POLARIZED MULTIANGULAR REFLECTANCE MEASUREMENTS OF DIESEL, MOTOR OIL AND LEAD: IMPLICATIONS FOR DETECTING AND CHARACTERIZING SOILS CONTAMINATED WITH PETROLEUM HYDROCARBONS AND HEAVY METALS

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Abstract

Petroleum hydrocarbons (PHCs) and heavy metals are common soil contaminants, which when released in the environment have the potential to damage plants as well as endanger the health of both humans and animals. Investigating these contaminations for cleanup purposes is therefore important, and developing new rapid techniques to aid in this process would be beneficial. VNIR-SWIR (350-2500 nm) reflectance spectroscopy is a well-known method that has been shown to be a promising tool for the rapid and costeffective mapping and monitoring of various soil contaminations. However, previous studies have primarily focused on the spectral features of soil contaminants; the anisotropic nature of reflectance and polarization have been largely ignored. Characterization of these reflectance properties has the potential to provide valuable additional information, that can be used to improve remote-sensing methods and help develop reflectance models for the quantitative and qualitative analysis of contaminants in soil. To study the bidirectional reflectance and polarization properties of petroleum hydrocarbons and lead, the Finnish Geodetic Institute Field Goniospectrometer (FIGIFIGO) was used to measure samples artificially contaminated with diesel, motor oil and lead in the laboratory as well as lead contaminated soil and vegetation at Suomenlinna, Finland. In total, 23 samples were measured. It was confirmed that petroleum hydrocarbons can be detected from their characteristic absorption bands, and that the 1730 nm band is the most significant for this purpose. However, clay minerals were found to considerably lower the intensity of these bands and affect the reflectance. Despite this, hydrocarbons were successfully detected from all samples at a lowest measured concentration of 0.5 wt.%. The polarization in the backward direction was found to decrease when diesel or motor oil was added, while the polarization increased in the forward direction on low zenith angles. In order to better understand the relationships between clay, water, hydrocarbon and quartz contents and their combined effects on the reflectance, more studies are needed. The reflectance and polarization of the laboratory Pb samples were found to increase significantly in the forward direction, while the polarization decreased in the backward direction in the SWIR region. This characteristic, if investigated further, could prove useful for the detection of heavy metals in soil. Lead was not reliably detected from the field samples, but more controlled studies on the relationship between soil contaminations and polarization properties of vegetation should be considered.

CONTENTS

1. INTRODUCTION	4
2. REFLECTANCE SPECTROSCOPY	5
2.1. Theory	6
2.1.1. Absorption	6
2.1.2. Reflectance	7
2.1.3. Bidirectional Reflectance Factor	8
2.1.4. Polarization	
2.2. Reflectance spectroscopy of soil	10
2.2.1. Absorption features of soil	
2.2.2. Bidirectional reflectance characteristics of soil	
2.2.3. Polarized reflectance characteristics of soil	
2.2.4. Limitations and challenges	13
2.3. Reflectance spectroscopy of PHCs	13
2.3.1. Chemical composition of PHCs	13
2.3.2. PHCs as soil contaminants	14
2.3.3. Absorption features of PHCs	15
2.3.4. Polarized reflectance characteristics of PHCs	16
2.4. Reflectance spectroscopy of lead	16
2.4.1. Lead as a soil contaminant	
2.4.2. Absorption features of heavy metals	
2.4.3. Vegetation as an indicator of heavy metal contaminations	
3. MATERIALS	18
3.1. Laboratory samples	
3.1.1. Uncontaminated sands	19
3.1.2. Diesel and motor oil	20
3.1.3. Lead pellets	
3.2. Field samples	23
4. METHODS	24
4.1. FIGIFIGO	24
4.1.1. Operation	26
4.1.2. Noise levels	26
4.2. Laboratory measurements	27

4.2.1. Laboratory setup	
4.2.2. Measurement procedure	
4.3. Field measurements	
4.4. Data processing	
5. RESULTS	29
6. DISCUSSION	43
6.1. Diesel and motor oil	43
6.2. Lead	
6.3. Lead contaminated soil and vegetation	
7. CONCLUSIONS	45
8. ACKNOWLEDGMENTS	
9. REFERENCES	

1. INTRODUCTION

Soil contamination is an increasing concern worldwide. Soil is a complex system, which consists of organic matter, minerals, gases and liquids; and is of great significance to life on earth. Soil affects the atmosphere; stores, supplies and purifies water; and provides a medium for plant growth and a habitat for organisms. Thus, soil contamination by harmful substances may damage plants as well as endanger the health of both humans and animals.

Methods commonly used for investigating soil contaminations can be time-consuming, expensive, and require rigorous field sampling (Dent and Young 1981) as well as laboratory analysis, which sometimes utilize environmentally damaging chemicals (Schwartz et al. 2011). For these reasons, it is challenging to conduct wide-scale assessments on suspected contaminated regions; and therefore examining more rapid, environmentally friendly, and cost-effective alternative techniques for the detection and monitoring of soil contaminations is warranted.

Reflectance spectroscopy is a well-known method that can be used to obtain large quantities of information on soil characteristics, and that has been shown to be a promising tool for the rapid detection and monitoring of soil contaminants, such as refined petroleum products and heavy metals (e.g. Malley et al. 1999, Pandit et al. 2010, Chakraborty et al. 2012, Shi et al. 2014). However, more studies with various contaminants and soil samples are needed until the method can be developed to a stage where it is routinely used for investigating soil contaminations. Better characterization of contaminated soil reflectance features could, for example, enable the reliable use of remote sensing methods for assessing suspected contaminant concentrations and types quickly.

Previous studies on the relationships between reflected radiation and soil contaminations have primarily focused on spectral features; polarization and the anisotropic nature of reflectance have been largely ignored. Expanding research on characterizing directional reflectance and polarization properties of contaminated soils has the potential to provide valuable additional information that is especially useful when improving remote sensing methods. These properties can be measured using a goniospectrometer, which is essentially a spectroradiometer with mechanics that enable multiangular reflectance measurements. In this master's thesis, the Finnish Geodetic Institute Field Goniospectrometer (FIGIFIGO) was used to measure sands artificially contaminated with diesel, motor oil, and lead. Moreover, lead contaminated soil and vegetation were measured in the field. The purpose was to study the directional reflectance and polarization characteristics as well as spectral features of the samples.

2. REFLECTANCE SPECTROSCOPY

Reflectance spectroscopy studies the interactions between matter and electromagnetic radiation. When radiation interacts with matter, it can be either reflected, absorbed, or transmitted. For most materials, this interaction is observable in the range of solar spectrum (350–2500 nm) (Hunt 1980), which can be divided into visible and near-infrared (VNIR, 350–1100 nm) and shortwave infrared (SWIR, 1100–2500 nm) regions (Ben-Dor et al. 1999).

The way that radiation and matter interacts is dependent on the wavelength of incident radiation as well as on the properties of the material; a specific material can reflect light at one wavelength but absorb at another, while partially absorbed light is emitted at a third wavelength (Winkelmann 2005). Hence, the observed reflectance is a function of incident radiation wavelength, emissivity, and surface material absorption and reflectance properties (Schwartz et al. 2011). Measuring and studying this reflectance can therefore be used to derive information on the samples chemical and physical characteristics (Ben-Dor et al. 1999).

2.1. Theory

2.1.1. Absorption

VNIR-SWIR spectroscopy is based on the fundamental electron vibrations in atoms and molecules. Absorption occurs when an atom or molecule transitions to a higher energy state, and there is a redistribution of electric charges, or a reorientation of nuclear or electron spins (Hunt 1980). A transition to a higher energy state requires that the natural vibrational frequency of an atom or molecule is the same as that of an interacting photons frequency, and this dependency results in absorption at specific wavelengths (Jensen 2009). When an atom or molecule subsequently makes a transition from the excited energy state to a lower one, a photon with energy equal to the difference between the energy levels is emitted (Ben-Dor et al. 1999). Since part of the incident photon's energy is generally transformed into other forms of energy in the absorption process, the emitted photon has a longer wavelength than the original (Jensen 2009). The electron transitions of outer valence electrons commonly produce absorption bands in ultraviolet and visible spectral regions due to relatively large differences between their energy states (Ben-Dor et al. 1999). The absorption by an outer valence electron is illustrated in Figure 1.



Figure 1. Absorption by an outer valence electron. a) An outer valence electron interacts with a photon. b) Absorption occurs and the electron transitions to a higher energy state. c) The electron makes a transition to a lower energy state, and a photon with energy proportional to the changes in the energy states is released with a longer wavelength than the original.

Part of the energy of molecules is located in their molecular bonds that have vibrational motion oscillations, and these oscillations can stretch molecular bonds (asymmetrically or symmetrically) or bend their angles (Figure 2). Transitions involving these vibrational motions significantly affect a molecules interaction with radiation. (Ben-Dor et al. 1999).



Figure 2. An illustration of stretching and bending of molecular bonds by using C-H bonds in CH2 group as an example. Stretching can shorten or lengthen the bonds asymmetrically or symmetrically, while bending changes their angles. Energy state transitions involving these processes affect the interaction between a molecule and electromagnetic radiation.

A molecule can have multiple vibrational modes, which are dependent on the number of atoms in a molecule as well as its structure (Ben-Dor et al. 1999). Each of these vibrational modes have a characteristic vibration frequency, and each mode can be excited individually (Winkelmann 2005). Therefore, transitions between the energy levels of each mode results in absorption at certain wavelengths (Ben-Dor et al. 1999).

When a transition happens between the lowest possible energy level of a vibrational mode and the next highest energy level, absorption in the infrared (IR) spectrum typically occurs. The resulting absorption bands are called fundamental bands, which are generally not observable in the VNIR-SWIR spectrum. However, when the transition between modes energy levels is more than one energy level up or down, absorption bands called overtones occur. Furthermore, combination bands are produced when a transition involves more than one mode due to the distribution of absorbed energy between multiple modes. These overtone and combination bands give rise to characteristic absorption features in the VNIR-SWIR spectrum, albeit their intensities are significantly lower than those of fundamental bands, and they often produce overlapping and complex absorption features. (Ben-Dor et al. 1999).

2.1.2. Reflectance

Reflectance describes the portion of radiation that is re-emitted from a surface by atoms and molecules. Reflectance is a directional property and depending on the characteristics of the surface it can be specular or diffuse. In the case of specular reflectance, almost all light from a certain direction is reflected to another individual direction, and when

7

reflected radiation is equally or nearly equally distributed to all directions, it is said to be diffuse (Figure 3). A surface exhibiting perfect diffuse reflectance is called Lambertian. (Jensen 2009).



Figure 3. The behavior of specular and diffuse surfaces. Top-left: perfect specular surface reflects all light to a single direction that is dependent on the angle of incident radiation. Top-right: near-specular surface reflects most of the light in a single direction, while some is reflected diffusely. Bottom-left: near-diffuse surface reflects most light diffusely, while a specular component is present. Bottom-right: Lambertian surface reflects light equally to all directions without specular properties.

Most real surfaces have a combination of diffuse and specular properties, and when the directional distribution of reflected radiation is unpredictable, it is said to be scattered. However, a surface such as still water would have a near-specular reflectance, while a smooth and white surface would have a near-diffuse behavior. (Jensen 2009).

2.1.3. Bidirectional Reflectance Factor

Reflectance varies with the angles of observation and illumination, and reflectance treated as a function of both view and illumination angles is called bidirectional. This bidirectional behavior is a fundamental property for all natural materials, and it is dependent on the geometrical and physical properties of a sample being measured (Schönermark von et al. 2004). Bidirectional Reflectance Factor (BRF) can be used to describe this phenomenon scientifically; BRF is defined as a ratio between reflected radiation from a surface and a Lambertian surface in same measurement conditions (Schaepman-Strub et al. 2006).

$$BRF = R(\theta_i \phi_i; \theta_r \phi_r) = \frac{L_r(\theta_i, \phi_i; \theta_r, \phi_r)}{L_r^{id}(\theta_i, \phi_i)}$$
(1)

Where θ_i is the zenith angle and ϕ_i the azimuth angle of incident radiation respective to the sample surface, and θ_r and ϕ_r are the zenith and azimuth angles for the observed radiances (Figure 4). L_r and L_r^{id} are the radiances from a sample and an ideal Lambertian surface; since there is no angular dependence for a Lambertian surface, it is $1/\pi$, and the view zenith and azimuth angles can be omitted. R is the reflectance factor.



Figure 4. Geometries of illumination and observation.

Due to the fact that ideal Lambertian surfaces do not exist, a white reference panel (e.g. Spectralon) that is close to a Lambertian surface is used and corrections are made:

$$BRF = \frac{L_r(\theta_i, \phi_i; \theta_r, \phi_r)}{L_{ref}(\theta_i, \phi_i)} R_{ref}$$
(2)

Where L_{ref} is the radiance and R_{ref} the reflectance factor of a reference panel, while the angular dependency for R_{ref} can be ignored.

2.1.4. Polarization

Polarization expresses the geometrical orientation of electromagnetic oscillation in an electromagnetic field. When radiation has equal distribution of polarization states, that is to say, all planes of propagation are equally probable, it is said to be unpolarized. This is the case with the majority of radiation sources, such as the Sun. However, when light interacts with matter and scattering occurs, the interaction often polarizes the reflected radiation, at least partially (Vanderbilt et al. 1991). If a minimum of two polarization directions are measured, the degree of linear polarization and polarized reflectance factor can be calculated.

2.2. Reflectance spectroscopy of soil

The complexity of soils is due to the many factors affecting their formation and the various processes that modify them. From a reflectance spectroscopy point of view this means that there are numerous changing variables that influence the observed reflectance; variables such as surface texture and roughness; mineral composition; water content, and organic matter content (Jensen 2009). These characteristics also influence each other; for example, with decreasing grain size, water is held in the soil more efficiently, which in turn greatly affects the observed reflectance properties.

Soil reflectance can be measured in the laboratory, in the field and from the air. The advantage of laboratory measurements is that they can be done in a controlled environment where problems such as those resulting from atmospheric effects, weather conditions and variations in illumination are not an issue, as is the case with field measurements. In addition, there are no time limitations and samples can be described and characterized more carefully. However, differences between laboratory illumination and sunlight bring about challenges for the direct comparison of field and laboratory data (Suomalainen et al. 2009a). Moreover, sometimes samples can't be brought to the laboratory or simultaneous measurements with aerial data are needed, and therefore field measurements are required (Suomalainen et al. 2009a).

2.2.1. Absorption features of soil

Materials that absorb radiation at distinct wavelengths in the spectral region of sunlight are called chemical chromophores (Ben-Dor et al. 1999). Chromophores responsible for significant soil absorption features over the VNIR-SWIR spectrum can be categorized roughly as minerals (mainly clay and Fe-oxides), organic matter (living and decomposing) and water (solid, liquid and gas phases) (Ben-Dor et al. 1999). The most common absorption feature of Earth's surface materials in the VNIR-SWIR region is the 1400 nm overtone band (Hunt 1980).

Spectral features of clay minerals (or phyllosilicates) are caused by overtone and combination bands related to OH, H_2O and CO_3 (Clark 1999). Among clay mineral elements, only the hydroxide group exhibits absorption features in the VNIR-SWIR spectral region (Ben-Dor et al. 1999). OH group can be present in the mineral structure (mostly as lattice water) or attached to the surface of the clay mineral (absorbed water). Substantial clay absorption features are located at three spectral regions: 1300–1400 nm, 1800–1900 nm, and 2200–2500 nm (Ben-Dor et al. 1999). Moreover, provided that signal-to-noise ratios are relatively high, it is possible to detect an additional overtone band at 950 nm (Goetz and Davis 1991).

Most Fe-oxides, such as hematite and goethite, have absorption bands in the VNIR spectral region due to orbital electron transitions of Fe^{2+} and Fe^{3+} (Torrent and Barrón 2002). These bands are located in the 400–900 nm spectral region (Ben-Dor et al. 1999), and therefore they affect the soil color significantly. Fe-oxides, especially hematite, are abundant typically in highly weathered soils (Ben-Dor et al. 1999).

Water in its different forms is active in the VNIR-SWIR region (due to OH group), and it has pronounced absorption features close to 1400 nm and 1900 nm wavelengths, as well as weaker overtones at 950 nm and 1200 nm wavelengths (Rossel and Behrens 2010). Water in soil can be categorized into three categories that each affect the spectra differently: hydration water (lattice water), absorbed water that exists as a thin layer on soil surfaces (hygroscopic water), and free water in the pores of soil (Ben-Dor et al. 1999)

Chemical bonds in organic materials (e.g. C-H, C-C, C=C, C-N, O-H) produce distinct overtone and combination bands in the VNIR-SWIR region (Shi et al. 2014). These bands are located near 2350 nm, 1750 nm, 1350 nm, and 1200 nm wavelength regions (Winkelmann 2005). Living plants affect different parts of the spectrum as plant composition and structure varies: the 500–750 nm band is characterized by absorption due to pigments, 750–1350 nm band is a region of high reflectance and low absorption due to internal leaf structure, and the 1350–2500 nm band is mostly affected by water in the tissues (Barrett 2013).

2.2.2. Bidirectional reflectance characteristics of soil

Measured BRF can vary over a wide range depending on the sample's characteristics. With increasing surface roughness, the reflectance and forward scattering typically decreases, backscatter features become more pronounced, and forward scattering diminish as the zenith angle increases (Cierniewski and Courault 1993). This relationship is influenced partly by the fact that irregularities of the soil surface cause shadowing when roughness is higher (Schönermark von et al. 2004).

With increasing water content soil reflectance decreases, forward scattering increases and backscattering becomes less pronounced at low zenith angles (Cierniewski and Courault 1993). The primary reason for the decrease in reflectance is the change of medium surrounding the particles from air to water, which decreases their relative refractive index (Ben-Dor et al. 1999). In completely water saturated or over saturated soils specular reflectance components are more probable than Lambertian components (Ben-Dor et al. 1999).

2.2.3. Polarized reflectance characteristics of soil

Polarization of reflectance is always bidirectional, and therefore it can be measured by using a polarizer when detecting bidirectional reflectance (Wu and Zhao 2005). Polarization is affected by various factors, such as moisture; minerals; vegetation; Feoxides; soluble salts, and surface roughness (Wu and Zhao 2005). There is also a relationship between wavelength and polarization (Wu and Zhao 2005, Suomalainen et al. 2009b).

Polarized reflectance is hypothesized to be generated mainly by the specular reflection component (Breon et al. 1995), and with low incident angles soils tend to exhibit more Lambertian characteristics (Wu and Zhao 2005). Hence, soils typically polarize more as the incidence angle increases, with very little polarization in the backwards direction and almost no polarization at nadir (e.g. Wu and Zhao 2005, Peltoniemi et al. 2009). In a study by Peltoniemi et al. (2009), various soil and vegetation samples were measured in field conditions and the polarization was found to be inversely but non-linearly proportional to reflectance.

2.2.4. Limitations and challenges

Many factors can affect the reflectance measurements and cause variation between results; some examples are movement of the fiber optics during measurements, changes in illumination, dust in the reference panel and mechanical noise originating from the instrumentation (Schwartz et al. 2011). Therefore, measurements with different spectrometers and even repeated measurements with a same spectrometer may result in variations, such as shifts in the peaks of absorption bands (Schwartz et al. 2011).

With reflectance spectroscopy, it is only possible to study the thin upper layer of the soil surface; soil crusting, soil sealing, snow, and vegetation can therefore prevent the measurement of main soil underneath. Moreover, it is not possible to acquire information on the soil profile. In addition, the results are strongly affected by water content; grain size distribution; measurement protocol, and the method used for calculating reflectance from the spectrometer data (Schwartz et al. 2011).

2.3. Reflectance spectroscopy of PHCs

2.3.1. Chemical composition of PHCs

Petroleum is a natural resource that can be refined to produce a wide range of products, such as liquid fuels, solvents and lubricants. These products are mainly a mixture of organic compounds called petroleum hydrocarbons (PHCs) and various metals in trace

quantities. Specifically, the chemical composition of refined petroleum products is predominantly C (83–97%), H (10–14%), N (0.1–2%), O (0.0005–1.5%) and S (0.05–6%). Metals, such as V, Fe, Ni and Cu, are present in concentrations of <0.1%. The classification of hydrocarbons is based on the kind of chemical structure (aliphatic or aromatic), and number of carbon atoms in the compound. These factors also determine several of the hydrocarbon's characteristics, including boiling point, solubility, absorption and toxicity. (Schwartz et al. 2011). Mineral oils such as diesel and certain motor oils have large amounts of polycyclic aromatic hydrocarbons (PAHs) (Okparanma and Mouazen 2013b).

2.3.2. PHCs as soil contaminants

Petroleum hydrocarbons are of particular interest among soil contaminants due to their extensive use and neurotoxicity. Exposure to PHCs can, for instance, affect the central nervous system, cause effects on the blood, immune system, lungs, skin and eyes (Agency for Toxic Substances and Disease Registry 1999). In addition, ecological systems and agricultural soils could be endangered (Fine et al. 1997).

Petroleum products are utilized all over the world for heating, energy production and in a range of transportation vehicles and machinery. According to the U.S. Energy Information Administration (2016), in 2015 global total liquid fuels production averaged at ~15.2 \cdot 10⁶ m³ d⁻¹. PHCs are typically released in the environment through broken pipelines, transport vehicle accidents, leaking underground storage tanks and spills at gas stations.

PHCs with different characteristics behave differently in soil or water. Some hydrocarbons can be more volatile than others, while some tend to migrate to groundwater due to higher water-solubility. Furthermore, many of the PHCs are susceptible to biodegradation (Tetra Tech EM Inc. for EPA 2000). Thus, shortly after hydrocarbons have been released in the environment, they may have drastically different characteristics compared to their parent substances.

2.3.3. Absorption features of PHCs

Petroleum hydrocarbon spectral features are generally dominated by absorption bands originating from overtones and combinations of C-H stretching vibrations in aliphatic C-H bonds as well as methylenic, olefinic or aromatic C-H functional groups (Aske et al. 2001). Hydrocarbon absorption bands in the VNIR-SWIR spectrum were first determined by Cloutis (1989) in a study where bituminous tar sands were measured. Multiple absorption signatures for hydrocarbons were found, and the intensities of the absorption features showed correlation with abundancies. However, various other materials, such as clays, organic matter and water, also exhibit absorption features in many of the same wavelengths, and this results in overlapping spectral signatures. Fortunately, many of the problems related to overlapping signatures can be solved by using advanced chemometrics and data processing techniques (Pasquini 2003).

The best spectral regions for detecting various C-H absorption bands were argued by Cloutis (1989) to be located at around 1730 nm and 2310 nm wavelengths. Mainly hydrocarbons produce prominent absorption features at 1730 nm (Kühn et al. 2004), and it is therefore considered to be the most important for investigating hydrocarbon contaminated soils (Chakraborty et al. 2012).

Although the 1730 nm region is close to a major water absorption band (around 1900 nm), it was demonstrated by Hörig et al. (2001) to be reliable for detecting petroleum hydrocarbons, and both the 1730 nm and 2310 nm wavelength regions have been successfully used in hyperspectral remote sensing studies (Hörig et al. 2001). Specific spectral signatures for most PHCs, according to Chakraborty et al. (2012), have been established by Mullins et al. (1992) and are located at 917 nm; 1020 nm; 1190 nm; 1388 nm; 1725 nm, and 2298 nm wavelengths.

The complex composition of petroleum products makes detection of hydrocarbon signatures challenging, especially when they are mixed with another heterogeneous mixture, such as soil (Wang and Fingas 1997, Okparanma and Mouazen 2013a). Cloutis (1989) argued that the general spectral properties of hydrocarbons in soils are only visible at a minimum concentration of 4 wt.%. However, in a study by Zwanziger and Förster (1998), three types of soils were artificially contaminated by diesel and gasoline in a

laboratory, and minimum detection limits of 0.1 wt.% and 0.5 wt.% were achieved (Schwartz et al. 2011). Furthermore, Hörig et al. (2001) successfully identified hydrocarbon contaminated soils using airborne hyperspectral sensors at minimum concentrations of 2.5 wt.%. Later Chakraborty et al. (2010) showed that it is possible to classify and quantify PHCs in soils at high precision using reflectance spectroscopy without any prior sample preparation, and with concentrations as low as 0.01 wt.%.

2.3.4. Polarized reflectance characteristics of PHCs

Wang et al. (2009) studied polarization characteristics of hydrocarbon contaminated soil samples with varying water and hydrocarbon contents at 630–690 nm and 760–1100 nm wavelength regions from 10°, 30° and 50° zenith angles by using a bidirectional reflectance photometer. The degree of polarization (DOP) was established as a quantitative index for hydrocarbon contamination, and the results indicated that the polarization is dependent on both the water and hydrocarbon content; with rising oil concentrations, DOP of the reflected light increased when the water content was low, and decreased when it was high. In the study, it was concluded that hydrocarbon contamination can be quantitatively determined by polarization at 180° relative azimuth angle.

2.4. Reflectance spectroscopy of lead

2.4.1. Lead as a soil contaminant

Lead is neurotoxic heavy metal that has been widely used, for instance, as an additive in gasoline, paint and water pipes. In addition, mining industry and lead ammunitions used at shooting ranges pose a lead contamination risk. Lead poisoning can affect the brain's functioning and cause permanent developmental and behavioral disorders especially in young children (Laidlaw et al. 2005), who are most susceptible to exposure due to hand-to-mouth behavior (Pandit et al. 2010).

As a consequence of lead usage in gasoline and paint alone, estimated $5 \cdot 10^6 - 6 \cdot 10^6$ mt of lead has been released into the atmosphere and accumulated in the environment

(Laidlaw et al. 2005). When a particulate lead is deposited, it tends to remain in the surface soil due to its insolubility and complexation of Pb and Pb-oxides with organic matter (Filippelli et al. 2005). The increased awareness of Pb's neurotoxicity has fortunately induced many regulatory measures, including a complete phase-out of lead usage in many cases. However, although sources of anthropogenic lead in the environment have been successfully reduced, it continues to be a common threat to human and animal health.

2.4.2. Absorption features of heavy metals

Heavy metals do not typically show characteristic absorption features in the VNIR-SWIR wavelength region (Schwartz et al. 2011) Since VNIR-SWIR spectral region is insensitive to the presence of heavy metals, using the reflectance spectroscopy method as a tool for detecting heavy metal soil contaminants is in general consider to be either impossible, or of only limited practical use (Winkelmann 2005, Baveye and Laba 2015).

Although heavy metals intrinsically in their pure form do not absorb light in the VNIR-SWIR region, it may be possible to detect them indirectly through their complexing with organic matter (OM) associated with detectable moieties, such as hydroxides, sulfides, carbonites and oxides (Schwartz et al. 2011). In addition, clays tend to absorb heavy metals and can be detected from the VNIR-SWIR spectra (Malley and Williams 1997). These complexes may then be differentiated from similar minerals by their peak shifts in absorption bands (Ben-Dor et al. 1999).

Most of the wavelengths that has been found to be the most important for predicting heavy metal concentrations are the absorption features of Fe and Fe-oxides (Kemper and Sommer 2002). In addition, Pandit et al. (2010) measured lead contaminated soil samples and confirmed that the reflectance would consistently decrease as the Pb concentrations increased. Nonetheless, it is difficult to determine small concentrations of heavy metals (Pandit et al. 2010), and according to Wu et al. (2007), they cannot be detected using reflectance spectroscopy at concentrations under 1000 mg kg⁻¹.

The notion of using vegetation as a heavy metal contamination indicator has been investigated. When plant's roots extract toxic metals from the soil, which are then distributed to other parts of a plant, vegetation stress may result depending on the contaminant, concentration, and plant type in question (Schwartz et al. 2011). This vegetation stress induced by toxic heavy metals can subsequently cause plants to show symptoms that are detectable from its spectra, as many studies have reported (e.g. Davids & Tyler 2003, Kooistra et al. 2004, Dunagan et al. 2007, Zhou et al. 2010). The overall spectral shape between Pb stressed and healthy vegetation largely remains the same, but there are distinct differences in the reflectance at 700–1350 nm region (Kooistra et al. 2004). In addition to spectral features, polarization might provide information on the internal properties of vegetation at wavelengths longer that 800 nm for many plant species (Vanderbilt et al. 1991). However, not all plants are sensitive to heavy metal contaminants (Shi et al. 2014), and relating vegetation stress symptoms and corresponding reflectance characteristics specifically to a stress caused by heavy metals is problematic (Kooistra et al. 2004).

3. MATERIALS

3.1. Laboratory samples

Artificially contaminated laboratory samples were prepared by manually mixing quartz sand with diesel and motor oil. In addition, diesel was mixed with regular sand and lead pellets were measured together with quartz sand. Quartz sand and regular sand were purchased from a hardware store, and diesel and motor oil from a gas station; a summary of the sample materials and additional information is in Table 1. The quartz sand is of a type which is utilized in abrasive blasting; it was chosen as a sample material due to its lack of strong spectral features and low clay, iron, water and organic material contents. This was hypothesized to allow the reflectance features of the contaminants to stand out as much as possible. The acquired regular sand is sold as sandbox sand; it has visible

organic material content, relatively wide grain size distribution and clay minerals in abundance.

Material	Product	Description
Quartz sand	Nilsiän kvartsi / Sibelco Nordic	White color, grain size $0.1 - 0.6$
		mm
Regular sand	Leka hiekkalaattikkohiekka / Boke	Grain size <3 mm
Diesel	Futura D / Neste	H2O < 200 mg/kg Polyaromatics <8.0 wt.% colorless
Motor oil	4-stroke motor oil / Teboil	100% mineral oil Brownish-yellow color
Lead pellets	Roundball pellets / Gamo	100% lead Diameter 4.5 mm

Table 1. A summary of laboratory sample materials acquired from various hardware stores and a gas station.

The diesel is regular diesel fuel used in motor vehicles, and the acquired motor oil is meant for lubricating light machinery, such as lawnmowers. The motor oil is less refined than diesel; it is heavier, more viscous and has dark, brownish-yellow color. The lead pellets are ammunition for air based rifles, and they have no coating of any kind.

3.1.1. Uncontaminated sands

Uncontaminated quartz and regular sand were carefully spread on the sample table before measurements to minimize surface roughness. In Figure 5 is a comparison of these samples. The surface roughness is clearly higher in the regular sand sample; this is due to the wider grain size distribution.



Figure 5. A picture of the uncontaminated quartz sand sample on the left and uncontaminated regular sand sample on the right. Surface roughness is greater in the regular sand sample due to larger grains. The quartz sand is highly homogeneous and white in color, while the regular sand is more heterogeneous.

In order to make the surface of the regular sand as even as possible, a 30-cm ruler was used for gently leveling it out. The quartz sand was spread on the sample table by passing it through a sieve from a height of approximately 1 m, without any further actions.

3.1.2. Diesel and motor oil

Diesel and motor oil samples were prepared in various concentrations (by weight), and a total of 12 samples were created. Diesel oil, motor oil and sands were weighed using a weighing scale before mixing, and the total end weight for each sample was 1000g. Concentrations were calculated using the following equation:

$$Wt.\% = \frac{weight of contaminant}{(weight of contaminant + weight of sand)} x \ 100$$
(3)

The reported concentrations have a margin of error up to 10% due to accuracy of the weighing scale (1g). Moreover, the manual mixing and homogenization process, however carefully executed, produces an additional uncertainty which is hard to quantify. Nonetheless, these uncertainties are considered to be well within an acceptable range for the purpose of this work.

The concentrations as well as descriptions of the diesel and motor oil samples are summarized in Table 2. The concentration range was decided based on previous studies that have generally suggested minimum detection limits for hydrocarbons in soil to be from around 0.5 wt.% to 4 wt.% when using the reflectance spectroscopy method (e.g. Cloutis 1989, Zwanziger and Förster 1998). Additionally, preparing samples with lower concentrations using the currently available laboratory equipment would be challenging and produce large margins of error.

Sample	Concentrations	Description
Diesel and quartz sand	0.5wt.%, 1wt.%, 2wt.%, 4wt.%	Diesel and quartz sand manually mixed, darkening with increasing concentration
Motor oil and quartz sand	0.5wt.%, 1wt.%, 2wt.%, 4wt.%	Motor oil and quartz manually mixed, a brownish-yellow hue when motor oil is added
Diesel and natural sand	0.5wt.%, 1wt.%, 2wt.%, 4wt.%	Diesel and regular sand manually mixed, darkening with increasing concentration. Clay minerals efficiently absorbed diesel.

Table 2. A summary of diesel and motor oil samples and their concentrations

After the mixing, samples were immediately spread out on the measurement table and evened out by using a ruler. During the sample preparation process, it was observed that with the more viscous motor oil the surface roughness of the quartz sand samples were more prominent than with diesel (Figure 6).



Diesel 4 wt.%

Motor oil 4 wt.%

Figure 6. A comparison between a diesel and motor oil sample. Surface roughness is greater in the sample that is contaminated with motor oil.

As expected, with diesel there was no significant change in color as the concentration increased, apart from a moderate darkening. However, the motor oil samples exhibited a slight brownish hue which became more noticeable at higher concentrations. When diesel

and regular sand were mixed, clay minerals in the sand instantly absorbed a portion of the diesel. This increased the surface roughness of the sample when it was prepared (Figure 7).



Figure 7. A comparison of regular sand mixed with diesel between concentrations of 0.5 wt.% (on the left) and 4 wt.% (on the right). Due to absorption of diesel by clay minerals the surface of the 4 wt.% sample has an increased roughness.

Diesel and motor oil sample preparation process was relatively straightforward and produced homogeneous samples when observed visually. The number of samples and the concentration range is considered to be adequate for examining reflectance properties of hydrocarbons in the scope of this work.

3.1.3. Lead pellets

The lead pellet samples were created by carefully placing lead pellets on top of a layer of quartz sand as evenly as possible. The number of lead pellets in the samples were 1, 9 and 363. (Figure 8).



Figure 8. Lead pellets on quartz sand. The sample on the left has 1 lead pellet in the center, the middle one has 9 lead pellets, and the sample on the right has 363 lead pellets that are placed on even rowes by first pressing slight dents on the quartz sand and then placing the pellets on the dents.

There was small variations between the depths at which the lead pellets settled on the surface of the quartz sand. The sample with 363 pellets was created by first pressing slight dents on the quartz sand surface and then by placing the pellets in the dents.

3.2. Field samples

Field samples consist of vegetation and exposed soil at a lead contaminated area in Suomenlinna, Finland. The lead concentrations in the target area have been mapped by Nurmi (2010) in his master's thesis, and spots for the measurements were chosen based on that work (Figure 9). Measurement of 1 vegetation and 1 soil sample failed, and this was noticed later in the post processing stage; the reason for the failed measurements is likely a user error at some point in the measurement process.



Figure 9. Measurement locations and Pb concentrations are on the left (Map based on Nurmi 2010). On the right is a map of Suomenlinna, Finland, and a location of the field measurements (Kustaanmiekka) (Nurmi 2010). The distribution of Pb in the area is uneven, with highest concentrations located near the road.

The vegetation was mostly short grass and no sample preparations were made before the vegetation measurements. Measurement locations were recorded using GPS coordinates. After measuring the grass, a layer of vegetation approximately 1-2 cm deep was peeled off at the same spot using a shovel in order to expose the soil (Figure 10).



Figure 10. A vegetation sample at the field measurement site on the left (Vegetation 1), and an exposed soil sample on the right (Soil 2). The measurements were done in Suomenlinna, Finland, September 2016.

A summary of the field samples is in Table 3. When the vegetation was peeled off, measurements were done without long waiting periods.

Sample	Measurements	Description
Vegetation 1	3 total measurements	Green grass at lead contaminated
Vegetation 2	1 failed (vegetation 3)	soil
Soil 1	3 total measurements	Exposed soil after vegetation have
Soil 2	1 failed (soil 3)	been peeled off

Table 3. A summary of the field samples.

Weather during the field measurements was sunny with very little or no clouds, and there was no visible water on the surface of the vegetation. Considering that only 6 samples were measured and from those 2 failed, these samples do not adequently represent the area as a whole.

4. METHODS

4.1. FIGIFIGO

FIGIFIGO is a device for multiangular reflectance measurements. It mainly consists of a casing, spectroradiometer, measurement arm, optics and a laptop. The measurement arm

is adjustable from 1.5 m to 2.6 m and can be tilted 90° from vertical to both directions by a motor inside the casing, while an inclinometer provides the control computer the measurement zenith angle. The spectroradiometer used is ASD FieldSpec Pro FR spectroradiometer (350–2500 nm) and it is inside the casing. At the top of the measurement arm is a horizontal rail where optics can be attached, and at the tip of the rail is a servo-driven mirror through which optics view the sample (Figure 11). A fiber optic cable that is attached to the arm runs from the optics to the spectroradiometer inside the main casing.



Figure 11. On the left is a concept drawing of FIGIFIGO (edited image; original drawing by Juha Suomalainen): spectroradiometer and most of the electronics are inside the casing, optics are attached to the top of the measurements arm and at the tip of the horizontal rail is a mirror through which optics view the sample. Two laser pointers indicate the area of optics field of view. On the right is a picture of FIGIFIGO taken during the field measurements at Suomenlinna, Finland, September 2016. Picture was taken by the author.

In addition to the standard optics used in regular BRF measurements, FIGIFIGO can be equipped with polarizing optics that enable linearly polarized BRF measurements. The polarizing optics utilize a Glan-Thomson linear polarizer that has been mounted in a software-driven rotator. Reference measurements are taken using a Spectralon white reference (WR) panel (manufactured by Labsphere Inc.), which has a high isotropic reflectance (close to a Lambertian surface). Samples with diameters ranging from 10 cm to 50 cm can be measured depending on the used arm length. (Suomalainen et al. 2009a).

In the field, a sky camera that is attached to the casing is used to detect the orientation of the spectrometer, while the direction of the Sun is determined based on GPS coordinates and time. Additional purpose for the sky camera is to take pictures that can be later used to review the weather conditions at the time of the measurements. In addition, solar irradiance is monitored by a pyranometer and readings from the pyranometer is used to make corrections in the field data. This is required due to atmospheric effects on incident radiation. (Suomalainen et al. 2009a).

4.1.1. Operation

When a measurement is initiated, the motor tilts the arm to a starting zenith angle defined earlier by the user, after which the arm is driven by the motor at a constant velocity over the sample to a same angle on the other side while the spectrometer measures reflectance. When measuring with polarizing optics, this process repeats for every polarizer orientation. After the measurement is over for one azimuth angle, the device is turned and the measurement process is initiated again. This procedure is repeated until the sample has been measured from all desired azimuth angles.

The spectrometer is calibrated both between and after measurements by using the Spectralon reference panel; in the field, the calibration is sometimes additionally done before or after the instrument has been rotated to a new azimuth angle, if changes in the radiance due to weather is suspected.

4.1.2. Noise levels

Noise levels vary over the VNIR-SWIR spectrum depending on the sensor sensitivity and the irradiance of illumination (Suomalainen et al. 2009a). When measuring in the field using sunlight, the noise is greatest at the atmospheric absorption bands at around 1200 nm, 1400 nm and 1900 nm (Figure 12). These absorption bands are not as prominent in the laboratory under artificial illumination, but otherwise noise levels are mostly the same or higher.



Figure 12. Noise levels of FIGIFIGO when measuring a Spectralon white reference panel (Suomalainen et al. 2009a). For the sunlight measurement, the high noise in the 1200 nm, 1400 nm, and 1900 nm wavelengths is caused by atmospheric absorption. Low illumination irradiance increases the noise levels at around 986 nm 1760 wavelengths for the laboratory measurement.

Due to low irradiance of the artificial laboratory illumination, the SWIR sensor is using high gain and this increases the noise levels at around 986 nm and 1760 nm wavelengths (Suomalainen et al. 2009a).

4.2. Laboratory measurements

The laboratory samples were measured in Finnish Geospatial Research Institute's laboratory at Masala, Finland. Measurements were done using the polarizing optics with maximum zenith angle of 65° and relative azimuth angles of 0°, 10°, 30°, 60° and 90°. The angle of incidence for all the measurements were 42°, and the measurements were always started at an azimuth angle of 0° .

4.2.1. Laboratory setup

In a laboratory, FIGIFIGO is placed on a steel ring that is 2 m in diameter; this allows the device to be rotated and the azimuth angle changed while having the optics field of view

at the center of the ring. For recording the rotation of the device, the ring has been equipped with an optical encoder. For illumination, a stabilized light source (1,000-Watt QTH light bulb) is used, and an off axis parabolic mirror is placed close to the lamp which reflects the light from the lamp to a regular flat mirror mounted to a telescopic pole. The flat mirror can then be used to direct the collimated beam to the sample (Figure 13).



Figure 13. Laboratory setup. Illumination from a 1,000-Watt QTH light bulb is reflected by using an off axis parabolic mirror to a flat mirror mounted to a telescopic pole. By adjusting the pole, the collimated light is then directed to the sample. FIGIFIGO is placed on the measurement ring that allows the device to be rotated while having the optics field of view at the center of the ring. (Image by Hakala (2009)).

The height of the pole where the flat mirror is mounted is adjustable from 1.5 m to 4 m and the illumination zenith angle can be altered between 20° and 70° by moving the pole and orienting the mirror (Hakala 2009).

4.2.2. Measurement procedure

Samples were measured right after the preparation process of each sample. Reference measurements using a Spectralon white reference panel were taken in the beginning and at the end of each measurement from nadir view direction; before measuring, the panel was leveled using a bubble level and cleaned from dust using compressed air. The spectrometer was allowed to warm up at least 15 minutes before starting measurements.

4.3. Field measurements

In the beginning the instrumentation was set-up and samples selected. The diffuse light originating from atmospheric effects and the environment was measured by shadowing the target from direct sunlight. This was done for the reference panel as well as for the samples. The reference panel was measured in the beginning and at the end of a sample measurement, and sometimes additional reference measurements were done during the measurement or before a new measurement sequence if changes in illumination was suspected. Before each reference measurement, the panel was cleaned and leveled. The azimuth angle was changed by manually lifting and rotating the device around the sample. A maximum zenith angle for the measurements were 75°.

4.4. Data processing

After the measurements, raw data files were downloaded from the control computer and processed in Mathlab; processing involved checking the data for possible errors and eliminating outliers. Next, reflectances were calculated at Finnish Geospatial Research Institute using precoded algorithms and figures were created for data interpretation.

5. RESULTS

The measured reflectances for uncontamined sand samples (Figure 14) show high overall reflectance for quartz sand but less prominent backscattering than that of regular sand. In addition, both samples have absorption bands at 1400 nm and 1900 nm regions.



Figure 14. The reflectance of quartz sand and regular sand samples at 0° , 30° (backward and forward) and 55° (forward) zenith angles.

For quartz sand, polarization is highest in the 1000–1350 nm region and increases at forward direction with increasing zenith angle. Polarization in the backward direction increases after 1350 nm wavelength, while polarization in the nadir and forward direction at low zenith angle drops. For regular sand, polarization in the 1000–1100 nm region drops for all zenith angles, but the drop is less in 55° forward direction (Figure 15).





Figure 15. The degree of linear polarization and polarized reflectance for quartz sand and regular sand.

Diesel contaminated quartz sand shows distinct absorption band appearing at around 1730 nm starting from the lowest concentration of 0.5 wt.% (Figure 16), and the band becomes more prominent with increasing hydrocarbon content. In addition, absorption at the 1400 nm band increases, and another absorption band appears at 1200 nm wavelength region starting from diesel content of 1 wt.%. There is also an increasing drop in reflectance at around 2300 nm, while the overall reflectance decreases over the whole VNIR-SWIR spectrum.





Figure 16. Reflectances for diesel contaminated quartz sand samples.

The uncontaminated quartz sand polarization at 1000–1350 nm region turns negative when diesel is added. In addition, there is no decrease in polarization after 1350 nm region, the angular dependency for polarization decreases, and there is negative polarization or no polarization in the backward direction (Figures 17-18).





Figure 17. The degree of linear polarization for diesel contaminated quartz sand.

Figure 18. Polarized reflectance of diesel contaminated quartz sand.

When diesel is mixed with regular sand, an absorption band appears at 1730 nm and backscattering decreases with inreasing diesel content. However, there is no additional absorption band appearing at 1200 nm region (Figure 19).



Figure 19. The reflectances for diesel contaminated regular sand samples.

When diesel is added, the polarization decreases in the SWIR region (Figures 20-21).



34



Figure 20. The degree of linear polarization for diesel mixed with regular sand.



Figure 21. Polarised reflectance of regular sand mixed with diesel.



Motor oil exhibits similar absorption bands as diesel, but they are more prominent (Figure 22).

Figure 22. Reflectances for quartz sand mixed with motor oil.

With motor oil, the polarization seems to be lower overall, but increase in longer wavelengths in forward direction at 4 wt.% concentration (Figure 23–24).



Figure 23. The degree of linear polarization for quartz sand mixed with motor oil.





Figure 24. Polarized reflectances for motor oil mixed with quartz sand.

Overall reflectance decreases with the increase of lead pellets, and with 363 lead pellets there is higher difference between reflectance at nadir and in forward direction at greater zenith angle (Figure 25).



Figure 25. Reflectances for quartz sand and lead pellets.

When lead pellets are placed on the quartz sand, the polarization increases in the forward direction and at nadir in the SWIR region, while the polarization decreases in the backward direction (Figures 26–27).



Figure 26. The degree of polarization for lead pellets and quartz sand.





Figure 27. The polarized reflectance for lead pellets and quartz sand.

Reflectance between vegetation 1 and 2 is very similar, but vegetation 2 has slightly lower reflectance at 750–1350nm region, which is associated with internal structure. There is also decreased polarization at 1100nm region in nadir position with Vegetation 1, and increased polarization in the backward direction (Figures 28–30).



Figure 28. Reflectances for the vegetation samples.

40



Figure 29. The degree of polarization for the vegetation samples.



Figure 30. The polarized reflectance for the vegetation samples.

The overall reflectance of soil 1 is slightly lower, and there is variation in polarization between the samples at 800–1200 nm region (Figures 31–33).



Figure 31. Reflectances for the soil samples.





Figure 32. The degree of polarization for the soil samples.



Figure 33. Polarized reflectance for the soil samples.

6. DISCUSSION

6.1. Diesel and motor oil

The diesel and motor oil measurements show distinct hydrocarbon absorption features as predicted based on previous studies, such as Cloutis (1989) and Aske et al. (2001). The 1730 nm overtone band appeared for all measured samples and became more prominent with increasing diesel and motor oil contents. However, this overtone band was significantly less prominent when measuring diesel with regular sand; this is likely due to clay minerals that sorbed a portion of the diesel. The presence of clay minerals even in low quantities has a tendency to significantly lower the intensity of spectral features of sorbed hydrocarbons (straight chain alkenes) through the shielding of hydrocarbons from incident radiation due to clay mineralogy (Forrester et al. 2010). This effect is affected by moisture content (Okparanma 2013b), which was not taken into account in this work.

Both diesel and motor oil when mixed with quartz sand show an additional absorption band at 1200 nm, which can generally be associated with C-H stretching in methyl and methylene (Stuart 2004). This band is where variations between different hydrocarbons most likely occur (Meijde van der et al. 2013), however both diesel and motor oil show similar absorption in that region. Diesel mixed with regular sand does not show this absorption band, which can be due to the lower intensity of the band as well as clay minerals. The increasing absorption near 2300 nm region is distinct for all samples, but since the noise levels of FIGIFIGO are high in that region, it is mostly ignored in this work.

Polarization show decrease in the backward direction in the SWIR region. This can be due to the diesel and motor oil filling the pores and lubricating the grain surfaces, creating a more even and oily surface, which consequently increases the specular components in the reflectance and hence increases the polarization in the forward direction. The changes in polarization are greater on low zenith angles relative to higher angles, but the polarization remains greatest on the highest zenith angle in the forward direction. Overall, the polarization relationships with increasing hydrocarbon content is not drastic, this could be due to the low contaminant concentrations; the concentrations used by Wang et al. (2009) to study hydrocarbon polarization were as high as 20 wt.%, and at the lowest 7.5 wt.%. However, the polarization changes drastically when adding hydrocarbons to quartz sand and this effect was not visible for regular sand with high clay content; it would be beneficial to study the relationships between clay, quartz and hydrocarbon contents in terms of polarization in the future.

6.2. Lead

Lead showed a decrease in overall reflectance with increasing numbers of lead pellets, but no absorption features; this confirms the findings of previous studies (e.g. Pandit et al. 2010). The reflectance increased moderately in the forward direction with increasing zenith angle, while the polarization increased dramatically in the forward direction (in the SWIR region) with the addition of lead pellets; this is due to the way the free electrons in lead interact with the incident radiation and generate polarization. This suggests that soils contaminated with lead and other heavy metals may possibly be characterized based on directional reflectance and polarization; just adding one lead pellet greatly affected the results. These reflectance characteristics could be most readily exploited when mapping soils near shooting ranges. However, Pb complexing with organic matter as well as other soil constituents that are present might affect the polarization in natural soils and make the characterization challenging.

6.3. Lead contaminated soil and vegetation

Soil samples have similar spectral shape and reflectance characteristics with slight difference in overall reflectance; some variation between the two samples occur in polarization between 900 nm and 1150 nm, which is a region associated with plant structure. However, although this variation cannot be related to heavy metals based on these measurements, it can be speculated that this region would be potential for future research as the observed variation is consistent with the hypothesis that polarization in longer wavelengths than 800 nm can provide information on the internal structure of

plants (Vanderbilt et al. 1991), and heavy metals can affect these wavelengths (Kooistra et al. 2004). In addition, also vegetation showed similar variation in the same region. Despite the fact that the spectral shapes are mostly the same, there are differences between the overall reflectance and this is in line with previous studies involving lead contaminated vegetation (Davids and Tyler 2003, Kooistra et al. 2004).

7. CONCLUSIONS

Petroleum hydrocarbons in common diesel fuel and mineral motor oil show a distinct absorption feature at around 1730 nm as well as a minor one at around 1200 nm. However, the 1200 nm band is significantly less intense, and therefore the 1730 nm band is considered more preferable for detecting hydrocarbons in soils. Clay minerals effectively masked these spectral signatures, and thus it is deduced that it is more challenging to detect petroleum hydrocarbons in soils with high clay content. Despite this, it was found that it is possible to detect hydrocarbon spectral signatures with concentrations as low as 0.5 wt.% even when the clay content is high. Polarization and bidirectional reflectance of hydrocarbons follows the same principles as that of water in soil; characteristic properties specifically relatable to petroleum hydrocarbons was not found. Further studies on the relationships between water, clay, quartz and hydrocarbon contents and their combined effects on the observed reflectance properties is recommended.

The presence of lead was characterized by its tendency to reflect light specularly, which consequently resulted in strong polarization in the forward direction with increasing zenith angles as well as a significant decrease in polarization in the backward direction in the SWIR region. However, more research with different types of soil materials is needed in order to determine if these properties can be detected in heterogeneous soils with smaller Pb concentrations, and to investigate how the complexing of Pb with organic matter affects the results. In addition, it was confirmed that the overall reflectance decreases with increasing lead content.

It was not possible to reliably detect lead contaminations from the reflectance of soil and vegetation at the field measurement site due to small sample size and lack of accurate

information on the lead concentrations at the measurement spots. Nonetheless, the observed variation in reflectance was consistent with previous studies, and thus the possibility of lead being the cause cannot be ruled out. Moreover, the 900–1200 nm region showed the most potential for characterizing polarization of heavy metal stressed vegetation at contaminated areas.

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