0.45- to 1.1-μm Spectra of Prudhoe Crude Oil and of Beach Materials in Prince William Sound, Alaska

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PREFACE

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The author thanks Dr. Jaqueline Michel, for helicopter transportation from Anchorage to Prince William Sound, and Dr. Richard Birnie and Dr. Donald Perovich for the use of their SE590 instruments. Dr. Birnie is also thanked for providing a copy of software he and others developed at Dartmouth to analyze SE590 data on a Macintosh computer. Steven Willis kindly ran the spectra through the mixing model program developed at the University of Washington. Dr. Donald Perovich and Dr. Robert Davis reviewed the manuscript and their comments improved the paper.

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CONTENTS

Preface ........................................................................................................... ii
Introduction .................................................................................................... 1
Instruments and methods.............................................................................. 2
Results ........................................................................................................... 4
Conclusions ................................................................................................... 13
Literature cited .............................................................................................. 14
Abstract ......................................................................................................... 15

ILLUSTRATIONS

Figure
1. Experimental setup showing water filled tanks and the radiometer head at the end of the L-shaped metal pipe ........................................................................ 2
2. Spectral measurements of oil on water .......................................................... 4
3. Location of field sites in Prince William Sound ........................................... 6
4. Average spectra of cobble and pebble beaches .......................................... 8
5. Average spectra of a flat rock and adjacent cobbles of same lithology ....... 9
6. Average spectra of beach materials with oil .............................................. 9
7. Average spectra of organic materials ......................................................... 10
8. Average spectrum of drift wood ................................................................. 11
9. Average spectrum of barnacles ................................................................. 12
10. Average spectrum of mussels ................................................................. 12
11. Average spectrum of rock weed and oil ................................................. 13
12. Average spectrum of rock shown in Figure 5a and oil .............................. 13

TABLES

Table
1. Wavelengths of Landsat thermatic mapper bands and the band centers of Innotech’s MEIS II sensor ................................................................. 3
2. Percent reflectance of different targets as seen by Landsat thermatic mapper filters 1–4 ......................................................................................... 12
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INTRODUCTION

Eleven million gallons of Prudhoe crude were spilled in Prince William Sound on 24 March 1989. The large scale of this spill and the low population density along the affected shorelines highlighted the need for remote sensing systems that can detect oil on water and on land.

Identification of oil on water has been investigated at ultraviolet, visible, infrared and radar wavelengths, and a combination of these has been used to better detect oil (Vizy 1974, Estes and Senger 1972, Stewart et al. 1970). Most remote sensing devices measure differences in reflected radiation between the target and the background. In the case of oil on water, these differences in reflected radiation are caused by oil’s ability to suppress capillary waves, thereby smoothing the water and increasing the specular component of the reflected radiation (O’Neil 1983). Side looking airborne radar can detect the roughness change. Ultraviolet, visible and infrared sensors may see small changes in the reflectivity of the surface as well as oil windrows or other patterns formed by the oil.

Unfortunately, neither the reflectivity changes nor the surface patterns are specific to oil. For example, large-scale filamentous features, interpreted as oil windrows, could be windrowed algal blooms or sea foam. Only the laser fluorosensor, which induces characteristic fluorescence in oils, can positively identify oil (Fantasia and Ingrao 1974). Although a scanning fluorosensor would be the sensor of choice for this work, the prototype is under development and is not yet completed.

Reviews of the various remote sensing systems and their applicability to oil detection are presented by Estes and Senger (1972) and Fingas (1990).

Spectral differences between a material of interest and various backgrounds have been used to map the aerial distribution of distinct spectral units. These units can then, we hope, be correlated with something of interest such as a vegetation type, a rock type or, in this case, the presence of oil. Detecting oil depends upon the spectral contrast between the oil and its background. Terrestrial background surfaces are spectrally complex and changes produced by the addition of oil to a background spectrum are probably not unique. Crystalline mafic and ultramafic rocks have flat spectra with low reflectances, less than 10% (Adams and Filice 1967), and are probably indistinguishable from oil in the visible region. Other dark lithologies, such as shales, present the same problem. Small scale shadows, such as those seen on cobbled beaches, decrease the reflectance of the beach and can be confused with oil.

I made laboratory spectral reflectance measurements, defined as the ratio of radiation scattered from the surface to that impinging on the surface x 100, of Prudhoe crude, of fresh water and of different thicknesses of Prudhoe crude on water. Beach materials in Prince William Sound were also characterized with a spectroradiometer and a simple spectral mixing model was used to determine how an oil coating would change the reflectance of these background materials.

In an effort to see if existing remote sensing devices could detect spilled oil, filter functions for the Landsat Thematic Mapper (TM) spectral bands were used to calculate the percent reflectance for oil and different background materials for TM bands 1–4. The aerial distribution of most of these materials is smaller than a Landsat pixel, but it is anticipated that MEIS II (Multi-detector Electro-optical Imaging Sensor) data will be available for analysis and that the measurements presented here can be used in interpreting its imagery.
INSTRUMENTS AND METHODS

A Spectron Engineering SE590 spectroradiometer was used to characterize Prudhoe crude and different beach materials in Prince William Sound. The SE590 acquires a virtually continuous spectrum (with a point every 0.003 μm) from 0.368 to 1.114 μm. The microprocessor in the SE590 has 12-bit resolution and automatically subtracts the dark current from all 256 channels. The instrument was operated with a 6° field of view. For most measurements the spectrometer head was held 1 m above the target, resulting in a 10.5-cm-diameter footprint. The accompanying data logger was programmed to take eight consecutive measurements and save the average spectrum on tape. At least three spectra of each material were saved along with a spectrum of the standard.

A Spectralon standard was used to measure the incident radiation and is reported to have greater than 98% reflectance in the wavelength range of interest (Labsphere, Inc., no date). A computer program took each spectrum and produced a percent spectral reflectance curve by dividing the spectrum by its accompanying standard and multiplying by 100. The software also "trimmed" each spectrum by removing those parts of the spectrum below 0.45 μm and above 1.09 μm as these sections were noisy.

Variability in these measurements are the result of the precision of the instrument, the variability of the target (from location to location) and the variability introduced by changes in irradiance (cloud cover, sun elevation and time of year). Variability of the target was investigated by measuring different parts of the target. The effect of changes in the solar irradiance between measurements obtained at roughly the same time of day are minimized when radiance is converted to spectral reflectance.

Spectral measurements of Prudhoe crude oil were made between 10 am and 2 pm on sunny days in an outdoor test container at CRREL (Fig. 1). Two Plexiglas containers, each 60 cm³, were painted with flat black paint (to avoid introducing unwanted primary and reflected light) and filled with fresh water. Increasing amounts of Alaskan crude—1, 5, 19, 100 and 150

Figure 1. Experimental setup showing water filled tanks and the radiometer head at the end of the L-shaped metal pipe.
cm³—were poured into one of the containers and spectral measurements were made. Oil volumes of 1, 6 and 25 cm³ did not form continuous coatings, but the larger volumes of 125 and 250 cm³ formed oil coatings estimated to have thicknesses of 35 and 70 μm respectively. The other container was used as a control to monitor variability in the reflectance of fresh water under the same conditions as the oil, e.g., cloud cover, time of day and seasonal sun angle.

The spectral characteristics of the 70-μm-thick oil coating were measured intermitently over a 2-month period to see if there were any changes as the oil aged. The surface temperatures of the water and of the oil were also measured.

Field measurements were made at established NOAA sites in Prince William Sound and included various beach types and different beach materials, such as rock weed, black lichen, mussels, barnacles and drift wood. The beaches, representing high, intermediate and low energy conditions, had been described and monitored frequently since the Exxon Valdez accident and good information existed on the extent of initial oiling and on subsequent recovery (Michel et al. 1990). Spectral measurements were made on the mornings of 5–8 September 1990 and, except for 7 September, which was a cloudless day, the measurements were made under cloudy sky conditions. The measurements made on the clear day should be used for interpreting the satellite data as cloud cover may alter the reflectance of the target (Perovich 1990). The dates and times of the field work were set by the NOAA researchers who were measuring beach profiles at low tide.

MEIS II imagery and Landsat TM imagery are two multispectral data sets that exist for the Exxon Valdez oil spill. MEIS is an airborne, pushbroom-type sensor with silicon charge-coupled devices that respond to the 1.1-fm region of the spectrum. Interchangeable spectral filters allow us to tailor the sensor for specific applications. For the oil spill, six bands in the visible and two in the near infrared were selected (Table 1). For more information on the performance of the MEIS II system, see Neville et al. (1983).

Landsat satellite is in a north to south, sun synchronous orbit around the Earth. The near polar orbit provides repetitive coverage at the same local time; for Prince William Sound it is near noon time. The thematic mapper is a mechanical line scanner that acquires data in approximately 190-km swaths and has a resolution of 30 m. Of its seven band passes, four bands fall within the spectral range of the SE590 spectroradiometer; three are in the visible and one is in the near infrared (see Table 1).

The TM values for the various materials measured with the SE590 were calculated using eq 1.

\[
TM = \frac{\sum_{\lambda=1}^{n} T_{\lambda} R_{\lambda}}{\sum_{\lambda=1}^{n} T_{\lambda}}
\]

where \( T_{\lambda} \) = transmittance of the TM filter at a specific wavelength

\( R_{\lambda} \) = reflectance measured by the SE590 at a specific wavelength

\( n \) = number of wavelengths in each filter.

To obtain information on pixels containing more than one spectral unit (say a cobbble beach and an oil), the two spectral units can be treated as end-members in a linear spectral mixing model as in eq 2 (Singer and McCord 1979).

\[
R(\text{obs}) = (XaRaA.) + (XbRbB.) + (XabRaRbA.)
\]

where \( Xa + Xb + Xab = 1 \)

and \( \lambda \) = wavelength

\( R(\text{obs}) \) = observed reflectance at a specific wavelength

\( Ra = \) reflectance of material A

\( Rb = \) reflectance of material B

\( Xa = \) percent coverage of material A

\( Xb = \) percent coverage of material B

\( Xab = \) percent coverage of an A and B mixture.

This model adds \( X\% \) of the reflectance value at each wavelength of one material (end-member A) to \((100 - X)\% \) of the second material (end-member B). The resulting curve is a prediction of what the spectrum of an area would be if it were covered by \( X\% \) A and \((100 - X)\% \) B. The cross term in eq 2, representing a light ray passing through both materials A and B, is small for situations were the spectral units are of centimeter or meter scale and is therefore ignored. The linear mixing model generates a curve that reasonably approximates the measured reflectance of a surface with discrete spectral units that are centimeters or meters in size.

**Table 1. Wavelengths (μm) of Landsat thematic mapper bands and the band centers of Innotech's MEIS II sensor.**

<table>
<thead>
<tr>
<th>Band</th>
<th>Wave Length (μm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band 1</td>
<td>0.45–0.52</td>
<td>0.751</td>
</tr>
<tr>
<td>Band 2</td>
<td>0.52–0.60</td>
<td>0.676</td>
</tr>
<tr>
<td>Band 3</td>
<td>0.63–0.69</td>
<td>0.875</td>
</tr>
<tr>
<td>Band 4</td>
<td>0.76–0.90</td>
<td>0.642</td>
</tr>
<tr>
<td>Band 5</td>
<td>1.55–1.75</td>
<td>0.597</td>
</tr>
<tr>
<td>Band 6</td>
<td>10.40–12.50</td>
<td>0.518</td>
</tr>
<tr>
<td>Band 7</td>
<td>2.08–2.35</td>
<td>0.448</td>
</tr>
<tr>
<td>Band 8</td>
<td>0.549</td>
<td></td>
</tr>
</tbody>
</table>
RESULTS

Figure 2 shows the averaged spectra of water, water with 1 cm³ of oil, water with 25 cm³ of oil and water with 250 cm³ of oil. Of these only 250 cm³ of oil formed a continuous coating on the water's surface. Prudhoe crude has a low, featureless spectral reflectance signature. It is quite similar to that of water over the measured wavelength range, except that water is slightly more reflective than oil from 4.5 to 7.2 µm (Fig. 2a and d).

Increasing the oil thickness masks the signature of the underlying water. The addition of even a small amount of oil, as illustrated in Figure 2c, produces a flat, featureless spectrum much like that of oil. The spectra of 1 cm³ and of 6 cm³ of oil are similar to that of water because the discrete blobs of oil did not cover much of the water's surface. Not surprisingly, the variability among measurements is greater for the mixed oil–water cover than for either oil or water. Reflectance measurements of 1-mm to 1-cm-thick continuous coatings have not yet been made. Horvath et al. (1970) predict that increasing the oil thickness, a variable in their model, will have little effect in the ultraviolet portion of the spectrum but will increase the radiance at longer wavelengths.

The spectral properties of various beach types were measured in Prince William Sound. Figure 3 shows the location and appearance of the study sites. Spectral measurements were also made of beach materials with a significant (several square meters) aerial distribution.

Figure 2. Spectral measurements of oil on water. Each figure shows a spectrum (middle) obtained by averaging three or more spectra obtained from different 10-cm spots of the surface. The lines above and below are +σ and −σ. Also shown are TM wavelength ranges.

a. Water filled tank with no oil.

b. Water filled tank with 1 cm³ of oil.
These materials will contribute to the pixel value obtained by Landsat but should be visible from imagery obtained using the MEIS II, which has about a 2-m resolution.

The average spectra of cobble and pebble beaches generally show a maximum value around 0.6 μm, with small decreases in reflectance at shorter and longer wavelengths; there are no absorption features (Fig. 4). Although the shapes of the curves are similar, their reflectance values vary from 20% for a fully illuminated rock slab to 10% for an adjacent cobbled surface composed of the same rock type (Fig. 5). Shadows decrease the reflectance but do not change the shape of the spectrum. The addition of oil to a cobble or pebble beach material lowers the reflectance but also flattens the spectrum. Figure 6a shows the average spectrum for a cobbled beach with a tarry residue and Figure 6b was made on an elevated portion of sheltered pebble beach that was oiled. These last two spectra are much flatter than the other cobble and pebble spectra.

The organic materials, on the other hand, have very distinctive spectra and considerably higher reflectance. The rock weed and kelp show an increase in reflectance in the green and a large increase at 0.7 μm in the infrared, a spectrum characteristic of chlorophyll. Figures 7a and b are spectra of rock weed and kelp that had been washed ashore. Figure 7c is a spectrum of living rock weed. The spectrum of drift wood shows a steady increase in reflectance with wavelength, a shallow dip at 0.95 μm, and a decrease in reflectance at wavelengths

c. Water filled tank with 25 cm³ of oil.

d. Water filled tank with 250 cm³ of oil.

Figure 2 (cont'd).
Site 1, Point Helen, Knight Island—exposed, relatively high energy cobble/boulder beach.

Site 2, Evans Island—sheltered, low energy pebble/cobble beach.

Figure 3. Location of field sites in Prince William Sound. Except for site 2, all the site numbers and classifications are from Michel et al. (1990).
Site 3, Smith Island—exposed, relatively high energy cobble/boulder beach.

Site 4, Block Island—pebble beach and tidal mud flat.

Site 5, Naked Island—pebble/cobble beach.

Site 7, Knight Island—exposed, relatively high energy cobble/boulder beach.

Site 10, Herring Bay, Knight Island—rocky beach.

Site 13, Herring Bay, Knight Island—sheltered, steep, rocky beach.

Site 17, Perry Island—exposed, relatively high energy cobble/boulder beach.
Figure 4. Average spectra of cobble and pebble beaches.
Figure 5. Average spectra of a flat rock face and adjacent cobbles of same lithology.

Figure 6. Average spectra of beach materials with oil.
b. Oiled pebbles in Herring Bay, Knight Island.

Figure 6 (cont'd). Average spectra of beach materials with oil.

a. Dead rock weed.

Figure 7. Average spectra of organic materials.

b. A different type of kelp.
longer than 1.0 μm (Fig. 8). Barnacles have a complex spectrum reflecting their chitinous composition (Fig. 9). Mussel beds, which cover many of the intertidal rock faces, have low reflectance in the visible, which increases to about 20% in the infrared (Fig. 10).

The calculated TM values for the various materials are listed in Table 2. Only water and oil have large enough aerial coverage to be seen by the Landsat. The beaches would generally be less than one pixel in size and their spectra would be mixed with that of water or of the surrounding woodlands. The values at the four TM bands for oil are very similar and have a reflectance of about 1%. Water measured in the 60-cm-deep tank is twice as reflective as oil in the first three TM bands and similar to oil in band 4. A ratio of bands 2 or 3 to band 4 would most clearly show the difference between oil and water.

The change in the spectrum of a material caused by the addition of oil is modeled in Figures 11 and 12. Under most conditions one would expect a pixel to contain more than one target material. Spectral mixes were made using Prudhoe crude as one end-member and the spectrum of a cobble beach and rock weed as the other end-member. The curves shown between the two end-members are predicted spectra for an area containing 10, 25, 50, 75 and 90% oil coverage. If these spectral mixes are validated for oil, 75% oil coverage of a cobble beach would eliminate the latter’s signature in a MEIS.
Table 2. Percent reflectance of different targets as seen by Landsat thematic mapper (TM) filters 1–4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TM1</th>
<th>TM2</th>
<th>TM3</th>
<th>TM4</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>water + 1 cm³ oil</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>water + 6 cm³ oil</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>water + 25 cm³ oil</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>water + 25 cm³ oil</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>water + 250 cm³ oil</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>pebbles</td>
<td>5</td>
<td>7</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>pebbles</td>
<td>6</td>
<td>8</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>pebbles + oil</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>cobbles</td>
<td>5</td>
<td>7</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>cobbles + tar</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>flat rock face</td>
<td>19</td>
<td>22</td>
<td>23</td>
<td>21</td>
</tr>
<tr>
<td>cobbles of same lithology</td>
<td>9</td>
<td>11</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>dead seaweed</td>
<td>1</td>
<td>3</td>
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<td>dead seaweed</td>
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<td>31</td>
</tr>
<tr>
<td>living seaweed</td>
<td>4</td>
<td>11</td>
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<td>65</td>
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<tr>
<td>drift wood</td>
<td>11</td>
<td>16</td>
<td>22</td>
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<td>barnacles</td>
<td>14</td>
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<tr>
<td>mussels</td>
<td>1</td>
<td>1</td>
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<td>12</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Prudhoe oil has a very dark and uniformly flat reflectance spectrum. Even a thin layer of oil (less than 100 μm) will mask the spectrum of the underlying water. As the spectral reflectance of the oil is only slightly different from that of water (less than 2%), spectral detection of Prudhoe crude on water will be difficult given the lack of absorption features and structure in the spectrum of the oil. Under real conditions, changes in the oil's spectrum resulting from factors not addressed here, i.e., spreading and thinning, modification by weathering and emulsification (Estes and Senger 1972), will make the task even more difficult.

Beaches in Prince William Sound have flat spectra, which, although more reflective than the spectrum of oil, do not have characteristic absorption features. The spectra of the beaches show them to be remarkably similar despite having different clast sizes and being of different lithologies. Materials on the beaches, such as rock weed (fucus), lichen, mussels, barnacles and drift wood are spectrally distinct. These materials have areal distributions large enough to be visible in the MEIS II data and will be masked when coated with oil.

The lack of distinguishing features in the spectra of oil, the similarity of oil and water spectra and the large variability and unpredictability of background materials are the main problems encountered when using spectral reflectance for oil spill delineation. High resolution, multispectral devices such as MEIS II can better define the many backgrounds and combined with spectral mixing models (Adams et al. 1989) may be useful for mapping oil on beaches. The reflectance measure-
ments described here will be used for this purpose. Future work will also test the validity of using this mixing model for oil by coating small amounts of beach materials returned to the laboratory with Prudhoe crude and measuring their reflectance.

LITERATURE CITED


Horvath, R., W.L. Morgan and R. Spellicy (1970) Measurements program for oil-slick characteristics. Ann Arbor: Environmental Research Institute of Michigan, Willow Run Laboratory, University of Michigan, Report 2766-7-F.


The spectral response in the visible and near-infrared (wavelengths of 0.45 to 1.10 μm) of different amounts of Prudhoe crude oil on water was measured. Spectral reflectance measurements were made of selected beaches and beach materials in Prince William Sound to provide ground truth data for the MEIS II imagery collected during the Exxon Valdez spill. A spectral mixing model was used to predict how different amounts of oil would change the spectra of beach materials in Prince William Sound.