs. Wavelength (nm)

Control - baseline
- Samples - 0 mins
- Samples - 16 mins
- Samples - 31 mins
- Samples - 47 mins
- Samples - 61 mins
- Samples - 92 mins
- Samples - 111 mins
- Samples - 171 mins
- Samples - 237 mins
- Samples - 301 mins
- Samples - 344 mins
- Samples - 5 days
- Samples - 7.4 days
- Samples - 9.4 days
- Samples - 13.2 days
- Samples - 18.1 days
- Samples - 21.4 days
- Samples - 25.0 days
- Samples - 31.3 days
- Samples - 39.0 days
- Samples - 50.3 days
- Samples - 59.4 days
- Samples - 64.4 days
- Samples - 79.8 days
- Samples - 88.9 days

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Diesel Fuel on Quartzic Beach Sand

Diesel Fuel on Vegetation
Motor Oil on Asphalt

Motor Oil on Bentonite
Motor Oil on Concrete

Motor Oil on Gypsum Sand

205
Motor Oil on Quartzic Beach Sand

Motor Oil on Vegetation

Samples - 0 mins
Samples - 28 mins
Samples - 63 mins
Samples - 92 mins
Samples - 124 mins
Samples - 190 mins
Samples - 258 mins
Samples - 315 mins
Samples - 1.5 days
Samples - 3.4 days
Samples - 5.4 days
Samples - 9.5 days
Samples - 13.1 days
Samples - 23.0 days
Samples - 45.9 days
Samples - 87.1 days
Samples - 122.5 days
Samples - 169 days (#1 only)

Samples - 0 mins
Samples - 17 mins
Samples - 34 mins
Samples - 54 mins
Samples - 80 mins
Samples - 111 mins
Samples - 135 mins
Samples - 167 mins
Samples - 206 mins
Samples - 244 mins
Samples - 306 mins
Samples - 502 mins
Samples - 1.0 days
Samples - 1.3 days
Samples - 3.6 days
Samples - 6.5 days
Samples - 10.6 days
Samples - 14.3 days
Samples - 24.1 days
Samples - 47.0 days
Samples - 88.3 days
Samples - 123.6 days
Samples - 170 days (#1 only)
Intermediate, Sour Crude on Quartzic Beach Sand

Intermediate, Sour Crude on Vegetation
Heavy Crude on Quartzic Beach Sand

Heavy Crude on Vegetation
Water on Asphalt

Water on Bentonite

later data have significant offsets due to deformation of bentonite, causing major sample heterogeneity.
Water on Vegetation

Control - baseline
Samples - 0 mins
Samples - 15 mins
Samples - 30 mins
Samples - 45 mins
Samples - 60 mins
Samples - 89 mins
Samples - 119 mins
Samples - 145 mins
Samples - 175 mins
Samples - 235 mins
Samples - 300 mins
Samples - 362 mins
Samples - 429 mins
Samples - 686 mins
Samples - 1.0 days
Samples - 1.4 days
Samples - 2.2 days
Samples - 2.6 days
Samples - 3.4 days
Control - 0.8 days
Control - 1.4 days
Control - 2.2 days
Control - 2.6 days
Control - 3.4 days
LIST OF REFERENCES
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CURRICULUM VITAE

C. Scott Allen received his Bachelor of Arts from Mary Washington College in 1995, his Master of Arts from the State University of New York-Stony Brook in 1996, and his Master of Science from George Mason University in 2001.