

SPECTROSCOPIC AND HYPERSPECTRAL EVALUATION OF POSSIBLE HYDROCARBON OCCURRENCES IN ESTUARINE SEDIMENTS, NORTH CHARLESTON, SOUTH CAROLINA, USA

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ABSTRACT

Reflectance spectroscopy is becoming an important tool in remote identification and mapping of surface hydrocarbons, which may be very useful in determining past and present introduction of hydrocarbons into the environment. Using surface sediment samples in a complex urban/estuarine setting of North Charleston, SC it is possible to define the natural background of the area. By introducing common hydrocarbon pollutants (e.g. crude, motor oil, diesel) into typical background, a spectral library of background spectra, affected by a particular pollutant can be produced. Using the lab-derived hydrocarbon pollutant spectra as an input, it is possible to carry out classification of airborne hyperspectral data as a response to past events and baselining or current response and mapping of a potential spill. The results show that introduction of hydrocarbons produces observable effects, which can be used to delineate presence of affected areas. Relatively simple spectral-similarity algorithms (SAM, Spectral Unmixing) can be successfully used to extract the similar spectral matches in the hyperspectral image data on the basis of the library spectra produced.

Index Terms— Hydrocarbon, Spectroscopy, Hyperspectral, PAH, Estuary

1. INTRODUCTION

Remote detection of hydrocarbons and poly-aromatic hydrocarbons (PAH) using visible-near infrared (VNIR) and short-wave infrared (SWIR) spectroscopy has gained popularity over the last decade as a useful technique in establishing baselines, monitoring past and current spills, accidents, pollution sites etc. Charleston, South Carolina has been a thriving port city for over three centuries, and through its development might have experienced occurrences of hydrocarbon introduction into the environment, due to shipping, industrial activity, heavy military presence and development [1, 2]. This study focuses on determining ground and airborne spectroscopic evaluation of suitable characteristics, attempting to outline

possible leads and clues to possibilities of past and present hydrocarbon occurrences in a complex estuarine setting.

2. BACKGROUND

North Charleston, SC has developed as an industrial and military complex in an estuarine area, near the confluence of Wando and Cooper Rivers (**Figure 1**). The primary function of the city was to provide wide array of services required for the Charleston Naval Base and Shipyard, including metal works, fuel storage, energy, chemical industry and infrastructure. Of particular concern were the sites used for storage of heavy fuel oils, petrochemicals, dredged shipping channel sludge, scrapping yards, waste incinerators, creosote treatment and coal-gasification plants [1].

Several other studies have addressed the zones of hydrocarbon occurrence within the Charleston area, establishing the baseline for concentration of PHA/hydrocarbons in the water column [2], near accident spill sites [3], creosote-treated railways [4], dredge spoils [5], and have all concluded elevated concentrations at sampled locations, consistent with the overall industrial-character of an area. The previous studies were mainly utilizing standard water-quality, geo-chemical and/or fluorescence spectroscopy to investigate for the presence of contamination.

This study uses the advances in hyperspectral and field-based VNIR/SWIR spectroscopy to delineate any spectral characteristics consistent with the hydrocarbon contamination of sediment [6], estuarine environment and/or overall presence of hydrocarbon absorption features [7] characterized by the main 1730 nm and 2310 nm absorption features.

3. AREA CHARACTERISTICS

The study area presents an interesting confluence of urban/industrial area situated within a dynamic, tidal estuary system with two main rivers and numerous tidal creeks, flats and marshes. The surface and near-surface lithology is dominated by the fine-grained, loamy mud and

sand, mixed with organic plant and shell fragments. In the industrial areas, there are also zones of artificial gravel, masonry and debris fill mixed in with sand or marsh mud. Occasional occurrences of phosphate nodules have been observed. As a whole, the majority of the samples are dominated by the clay minerals. The previous studies [8] have shown that the majority of mineral constituents of estuarine marsh are represented by clay minerals kaolinite and montmorillonite [9], derived from the disintegration of Carolina Slate Belt [10]. Comparison of collected sample spectra with USGS spectral library [11] partially supports this observation, but suggests that it may present an intimate mixture with other minerals.

4. METHODOLOGY

The main goal of the project was to determine the possible spectral observable elements that could help isolate and define hydrocarbon-affected estuarine sediments. In the preliminary phase we have collected the spectra of likely pollutants: diesel, bio-diesel, crude oil, gasoline, kerosene, motor-oil and transformer oil. In addition, we have sampled numerous, possibly-affected and presumably-clean sites in the Charleston area for lab spectroscopic study using a full VNIR-SWIR range spectrometer. Some of the spectroscopic-determined clean samples were artificially polluted with a known-quantity of likely hydrocarbons (e.g. diesel, crude oil, motor oil) to determine spectral changes. Based on the information derived from the lab and field study, we have attempted a hyperspectral-scene classification/matching using the derived input and attempt delineating any areas of possible hydrocarbon occurrence on an AVIRIS image, acquired in August of 1997.

4.1. Field spectra and spectral library

The reflectance spectra used in this study have been collected from 30 samples in North Charleston area, mainly from the banks of Cooper River, which also represents the main arterial transportation route. The presumably clean samples have been collected from the areas west of the major industrial zone, in the former 19th century rice-growing and tributary creek areas. Sample locations were marked with GPS and were analyzed in the lab within hours of collection and results stored in a spectral library with sample description and location.

In order to establish a more-descriptive mineralogy of the estuarine soil samples and overall contribution of water and organic materials to the presumed clay-dominated base, five representative samples from the area have been baked at 105°C temperature for 48 hours to burn-off the excess water and then at 500°C to burn-off the organic constituents. The samples were spectrally measured before

the baking, after the de-watering and after organic removal. The **Figure 2** shows the apparent spectral differences in de-watered and organic-removed samples compared with the minerals from the USGS spectral library.

4.2. Artificial hydrocarbon pollution

A representative subset of 5 samples from the presumably “clean” category was chosen as the set for artificial creation of hydrocarbon pollution. The reflectance baseline spectra for the “clean” samples were collected and did not exhibit any of the known hydrocarbon features [7]. The samples were measured in their natural “wet” state, to simulate real, field-like conditions that would likely be encountered during the spill or remote-detection in the environment. Each sample was measured by volume and an appropriate volume of hydrocarbon was introduced via pipette to represent the 10%, 30% and 50% of the “clean” sample volume. The samples were polluted with crude, motor oil, diesel and kerosene and reflectance spectra collected on each and every of the pollutants and concentration levels.

4.3. AVIRIS image comparison

The input spectra showing hydrocarbon presence were compared with 1997, high-altitude AVIRIS [13] hyperspectral scene acquired over Charleston. The main objective was to test the validity of input spectra to delineate any possible zones of hydrocarbons within the AVIRIS scene. The AVIRIS scene was calibrated to reflectance using flat-field and empirical line calibration methods using a ground target of spectrally-flat, clean, quartz-rich beach sand on Kiawah Island, in the southeastern portion of the AVIRIS flightline.

The input spectra were re-sampled to AVIRIS spectra and compared with the scene using Spectral Angle Mapper (SAM) technique with 0.10 and 0.15 radian thresholds. The spectra were also compared with in-scene reflectance using the match filtering (MF) method, comparing the possible mixtures of input and classified image classes [13]. The results of match-filtered spectral classes have been ratioed against SAM-derived results to outline best possible matches in the scene with input hydrocarbon-model spectra.

5. OBSERVATIONS

Generally, the results show that even 10% of the hydrocarbon contaminant (irregardless of its derivative) is sufficient to produce observable spectral features in the otherwise uncontaminated muddy and/or sandy estuarine sediments.. The contaminant features were more apparent in

the sandy samples than in darker, loamy mud samples possibly relating to the apparent greater albedo/intensity in the brighter sandy samples. The **Figure 3a** shows some of the characteristic hydrocarbon occurrences noted. In addition to standard C-H stretching overtones and combination bands in the 1720-1750 nm region. In some of the samples, this feature may be well developed and will show asymmetric doublet with the strongest absorption at 1720 nm and a second, less pronounced at 1750 nm. The region between 2200 and 2500 nm is reportedly affected by the numerous overlapping combination and overtone bands of H-C [6]. These occurrences cause the strong reflectance attenuation beyond 2200 nm, which will often result in the destruction of any O-H absorption features present in the samples containing clay minerals. The absorption effects of H-C are particularly strong in the 2300 nm. In addition to these well-established absorptions, we have noted additional absorptions at 1155 and 1190nm in all of the analyzed samples (**Figure 3b**), contaminated with pollutants. Another apparent occurrence is the flattening of clay-mineral absorption at 2200nm in samples containing more than 30% of hydrocarbon pollutant by volume.

The spectral library of artificially polluted samples were compared with the AVIRIS scene to look for in-scene spectral matches. The results from SAM, MF and subsequent ratios of spectral classes indicate that the majority of “hits” represent asphalt roads and tar-covered rooftops, chiefly because their good exposure and size, sufficient to produce a good spectral response in 20m AVIRIS pixels. However, several clusters of good matches are noted in a non-urbanized portion of the scene, in vicinity of the harbor dredge spoils piles or in the vicinity of abandoned landfills and shipping terminals. Even though they are diffuse, the clustering of pixels presents an interesting occurrence. These locations of interest are identified on **Figure 4** and corresponding spectral matches are shown on **Figure 5**. The locations present zones of interest that will be followed with more detailed ground verification.

6. CONCLUSIONS

The results indicate that there are usable observable features for hydrocarbon detection in an estuarine setting. Even in water-saturated sediments, the presence of small amount of hydrocarbon is likely to produce apparent changes in the reflectance spectra. However, for remote-sensing identification and follow-up on a detailed level, higher-spatial resolution sensor is desirable to help discern the zones of interest better and mask the false-positives of asphalt/tar surfaces occurring in an urban setting. The results suggest that some of the older harbor dredge-spoils

may possibly contain some observable spectral features warranting further appraisal and investigation.

7. REFERENCES

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8.FIGURES

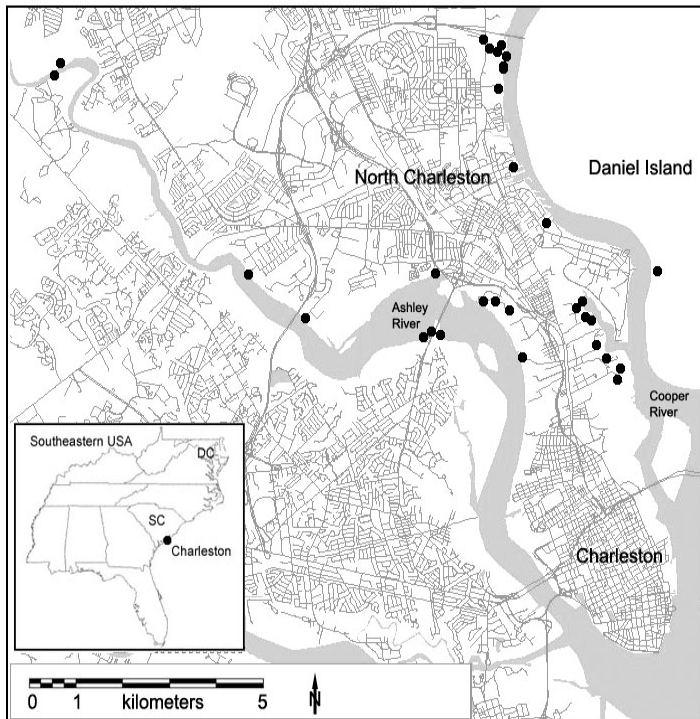


Figure 1 – Area map and sample locations

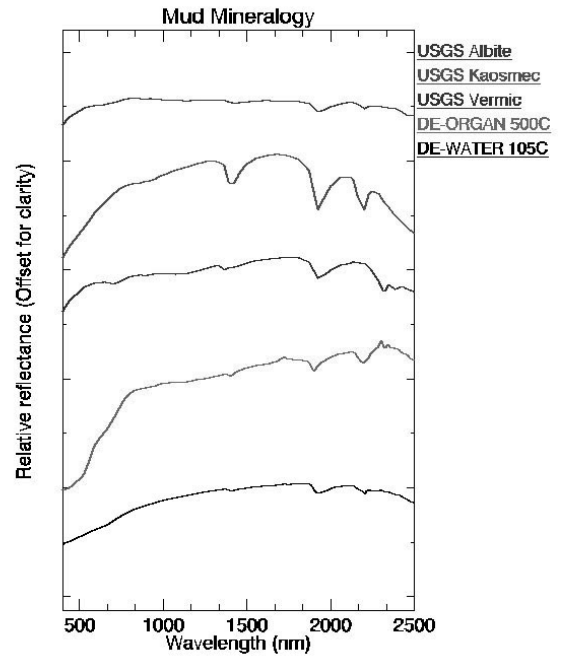
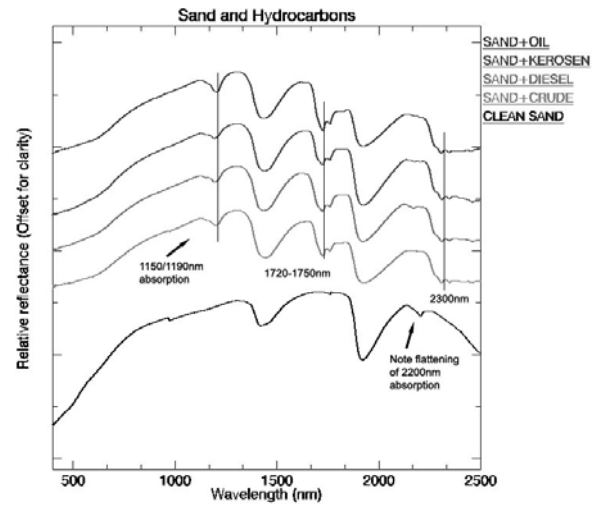
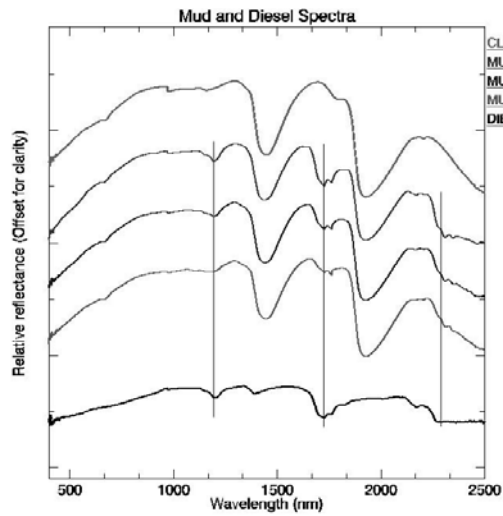


Figure 2 – Marsh mud mineral constituents comparison



Figures 3a and 3b – a) spectral effects of adding diesel to marsh mud and b) marsh sand mixed with various hydrocarbon pollutants.

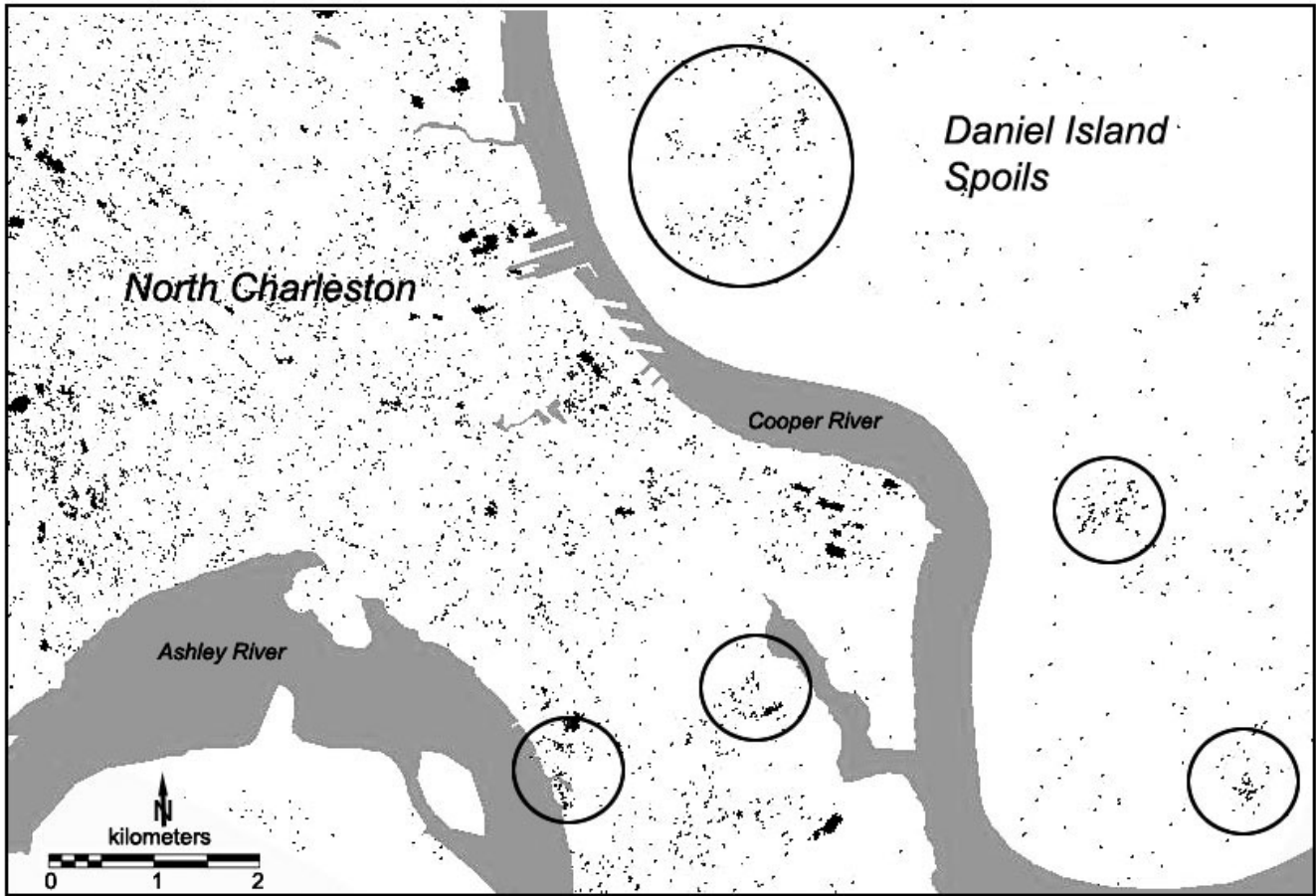


Figure 4 - SAM/MF Classification of AVIRIS scene: circles shows potential zones of interest due to clustering of H/C pixels.

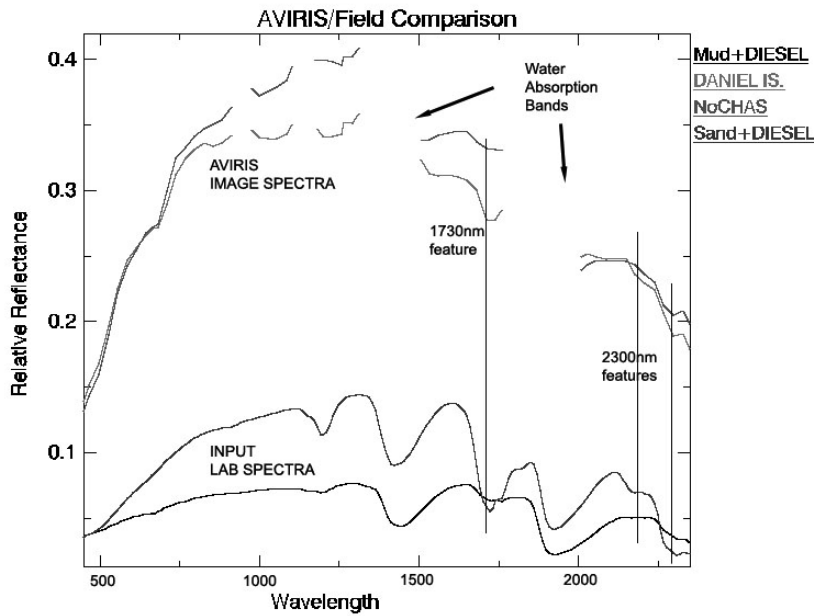


Figure 5- Image results and lab spectra comparison. Note 1730 and 2300nm absorption features.