Remote Sensing for the Geobotanical and Biogeochemical Assessment of Environmental Contamination

by

James Wickham¹
Matthew Chesley²
Judith Lancaster¹
David Mouat¹

Desert Research Institute
University and Community College System of Nevada
Reno, Nevada

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¹Biological Sciences Center

²Water Resources Center

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PREFACE

This document has been written to provide the Department of Energy (DOE) with a literature review of current remote sensing techniques that have been or can be used to examine the spectral properties of vegetation as affected by environmental stress. As pollutants may often be the cause of vegetation stress, the ability to identify such stresses may help DOE in their efforts to locate, map, and monitor zones of contamination on DOE sites. The remote sensing studies reported in the literature have been examined with respect to their potential usefulness, and it is hoped that this resulting document will aid DOE in the development of remote sensing programs in support of Environmental Restoration and Waste Management (ERWM) activities.

To adequately cover the many aspects of detecting vegetation stress using remote sensing techniques, a relatively lengthy document is required to discuss techniques appropriate to laboratory, field, airborne, and satellite platforms, in addition to a basic review of plant physiology and vegetation response to stress. To provide a more useful and comprehensible resource, this document has been split into chapters that, to some extent, can be read independently of one another.

The document consists of seven chapters: 1) Background/Introduction; 2) Detection of Red Edge Shifts in Plant Reflectance Spectra; 3) Full Spectral Matching and Fluorescence; 4) Ratio Techniques; 5) Results of the Sacramento River Study; 6) Review of Plant Physiology; and 7) Summary and Conclusions. The Introduction provides a brief overview of the unique spectral response of vegetation and how this response has been examined in vegetation stress detection studies. Chapter 2 discusses previous studies using laboratory, field, and airborne spectral data, focusing on the detection of red edge shifts to shorter or longer wavelengths. Chapter 3 presents full spectral matching techniques that have expanded on red edge shift detection studies, and introduces fluorescence. Chapter 4 presents studies that have used ratio techniques to study vegetation, and discusses the relationships between ratio and red edge shift detection techniques. Chapter 5 presents the application and results of some of these techniques in the Desert Research Institute's (DRI) study of vegetation following the July 13, 1991, contaminant spill along the Sacramento River in northern California. Chapter 6 reviews the basic plant physiology functions related to primary production and chlorophyll development. The Summary and Conclusions tie together the results of the preceding chapters, and highlights potential challenges and applications of future data collection and analysis efforts.

As mentioned previously, each of the chapters can be examined independently of each other. A summary and conclusions section closes each chapter to facilitate its independent treatment. The separation has been done for convenience, based on different aspects of remote sensing of vegetation stress. However, the chapters are naturally connected; therefore, we recommend that each chapter be read in turn.

1.0 BACKGROUND/INTRODUCTION

Under Contract Number DE-AC08-90NV10845, the DOE has funded the Desert Research Institute (DRI) to examine several aspects of remote sensing, specifically with respect to how its use might help support Environmental Restoration and Waste Management (ERWM) activities at DOE sites located throughout the country. This report represents partial fulfillment of DRI's obligations under that contract and includes a review of relevant literature associated with remote sensing studies and our evaluation and recommendation as to the applicability of various remote sensing techniques for DOE needs.

With respect to DOE ERWM activities, remote sensing may be broadly defined as collecting information about a target without actually being in physical contact with the object. As the common platforms for remote sensing observations are aircraft and satellites, there exists the possibility to rapidly and efficiently collect information over DOE sites that would allow for the identification and monitoring of contamination related to present and past activities. As DOE sites cover areas ranging from tens to hundreds of square miles, remote sensing may provide an effective, efficient, and economical method in support of ERWM activities.

For this review, remote sensing has been limited to methods that employ electromagnetic (EM) energy as the means of detecting and measuring target characteristics. The EM spectrum and properties thereof are displayed in Figure 1.1 and Table 1-1. DRI's focus excludes electrical, magnetic, and gravity methods that are being considered by other researchers for DOE. More specifically, this review primarily encompasses passive remote sensing techniques between 0.4 and 2.5 micrometers (μm). The reasons for this are straightforward: a large number of laboratory, field, airborne, and satellite instruments currently exist that have successfully demonstrated collection of data in this manner and in this region of the EM spectrum, thereby allowing the implementation and application of successful methodology with a minimum of development time.

This review discusses passive techniques between 0.4 and 2.5 μm , with an emphasis on vegetation and its use as a surrogate indicator of the presence of contamination. Vegetation is in contact with both the surface and subsurface allowing it to be an integrator of conditions in both environments. Properties of vegetation, vegetation stress associated with contamination, and primarily, remote sensing techniques that allow vegetation stress to be detected are the focus of this literature review. Where warranted, aspects of the reviewed remote sensing studies and techniques are discussed with respect to their relevancy and application to DOE concerns.

In examining the use of remote sensing techniques for application on DOE sites, methods are reviewed that primarily focus on detecting departures (or "anomalies") from normal or control reflectance spectra. Specifically, remote sensing techniques are examined with respect to the detection of vegetation spectral response resulting from the effects of contaminants and to use that response in the process of contamination assessment. There are several reasons for focusing on vegetation as a detection medium: plants are sessile and therefore cannot avoid environmental contaminants released into the environment; vegetation is fairly ubiquitous (even

Figure 1.1: The electromagnetic spectrum (from Sabins, 1987).

Table 1-1.: Electromagnetic spectral regions (from Sabins, 1987).

Region	Wavelength	Remarks
Gamma ray	$< 0.03 \text{ nm}$	Incoming radiation is completely absorbed by the upper atmosphere and is not available for remote sensing.
X-ray	$0.03 \text{ to } 3.0 \text{ nm}$	Completely absorbed by atmosphere. Not employed in remote sensing.
Ultraviolet	$0.03 \text{ to } 0.4 \mu\text{m}$	Incoming wavelengths less than $0.3 \mu\text{m}$ are completely absorbed by ozone in the upper atmosphere.
Photographic UV band	$0.3 \text{ to } 0.4 \mu\text{m}$	Transmitted through atmosphere. Detectable with film and photodetectors, but atmospheric scattering is severe.
Visible	$0.4 \text{ to } 0.7 \mu\text{m}$	Imaged with film, photodetectors, electro-optical systems, and CCDs. Includes reflected energy peak of earth at $0.5 \mu\text{m}$.
Infrared	$0.7 \text{ to } 100 \mu\text{m}$	Interaction with matter varies with wavelength. Atmospheric transmission windows are separated by absorption bands.
Reflected IR band	$0.7 \text{ to } 3.0 \mu\text{m}$	Reflected solar radiation that contains no information about thermal properties of materials. The band from $0.7 \text{ to } 0.9 \mu\text{m}$ is detectable with film and is called the <i>photographic IR band</i> .
Thermal IR band	$3 \text{ to } 5 \mu\text{m}, 8 \text{ to } 14 \mu\text{m}$	Principal atmospheric windows in the thermal region. Images at these wavelengths are acquired by optical-mechanical scanners and special vidicon systems but not by film.
Microwave	$0.1 \text{ to } 30 \text{ cm}$	Longer wavelengths can penetrate clouds, fog, and rain. Images may be acquired in the active or passive mode.
Radar	$0.1 \text{ to } 30 \text{ cm}$	Active form of microwave remote sensing. Radar images are acquired at various wavelength bands.
Radio	$> 30 \text{ cm}$	Longest wavelength portion of electromagnetic spectrum. Some classified radars with very long wavelength operate in this region.

in arid regions); vegetation grows in both the surface and subsurface environment allowing it be in contact with pollutants in several phases; plants may be sensitive to toxic concentrations far below that needed for direct detection; through bio-accumulation of toxins, vegetation may provide a potential pathway for exposure or method of remediation; and finally, vegetation has a spectral profile that is unique from nearly all other earth surface materials.

The region of the EM spectrum being used by most passive remote sensing systems is shown in Figure 1.2 along with atmospheric transmittance, which dictates the placement of many instrument channels. Figure 1.3 displays a typical vegetation reflectance spectrum (changing magnitude of reflectance across a series of wavelengths) detailing the red edge and atmospheric absorption bands. Vegetation has a unique reflectance spectra from that of most other earth surface materials. The photochemical pigments (principally chlorophylls) contained within plant tissues are primarily responsible for the unusual spectral response of vegetation in the visible and near infrared (NIR) regions of the EM spectrum. Chlorophylls use the energy contained in the sun's radiant flux to drive photosynthetic reactions. However, the amount of energy in the sun's radiant flux varies across the EM spectrum and is inversely proportional to the wavelength (see, for example, Breuer, 1975):

$$E = \frac{c}{\lambda}$$

where c is the speed of light, λ is wavelength, and E is energy. Wavelengths in the infrared (IR) region ($\approx 700 \text{ nm}$ to 1 mm) do not contain enough energy to drive photosynthetic reactions, and

Figure 1.2: An expanded diagram of the visible and infrared regions of the EM spectrum showing atmospheric windows and band placement of commonly used remote sensing systems (from Sabins, 1987).

Figure 1.3: Reflectance spectra for vegetation and rock and spectral regions dominated by specific plant attributes (adapted from Sabins, 1987).

are reflected. In contrast, wavelengths in the visible region (400 to 700 nm) of the EM spectrum contain the energy necessary to drive photosynthetic reactions, and are absorbed. Thus, the sharp increase in reflected energy from a vegetated surface at the change from the visible red to the NIR region of the EM spectrum (Figure 1.3) is the result of the energy contained in the respective regions and its utility in driving photosynthetic reactions (Salisbury and Ross, 1979). If ultraviolet (UV) radiation (less than ≈ 400 nm) is considered as a third region, it is found that too much energy is contained in this region to be useful in driving photosynthetic reactions. The utility of energy in the UV, IR, and visible regions in driving photosynthetic reactions can be thought of as “too hot,” “too cold,” and “just right,” respectively.

The sharp increase in vegetation reflectance from the visible red to the NIR portion (at approximately 700 nm or 0.7 μm) of the EM spectrum is referred to as the red edge (Figure 1.3). The red edge was first reported by Gates et al. (1965), and discussed in the remote sensing literature by Knipling (1970)¹. Detecting vegetation stress with remote sensor data often employs techniques that quantify horizontal changes (change in wavelength) or vertical changes (change in magnitude of reflectance) in the red edge by comparing the red edge positions of suspected stressed vegetation to known controls (non-stressed). The position of the red edge is most often defined by the point of maximum slope or greatest change in reflectance per unit of wavelength between the regions of strong absorption and reflection centered around 700 nm.

Comparisons of horizontal positions have often taken advantage of the fact that a vegetation spectral profile can be easily expressed as a mathematical function (e.g., $y=F(x)$; $F(x)=a_1+a_2x+a_3x^2$, where y = reflectance, x = wavelength, and the a 's are coefficients). The recent introduction of remote sensing instrumentation with high spectral resolution allows small changes in the position of the red edge to be observed directly in the resulting spectrum, and is more reliable than using functions to estimate red edge positions. Comparisons of vertical changes more often use ratio (or ratio based) calculations (e.g., NIR/red), and can be done with remote sensing instrumentation with a much lower spectral resolution.

Remote detection of vegetation spectral anomalies is not new. Many studies have been published reporting variations in vegetation reflectance spectra, focusing on such things as metal toxicity (Banninger, 1991; Horler et al., 1980a, 1980b; Roberts and Green, 1985; Milton et al., 1988; Lehman et al., 1990; Lichtenthaler, 1989; Lichtenthaler and Buschmann, 1987; Lichtenthaler et al., 1986; Lulla et al., 1982; Lyon, 1987; Suresh et al., 1989; Zilioli et al., 1992), plant chemical content (Card et al., 1988; Curran, 1989; Curran et al., 1991; Elvidge, 1988; Jensen et al., 1990; Marten et al., 1989; Schenk et al., 1979; Wessman et al., 1987; Norris et al., 1976; Williams, 1991), estimation of vegetation parameters and vegetation classification (Tucker et al., 1986; Quarmby et al., 1992; Williams and Nelson, 1984; Banninger, 1989; Curran et al., 1992; Huete et al., 1985), phenological development (Boyer et al., 1988; Miller et al., 1991; Schwaller and Tach, 1980; Schwaller et al., 1981; Labovitz et al., 1985; Williams et al., 1983), moisture/temperature stress (Carlson et al., 1971; Cure et al., 1989; Danson et al., 1992; Holben et al., 1983; Jackson et al., 1980; Kleman and Fagerlund, 1987; Pierce et al., 1990; Riggs and Running, 1991; Gulaid, 1986; Steinmetz et al., 1990), and airborne pollution and pest infestation (Khorram et al., 1989; Rosema et al., 1992; Rock et al., 1986). The "newness" of this effort is brought about by recent developments in instrumentation that allow the detection of much smaller variations in vegetation reflectance spectra from ground and airborne platforms at local and regional scales. Furthermore, this effort involves multi-disciplinary investigations combining knowledge of sensor development (laboratory, field, airborne, and satellite instruments), spectral mixing, vegetation characteristics, contaminant relationships, and computer programming. In addition, research is needed to define species-specific, normal or unstressed spectral reflectance properties and contaminant related affects to observe and detect variations due to contamination. The identification of these parameters is the stepping stone to effectively and efficiently characterize contamination on a regional scale.

¹Reviews by Knipling (1970), and others, have complicated somewhat the significance of the vegetation spectral profile by attributing high reflectivity in the near infrared (≈ 700 to $1,300$ nm) to leaf anatomical structure. While this is technically correct, it obscures the fact that this wavelength region of light does not contain sufficient energy to excite chlorophyll pigments, and would therefore be reflected or transmitted, since these are the only other outcomes possible. The article by Knipling is still widely cited in the literature, and is often accompanied by a typical vegetation reflectance spectrum that attributes its unique spectrum to chlorophyll pigment absorption, leaf anatomy, and water absorption among the three regions ≈ 400 to 700 nm, ≈ 700 to $1,300$ nm, and $\approx 1,300$ to $2,400$ nm, respectively.

While there have been an extensive number of vegetation contaminant exposure studies as referenced in Appendix 1, most were not concerned with changes in spectral properties and many do not include contaminants or vegetation species of concern to DOE. A list of pollutants of concern to DOE and other agencies is given in Appendix 2. Generally, the contaminants found on DOE sites can be placed into four groups (volatile organic compounds, heavy metals, radioactive compounds, and inorganic compounds). Of these four, metal toxicity has received the most attention in the remote sensing literature, largely due to its relationship to economic mineral deposits. Therefore, a significant need exists to define the spectral affects of previously untested contaminants on numerous vegetation species to efficiently apply remote sensing techniques at DOE facilities. Experiments must also be designed for optimal application of remote sensing methods, since the detection of stress in individual leaves does not guarantee that the same stress will be detectable or mappable in airborne or satellite remote sensing applications. Nor does success in humid environments guarantee successful implementation in arid environments. It will be necessary to define these unknown characteristics with careful consideration of future applications for maximum benefit to DOE and other agencies concerned with the detection, monitoring, and remediation of contaminated areas.

2.0 DETECTION OF VEGETATION STRESS THROUGH HORIZONTAL SHIFTS IN THE POSITION OF THE RED EDGE

As previously shown in Figure 1.3, properties of vegetation reflectance spectra include the absorption wells in the blue (400 to 500 nm) and red (600 to 700 nm) wavelength regions, the reflectance hump in the green region, and the area of rapid change in reflectance between the red and near infrared (NIR) regions (≈ 700 nm) known as the red edge. A majority of research has focused on detecting changes in the red edge, as it is one of the more significant features in vegetation reflectance spectra.

Detection of horizontal shifts in the position of the red edge can be calculated by subtracting the percent radiance (%R) at wavelength n (λ_n) from %R at λ_{n-1} . This series of simple subtractions is calculated across the entire series of wavelengths that constitute the red edge portion of the electromagnetic (EM) spectrum, approximately 670 to 760 nm. Many investigators compute the subtractions across the EM spectrum from 400 to 1,000 nm, or some subset of this range (Rock et al., 1988; Curtiss and Ustin, 1989; Karr and Mouat, 1990). This series of calculations simply creates the first derivative of the measured spectrum and is termed the simple difference spectra (SDS). Simple difference or first derivative spectra is discussed thoroughly by Boochs et al. (1990) and is summarized below. The Boochs et al. (1990) red edge equation is defined as:

$$dr(i) = r(i) - r(i - 1)$$

where $r(i)$ is the radiance at wavelength (i) . The authors used radiance values for 90 wavebands² from 623 to 802 nm. The graphical depiction of the original spectral profile (bottom) and simple difference spectra (top) is reproduced in Figure 2.1.

The actual position of the red edge is most often defined as the wavelength of maximum change (slope) in radiance, and is equivalent to the maximum inflection point (MIP) of the first derivative spectra. Figure 2.1 displays the MIP labeled $dr_{\max}$ and the corresponding wavelength position of the red edge (λ_{re}). An SDS typically has a parabolic shape between 670 and 760 nm, with the maximum difference in radiance defining the peak of the parabola where the slope begins to decrease. In the example illustrated by Boochs et al. (1990), the red edge inflection point occurs at about 730 nm.

It should be noted that variations of the red edge equation are also used. For example, Ambrosia et al. (1991) defined their red edge equation including the wavelength difference as a divisor as:

$$R_n - R_{(n-1)} / \lambda_n - \lambda_{(n-1)}$$

where R is the percent radiance for waveband n and λ is the wavelength midpoint for that waveband. This allows for limitations in the instrument to be accounted for.

²Waveband is a term that is used to describe the spectral resolution of a sensor when that resolution spans more than 1 unit (e.g., nanometers) of wavelength. In the case of Boochs et al. (1990), the wavebands spanned 2 nm (nanometers) of wavelength.

Figure 2.1: Reflectance spectra (bottom) and simple difference spectrum (top) (from Booch et al., 1990).

Laboratory Studies

Much of the work regarding detection of a horizontal shift in the position of the red edge has been carried out under laboratory conditions. The results from many of these studies are summarized in Table 2-1. The majority of the results show that vegetation stress is evident as a shift in the red edge position toward shorter wavelengths, known as a blue shift. However, observations of shifts towards longer wavelengths have been recorded as well (Milton et al., 1989).

Observation of a blue shift in several studies focusing on plant development has shown the position of the red edge to be related to chlorophyll concentration (Gates et al., 1965; Collins 1978; Horler et al., 1983). Each of these studies, with the exception of Horler et al. (1983), traced the position of the red edge through phenological development, showing that the red edge shifts

TABLE 2-1: Red edge shift detection: laboratory studies.

AUTHOR/ SPECIES	INSTRUMENT	BAND WIDTH	SPECTRAL RANGE	STUDY TYPE	TARGET SIZE	LEAF STACKING [†]	RESULTS
Westman & Price 1987 species: <i>jeffery pine</i> , <i>giant sequoia</i> , <i>California coastal sage scrub</i> species	Collins VIRIS	NR	NR	ozone sulfur dioxide fumigation	NR	NR	blue shift, magnitude not reported
Singhroy et al. 1989 species: <i>white birch</i> , <i>quaking aspen</i> , <i>jack pine</i> , <i>blue spruce</i> , <i>white and red oak</i>	Barringer HHRR	3 nm	7 bands @ 650, 680, 703, 713, 743, 782, 800 nm	mineral stress	6 cm ²	3+	8 blue shifts up to 5.8 nm, b shift to 5.8 nm, r shift to 3 nm, and no shift, 3 red shifts up to 3 nm, 3 no shifts
Chang & Collins 1980 species: <i>sorghum</i> , <i>mustard</i>	NR	NR	NR	mineral stress	NR	NR	blue shift of 10 nm with low soil conc. (100 ppm)
Milton et al. 1989 species: <i>soybean</i>	Beckman 5240	NR	NR	arsenic and selenium doping	2 cm ²	1	selenium doping produced 4 nm red shift arsenic doping produced 1 to 3 nm blue shift
Hoque & Hutzler 1992 species: <i>Beech</i>	Zeis MCS 512	2.4	680 to 760	damage classes	NR	NR	blue shift up to 7 nm across 4 damage classes
Milton et al. 1991 species: <i>soybean</i>	Beckman 5240	1 nm	400 to 800	Phosphorous (P) deficiency	2 cm ²	1	blue shift up to 7 nm with ↑ P deficiency
Horler et al. 1983 species: <i>corn</i>	Perkin Elmer 554	NR	NR	Cu, Zn stress	NR	3+	blue shift, magnitude not reported
Singhroy & Kruse 1991 species: <i>white birch</i> , <i>quaking aspen</i> , <i>jack pine</i> , <i>blue spruce</i> , <i>white and red oak</i>	SE590	2.8 nm	400 to 1,100 nm	mineral stress	6 cm ²	3+	6 blue shifts up to 9 nm 2 red shifts up to 3 nm 3 no shifts

[†] = number of layers of leaves within spectroradiometer field-of-view

NR = not reported

nm = nanometer

to longer wavelengths (an IR shift) as plants mature. It was inferred from these results that overall chlorophyll concentration was responsible for the wavelength position of the red edge. Horler et al. (1983) further documented this relationship by regressing red edge positions (λ_{re}) against chlorophyll concentration per leaf area ($\mu\text{g}/\text{cm}^2$). Correlation coefficients (R^2) and significance measures were strong for both monocot and dicot plants.

These studies have provided the basis for using positional shifts of the red edge as an indicator of vegetation stress. As pollution and/or other types of environmental stress impacts plants, a likely consequence is to impact the physiological and/or physico-chemical properties of the plant. The net result is often an overall reduction in chlorophyll concentration due to hindered metabolic process (e.g., photosynthesis, respiration). This reduction in chlorophyll should be detectable as a shift in the wavelength position of the red edge.

A valuable property of red edge shifts is its insensitivity to mixed pixel problems.³ Horler et al. (1983) have shown that varying the amount of vegetation and bare ground (i.e., rock or soil) within the spectrophotometer field-of-view or pixel does not appreciably affect the position of the red edge as long as vegetation comprises at least 20 percent (Figure 2.2). This finding has been replicated by Miller et al. (1990) and is important with regard to aerial and satellite remote sensing applications which have spatial resolutions ranging from tens to hundreds of square meters.

While the majority of results in Table 2-1 show a shift to shorter wavelengths, or a blue shift, in the red edge for stressed vegetation relative to control samples, they tend to be rather small, typically less than 10 nm (e.g., Singhroy and Kruse, 1991; Chang and Collins, 1980; Hogue and Hutzler, 1992; Milton et al., 1991). As these shifts are sometimes not present, or the shift is toward longer wavelengths (an IR shift), it is important to define properties responsible for these variations.

Unfortunately, because of differences in analytical techniques and instrumentation, it is difficult to find a single or suite of characteristics responsible for the variable results. These are in addition to differences in species studied and toxins used, or stresses applied. Indeed, Milton et al. (1989) showed that arsenic doping produced a blue shift while selenium doping produced a red shift in the same species. This emphasizes the need to delineate those species and contaminants that show potential in remote sensing applications.

Horler et al. (1983) showed that leaf stacking (increasing the number of layers of leaves above one within the spectrophotometer field-of-view) shifted the position of the red edge to longer wavelengths. This result is consistent with the results of the phenological studies presented earlier because leaf stacking places more chlorophyll within the field-of-view, thereby simulating increased chlorophyll concentrations due to phenological leaf development

³Mixed pixel refers to the phenomenon where more than one earth surface feature (e.g., vegetation, soil, water) contributes significantly to the signal received for that field-of-view or picture element (pixel). Current research is focusing on the ability to distinguish the contribution to the signal of each surface feature for a mixed pixel.

Figure 2.2: Change in the position of the red edge inflection point (λ_{re}) as amount of vegetation is reduced from 100 to 0 percent (reprinted from Horler et al., 1983).

and maturity. Increasing leaf stacking above one layer may increase the overall chlorophyll concentration of both stressed and control samples, potentially decreasing the magnitude of the difference between them. Westman and Price (1987) showed that infrared reflectivity reaches an asymptote at seven to eight leaf layers, which further supports this position. Singhroy et al.

(1989) and Singhroy and Kruse (1991) were the only studies using a leaf stack greater than one, and the only studies that reported instances of no shift between stressed and control samples.

Field and Airborne Studies

There have been relatively few red edge shift detection studies undertaken that have utilized field-measured spectral data (Table 2-2), and even fewer using airborne-measured data (Table 2-3). Notwithstanding the greater expense of data collection, the reasons for the few number of red edge shift detection studies using field- or airborne-collected data seem to be twofold. First, the high spectral resolution necessary to detect horizontal shifts in the wavelength position of the red edge is not readily available on most airborne remote sensing instrumentation. Ideally, many spectral measurements are needed along the entire red edge slope (≈ 670 to 760 nm). The majority of airborne systems do not have spectral resolution finer than 10 nm,⁴ which is approximately the maximum magnitude of red edge shifts reported in the literature (Singhroy and Kruse, 1991). Second, removing spectral measurements from the laboratory into the field introduces confounding effects of variations in atmospheric conditions, and canopy and illumination geometry. Table 2-4 tallies a number of studies that have investigated red edge shifts, according to whether they used laboratory measurements, field-, or airborne-collected data. Undoubtedly, many more field and airborne studies will take place in the near future as instrumentation development continues and the need for regional assessment of vegetation increases.

Most researchers have recognized the potential for atmospheric, canopy and illumination geometry effects to complicate the application of red edge shift detection studies (Schwaller, 1982; Chang and Collins, 1980; Collins et al., 1983; Shutt et al., 1984; Vanderbilt et al., 1985; Vanderbilt et al., 1988; Curtiss and Maecher, 1991). The results in Table 2-2 reflect to some extent the potential impact of these environmental parameters. Only two of the five studies (Demetriades-Shah and Steven, 1988; Curtiss and Maecher, 1991) conducted their experiments at the canopy level. Of these two, only Curtiss and Maecher (1991) attempt to control for differences in canopy and illumination geometry, by using principal components analysis. The significance of their results is that they indicated a shift of the red edge, while those of Demetriades-Shah and Steven (1988) did not. The three remaining studies collected spectral data at the branch level, which effectively eliminates any canopy and illumination geometry, and atmospheric effects.

The impact of a variable environment (e.g., atmospheric, canopy and illumination geometry) on the detection of red edge shifts between stressed and control sites is even more evident among the studies utilizing airborne data (Table 2-3). While two of the three studies

⁴Rock et al. (1988) used the Fluorescence Line Image (FLI) to collect their airborne data. The FLI has a spectral resolution of approximately 2.6 nm, and was manufactured by Moniteq, Ltd. A more complete description of the system is found in Hollinger et al. (1985). Also, Collins et al. (1983) used the Mark I system, which collects spectral data for 500 wavebands across the 450 to $1,100$ nm portion of the EM spectrum in 1.4 nm bands. Description of the Mark I system is found in Chui and Collins (1978).

TABLE 2-2: Red edge shift detection: field studies.

AUTHOR/ SPECIES	INSTRUMENT	BAND WIDTH	SPECTRAL RANGE	SAMPLING [†] DISTANCE	STUDY TYPE	TARGET SIZE	RESULTS
Demetriades-Shah & Steven 1988 species: <i>sugar beet</i>	LI-1800/Li-Cor	6 nm	400 to 1,100 @ 2 nm internals	2 m above canopy	chlorosis (virus infection)	NR	canopy red edge did not correlate, chlorophyll content ($\mu\text{g}/\text{cm}^2$)
Buschmann et al. 1989 species: <i>spruce</i>	VIRAF	NR	400 to 800 nm	NR	damage (forest decline)	NR	1) no shift for current year needles 2) 4 nm blue shift for 1-year-old needles 3) 10 nm shift for 2-year-old needles
Rock et al. 1988 species: <i>spruce</i>	VIRIS	2 nm	400 to 1,000 nm	NR	air pollution	1 x 3 cm	1) 5 nm blue shift for current year needles 2) 5 nm blue shift for 3-year-old needles
Curtiss & Maecher 1991 species: <i>lodgepole pine</i>	PSII	2.7	350 to 1,050 @ 1.3 nm internals	50 m	stress arsenic, lead, zinc	NR	blue shift, magnitude not reported
Curtiss & Ustin 1989	PIDAS	1 nm 5 nm	400 to 900 m 900 to 2,450	0.5 m	ozone	10 cm	red shift with ozone damage ↑
Karr & Mouat 1990	HHRR	10 nm	675 to 775 nm used	1.0 m	acid wastes heavy metals	10 cm	blue shift with increasing concentration

↑ = increase

† = distance between spectrometer and target

TABLE 2-3: Red edge shift detection: airborne studies.

AUTHOR/ SPECIES	INSTRUMENT	BAND WIDTH	SPECTRAL RANGE	PIXEL SIZE	# OF PIXELS PER TARGET	STUDY TYPE	RESULTS
Ambrosia et al. 1991 species: <i>ponderosa pine</i>	AVIRIS	9.7 to 11.6 nm	400 to 2,450	NR	154 to 375	drought and pest damage	no shift evident
Leprieur 1989	AVIRIS	9.8 nm	400 to 2,450	20 m	20 to 309	Δ in red edge with Δ in vegetation	$\uparrow$ in red edge from 705 to 721 nm across 8 sites
Rock et al. 1988	FLI	2.6 nm	400 to 800	8 x 17 m	NA	air pollution	1 nm blue shift, but this magnitude was not larger than wavelength standard deviation values

NA = not applicable

Δ = change

$\uparrow$ = increase

TABLE 2-4: Trends in detection of shifts in the red edge.[†]

STUDY SCALE	BLUE SHIFT	IR SHIFT ^Φ	NO SHIFT
Laboratory	21	6	6
Field	6	1	2
Airborne	2	0	1

[†] The tallies are based on the number of shifts reported in the reports cited. In some cases, authors reported results for several species, and in other cases, results were reported across time. Therefore, the number of shifts reported is greater than the number of studies listed in Tables 2-1, 2-2, and 2-3.

^Φ Shifts less than 1 nm were treated as no shift.

reported shifts, only Leprieur (1989) attempted to account for environmental constraints, such as atmospheric parameters, sun position, and canopy architecture. Illumination effects were controlled by acquiring all data at the same solar time. Atmospheric path length effects were controlled by application of the 5S model (Tanre et al., 1986), and canopy geometry effects by application of the SAIL model (Verhoef, 1984). While the number of airborne studies are too few for any broad conclusions, two of the three groups reported success that would focus greater scrutiny in those areas of suspected stress. This could have great economic benefit to ERWM activities.

A final observation pertaining to Table 2-2 is that Buschmann et al. (1989) reported an increasing magnitude in the blue shift with increasing duration of exposure. This is intuitive and may have significant application at sites with a history of contamination. While temporal effects have received little attention in the remote sensing literature, they may dictate the timing and repetition of remote sensing acquisition efforts.

Wave-Form Analysis

Collins et al. (1983) developed a technique for detecting vegetation stress that is a modification of the red edge shift detection technique previously discussed. The technique is called wave-form analysis, and is generally applied to airborne measurements with sufficient spectral resolution. The equation for calculation of the SDS can be summarized as function such as:

$$F(a + x) = \sum_{i=0}^{i=N} A_i X_i$$

where X is the reflectance at wavelength i , and A is a coefficient that changes as i changes and $(a+x)$ describes the change in reflectance X as wavelength (i) changes across the spectral region from i to N .

Collins et al. (1983) point out that background variations (canopy effects and topography) can cause variations in reflectance significantly greater than variations due to vegetation stress; they modified the above equation as follows:

$$F(x) = \sum_{i=0}^{i=N} A_i T_i X$$

where $T_i(X)$ is a polynomial. Hence, the primary difference between the simple difference equation and the wave-form equation is that the wave-form uses a polynomial ($T_i(X) = a_1 + a_2x + a_3x^2 \dots$) to estimate the difference in magnitude in reflectance between adjacent wavelengths, while the simple difference technique calculates this difference directly. Collins et al. (1983) use the Chebyshev polynomial for $T_i(X)$. The Chebyshev polynomial was selected because it is sensitive to lower frequency changes (the small changes in a spectral profile due to vegetation stress) while ignoring higher frequency changes (shifts in the spectral profile resulting from a variable canopy or topography).

After calculating a series of Chebyshev polynomials, principal components analysis was used to study the variance. It was found that 10 coefficients captured nearly all the variance, that is, 10 coefficients (a_1 to a_{10}) were needed in the polynomial to model the reflectance. Collins et al. (1983) found that sulfide toxicity in vegetation could be detected using ratios of the 9th and 5th coefficients, while canopy effects were evident in ratios of the 8th and 4th coefficients. Their method is important in that it allows the identification of various aspects responsible for reflectance features observed in collected spectra. Furthermore, it was developed specifically for data collected by the high resolution Mark I airborne spectroradiometer. The Mark I spectroradiometer acquires a 500-channel profile in 1.4 nm wavebands across the 400 to 1,100 nm region and is described more fully by Chui and Collins (1978). This suggests that as data from other high resolution instruments (e.g., Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) and Compact Airborne Spectrographic Imager (CASI)) become more widely available, new methods will be developed that more easily allow the detection of vegetation stress.

Inverted Gaussian Model

Singhroy and Kruse (1991) point out that shifts in the wavelength position of the red edge are generally small and would require spectral resolution beyond the capability of most airborne and satellite sensors for detection. However, a technique introduced by Hare et al. (1984) and Miller et al. (1985) calculates the red edge slope (see Figure 1.3) using only four data points, allowing red edge calculations with data from lower resolution, airborne sensors. The equation, called the inverted Gaussian (IG) function, is reprinted here from Miller et al. (1990):

$$R(\lambda) = R_s - (R_s - R_o) \exp(-(\lambda_o - \lambda) / 2\sigma)$$

where R_s is the maximum reflectance (shoulder) in the near IR region, R_o is the minimum reflectance in the chlorophyll absorption (red) region, λ_o is wavelength of peak absorption (minimum reflectance, R_o , in the red region), λ is wavelength, and σ is the distance between the wavelength of maximum absorption (λ_o) in the red region and the wavelength of the red edge inflection point (λ_{re}) (Gaussian function derivation parameter). These parameters are graphically presented here in Figure 2.3 where λ_{re} , the wavelength of the red edge inflection point, is labeled λ_p .

Initial estimates of R_s , R_o , λ_o , and σ are made, and the equation is iterated by incremental increases in λ (e.g., 1 nm) to determine $R(\lambda)$ for that λ . Once the iteration is complete for the spectral region being estimated (e.g., 660 to 810 nm), the iteration is repeated by incrementing λ_o , σ , and R_s in turn and in that order. The incremental steps suggested for λ_o , σ , and R_s are 0.10 nm, 0.03 nm, and 10 percent, respectively. Miller et al. (1990) note that the initial values selected and the spectral range chosen must be given careful consideration. When iterations are complete, least squares criterion are used to determine the best fit. $R(\lambda)$ values calculated from the least squares analysis are then used to calculate the SDS and the red edge inflection point.

Miller et al. (1990) successfully applied the IG fitting procedure to laboratory spectra of bur oak (*Quercu macrocarpa*) (Figure 2.3). Additional comparisons between laboratory spectra and data collected from the MEIS II airborne sensor for balsam fir (*Abies balsamea*) and sugar maple (*Acer saccharum*) also showed good agreement. While the authors indicate that the iterative, model-fitting characteristics of IG offer some ability to control for atmospheric effects as well, it should not be considered as a substitute for high resolution data when available.

Summary and Conclusions

Detection of wavelength shifts in the location of the red edge is a technique that has been widely applied in remote sensing of vegetation stress. Through a large weight of evidence, a shift in the red edge to shorter wavelengths can be linked to lower overall chlorophyll concentration in stressed versus control vegetation samples. The red edge shift technique, as reported by Horler et al. (1983) and Miller et al. (1990), also has the advantage of being insensitive to mixed pixel problems. This insensitivity to mixed pixels may be a significant advantage when analyzing data from airborne and satellite platforms, specifically over arid regions.

The results, however, do not constitute a panacea. Incidents of no shift and shifts to longer wavelengths have also been reported. The variable results, to some degree, can be attributed to the variable methodological practices as indicated in Tables 2-1, 2-2, and 2-3. However, if shifts in the red edge towards longer wavelengths can be accurately characterized for specific plants and contaminants, they may be just as valuable as documented blue shifts in the application of remote sensing for vegetation stress detection. Of greater concern is the small number of studies to apply these techniques with spatial or airborne data while accounting for environmental

Figure 2.3: Graphic representation of IG function parameters, and comparison of IG modeled (dashed line) and measured (solid line) reflectance (top) and simple difference (bottom) spectra (reproduced from Miller et al., 1990).

parameters (e.g., atmosphere, canopy and illumination geometry). This can be explained mostly due to a lack of high resolution instruments available and costs associated with acquisition.

Many of the studies reviewed did not discuss the influence of time on spectral measurements. Buschmann et al. (1989) presented time series showing spectral evidence of increasing stress in second and third year conifer needles exposed to very low concentrations of air pollution (Table 2-5), while Gates et al. (1965), Collins (1978), and Horler et al. (1983) presented changes in the red edge position as a function of phenological development. It is clear that temporal effects of red edge phenomena must be considered when planning data collection efforts and may require annual to seasonal acquisition for successful identification of stressed vegetation.

Rock et al. (1988) note that spectral measurements in the field include vegetation injury characteristic of the site, but do not quantify how that damage was assessed. Curtiss and Maeher (1991) presented evidence showing no clear relationship between visible symptoms of stress (e.g., needle/leaf yellowing and/or lack of retention) in samples from toxic and control sites. Since the red edge phenomena spans from the visible to the IR or nonvisible region of the EM spectrum, it is intuitive that instruments recording in these regions may allow the detection of subtle changes indicative of stress before they are visible to the human eye. Furthermore, recently developed airborne instruments can digitally record differences and detect changes in both visible and NIR regions with greater sensitivity than the human eye. These differences can then be easily highlighted through the use of computer image processing techniques for visible distinction. These qualities would suggest the use of more recently developed instruments in addition to, or instead of, traditional aerial photography in a remote sensing program.

TABLE 2-5: Time-series spectral data of stress and control samples (from Buschmann et al., 1989).

Samples	RED-EDGE INFLECTION POINT		
	1988	1987	1986
Control	707	704	707
Stress	707	700	697

Collins et al. (1983) developed wave-form analysis to model the red edge profile (≈ 670 to 760 nm) using a 10th-order polynomial. Their justification for this was that environmental effects on reflectance, such as canopy geometry and topography, introduced variations in reflectance that are much greater than variations due to stress such as metal toxicity. The methodology appears successful, but has been used by few other researchers. Lack of wider use of this technique is most likely the result of its development for a specific high resolution spectroradiometer that has had limited availability to other researchers.

A second technique, the IG function, was introduced by Hare et al. (1984), Miller et al. (1985) and Miller et al. (1990). It has the advantage of being able to model the red edge profile using only four data points, allowing red edge studies with lower spectral resolution instrumentation. Like the wave-form technique, IG is reported to be able to partially control for the affects of atmospheric, canopy geometry and illumination changes on reflectance. Perhaps IG's most significant contribution is in defining other critical points along the vegetation spectral profile; the IR reflectance shoulder, R_s ; the chlorophyll well reflectance minimum, R_o ; and the wavelength of the reflectance minimum, λ_o . Much of the data presented in the literature indicates that these parameters along with the red edge position, when considered as a whole, may provide greater reliability in predicting vegetation stress. While it is noted that the IG function represents an approach for using coarser resolution airborne data, it is an estimation technique that does not replace high resolution data when available.

The reported success of both the wave-form and IG modeling techniques is to some degree the result of accounting for atmospheric, illumination, and canopy effects on measured spectral reflectance. The importance of controlling for these effects cannot be discounted and may dictate the success or failure of an investigation.

Many techniques similar to those discussed are well developed for other uses in industrial applications and in the field of spectroscopy where high resolution instrumentation is readily available. As technological developments continue to improve remote sensing instrumentation, these techniques will no doubt become more widely used and accepted in remote sensing investigations.

3.0 FULL SPECTRAL MATCHING AND FLUORESCENCE

The inverted Gaussian (IG) model previously discussed introduces three new variables as important characteristics of a vegetation spectral profile: R_s , R_o , and λ_o . Each of these variables, along with the wavelength of the red edge inflection point (λ_{re}), represents a parameter that may be exploited in some fashion to determine the status of vegetation. Examining several critical points or the entire continuum along the vegetation spectral profile constitutes another approach to the detection of vegetation stress. Such an approach, referred to here as full spectral matching, is evident in the literature and in the field of spectroscopy, but is less frequently used in the field of remote sensing due, in part, to the low spectral resolution of most systems.

Full Spectral Matching

Both Singhroy and Kruse (1991) and Curtiss and Maccher (1991) point to the value of examining the depth (magnitude of absorption) and breadth (number of wavelengths) of the chlorophyll absorption band (red region of the EM spectrum) for the detection of vegetation stress. Singhroy and Kruse (1991) present a methodology for defining these parameters. Milton et al. (1989) report that arsenic and selenium doped plants showed an increase and decrease, respectively, in reflectance in the 550 to 660 nm (green) region of the EM spectrum when compared to control samples. Ager et al. (1989) similarly reported an increase in reflectance in the 550 to 650 nm region for metal-stressed vegetation growing in northeastern Minnesota. Rock et al. (1988), using the IG model, reported significant differences in R_s , R_o , and λ_o parameters between high and low damage sites. This signifies the importance of operationally using the best instrument available, analytical techniques appropriate to the data collected.

Other studies have looked at statistical differences in percent reflectance between stress and control sites or samples, using selected critical wavebands. Leckie et al. (1992) reported an R^2 of 0.91 between defoliation levels and the MEIS II blue spectral band (≈ 430 to 460 nm). Karr and Mouat (1990) used Student-t tests to show a significant difference between stress and control sites, using Landsat Thematic Mapper (TM) replicated wavebands. Mouat (1982) presents an example of the intent of full spectral matching. Citing Siegal and Gillespie (1980), he presented full spectral profiles for damage and control samples of red spruce (*Picea rubens*) and balsam fir (*Abies balsamea*), showing where profiles were significantly different through the use of 95 percent confidence intervals. These results are reproduced here as Figure 3.1.

Confidence intervals can be easily constructed for a sample of spectral profiles, using the standard equation (see, for example, Brower and Zar, 1977):

$$\mu = X \pm ts_x,$$

where μ is the population mean, X is the sample mean, t is a constant taken from the Student-t table (value dependent on significance level and degrees of freedom), and s_x is the standard error of the sample mean. This simple technique will allow statements of statistical confidence pertaining to measured differences in the magnitude of reflectance between stress and control

Figure 3.1: Difference in reflectance spectra for control (background) and stress (anomalous) balsam fir and red spruce samples. Thick black lines at top of the spectra show wavelength regions where stress and control samples are significantly different at 95 percent confidence interval (reproduced from Mouat, 1982).

sites/samples. Graphical presentations of the differences in the spectral profiles between stress and control vegetation are numerous in the literature, but statements of confidence pertaining to these differences are often lacking.

Fluorescence

The plant property of fluorescence has also been used to detect vegetation stress. Fluorescence is the emittance of red light by plants upon excitation of the chlorophyll molecules by higher energy light, namely blue light. The emittance of red light is caused by the rapid decay of electronic energy. Light, essentially, drives electrons away from the nucleus of the chlorophyll molecule, and the distance the electrons are driven away is a function of the energy contained in the radiant flux. As stated in the Introduction, blue light has more energy than red light and is, therefore, able to drive electrons further away from the nucleus. The farther the electron is

driven, the more likely fluorescence will occur. The phenomenon of fluorescence is difficult to visualize without the aid of graphics. It is discussed again in Chapter 6 under Photosynthesis, where graphics are included.

The property of fluorescence has been exploited to detect vegetation stress by calculating ratios of the light emitted at ≈ 690 nm versus that emitted at ≈ 730 nm. A decrease in the ratio has been interpreted as a sign of vegetation stress, as reduced fluorescence in the 690 nm region suggests an overall lower chlorophyll content. This research has been primarily carried out by Buschmann and Lichtenthaler (the references cited section of Buschmann et al. (1989) lists 11 fluorescence publications that include one or both of these authors), with some work by Chapelle (e.g., Chapelle and Williams, 1987; Chapelle et al., 1991). While a very promising technique, fluorescence has not been widely applied by other researchers in the remote sensing community, due mostly to the fact that fluorescence requires active as opposed to passive remote sensing. Since fluorescence requires radiating plants with an energy source, typically lasers, instrumentation for its use is relatively complex, expensive, and rare. While this may limit its wide-scale application in the near term, future development may increase its availability.

Summary and Conclusions

The introduction of the three additional points along the vegetation spectral profile, in addition to the red edge inflection point (λ_{re}), indicates that a more confident detection of vegetation stress can be ascertained by gathering a "full weight of evidence" through use of the entire profile. Full spectral matching, as presented by Mouat (1982), is an example of using all the "vertical" or reflectance data in the spectral profile. An addition to this technique would be the inclusion of "horizontal" or wavelength shifts where appropriate.

Finally, detection of vegetation stress using fluorescence was presented. This technique has not been widely applied, due to its requirement for active remote sensing instrumentations. However, research is continuing, as its application for stress detection is promising.

4.0 RATIO TECHNIQUES

Ratio techniques are methods that have been developed to expose relationships of spectral reflectance between different regions in the electromagnetic (EM) spectrum. They are typically performed by dividing the reflectance values in one band (or region) by corresponding reflectance values in another band. The closer the resulting value is to one, the more similar reflectance values are between bands and vice versa. Ratio techniques have been successfully applied in both mineral and vegetation investigations using both point and spatial data.

The use of ratio techniques probably has been the most widely applied approach to the study of numerous aspects of vegetation dynamics, including pest damage (e.g., Leckie et al., 1992), changing leaf area index values along a vegetation gradient (Running et al., 1986; Peterson et al., 1987), desertification (Tucker and Justice, 1986; Townshend and Justice, 1986), phenological cycles (Goward et al., 1985), and detection of moisture stress (e.g., Ambrosia et al., 1991). Richardson and Everitt (1992) reviewed several ratio techniques, which are presented in Table 4-1. The numerous ratio techniques listed and the length of time each has been in use

TABLE 4-1: Ratio techniques (from Richardson and Everitt, 1992).

NAME	VEGETATION INDEX (VI)	SOURCE
Ratio VI	$RVI = NIR/RED$	Pearson and Miller (1972)
Normalized Difference VI	$NDVI = (NIR - RED)/(NIR + RED)$	Rouse et al. (1974)
Greenness VI	$GVI(RED, NIR) - PVI$	Kauth and Thomas (1976)
Difference VI	$DVI = NIR - a RED$	Richardson and Wiegand (1977)
Perpendicular Vegetation Index	$PVI = \frac{NIR - aRED - b}{SQRT(1 + a^2)}$	Richardson and Wiegand (1977)
Soil Adjusted VI	$SAVI = \frac{(1 + L)(NIR - RED)}{(NIR + RED + L)}$	Huele (1988)
Transformed Soil Adjusted VI	$TSAVI = \frac{a(NIR - aRED - b)}{RED + aNIR - ab}$	Baret et al. (1989)
Soil Adjusted Ratio VI	$SAVI_2 = \frac{NIR}{(RED + b/a)}$	Major et al. (1990)

illustrate the comparatively long history of application these techniques have enjoyed. Furthermore, the introduction of one ratio technique has stimulated the development of another. The history of ratio techniques and continuing development is in large part due to their successful and easy application with satellite data, and its 20-year availability.

One of the most commonly used ratio techniques places near infrared (NIR) reflectance in the numerator and red reflectance in the denominator (NIR/red, e.g., TM bands TM4/TM3). The rationale for wide application of this technique is evident in Figures 1.2 and 1.3. Vegetation is highly reflective in the NIR region and strongly absorbing in the red region. NIR/red ratios quantify the magnitude of difference in reflectance in the two regions, and variations in the difference of this magnitude can be used to study various aspects of vegetation dynamics, such as those mentioned above. It can also distinguish between vegetation and rock/soil since these surfaces display relatively little difference between the red and NIR regions of the EM spectrum.

Forest Decline Studies

The studies utilizing ratio techniques to examine vegetation parameters are extensive (Rock et al., 1986; Petersen et al., 1988; Running and Nemani, 1988; Williams and Nelson, 1984; Tennakoon et al., 1992; Milton and Rollin, 1988). In general, ratio techniques have been successful in the identification and quantification of vegetation stress. The major difference between ratio techniques and those previously discussed is the types of data they are applied to and the magnitude of vegetation stress detected. Most vegetation stress studies use ratio techniques which are employed on instrument data with relatively wide band passes.

Some results of seven forest pest damage studies are presented in Table 4-2. These studies nearly exclusively use Landsat TM satellite data, and have been undertaken primarily on New England forests (Rock et al., 1986). Table 4-2 includes two columns (Air Photo Reference and Visual Estimate of Damage), which were generally not available for studies listed in Tables 2-1, 2-2, or 2-3. The fact that the information contained in these two columns was routinely reported for these studies and not for the studies in Tables 2-1, 2-2, or 2-3 suggests that the magnitude of stress is much greater in the studies utilizing ratio techniques. In each of the studies in Table 4-2, stress was calculated as the amount of foliage lost. Foliar loss was explicitly measured, and visually observed in aerial photography and satellite imagery. Moreover, the use of the word "stress" is generally lacking and, instead, replaced by the word "damage." As noted in the summary and conclusions to Chapter 2, most of the higher resolution studies did not report visual differences between stress and control samples.

It should also be noted that most of the studies presented in Table 4-2 applied some kind of radiometric adjustment to control for atmospheric and other environmental effects. As stated previously in Chapter 2, methods for controlling for atmospheric, canopy, and illumination effects are an important aspect in the ability to discriminate vegetation stress in spectral data acquired above the canopy. Since these methods have already been developed, their successful use with high resolution data, as it becomes more widely available, is promising.

Ratio Techniques Versus Wavelength Shifts

There is an interesting relationship between ratio techniques, which quantify the difference in reflectance between two portions of the EM spectrum, and the suite of techniques which focus

TABLE 4-2: Ratio and similar techniques applied to forest damage detections from airborne or satellite platforms.

AUTHOR	INSTRUMENT	PIXEL SIZE	PIXEL/SAMPLE ¹	RADIOMETRIC ² CONTROL	AIR PHOTO REFERENCE	VISUAL ESTIMATE OF DAMAGE	TECHNIQUE ³	RESULTS
Vogelmann and Rock 1986	NS001-TMS	17 m	89/1023	yes	no	% needles	5/4	$R^2 = 0.94$
Leckie et al. 1992	MEIS II	40 cm	55/tree	yes	yes	defoliation to nearest 5 percent	15 ratios 4 pc's orig. bands	$R^2 = 0.92$ (IR/red)
Hermann et al. 1988	Daedulus ATM	6 m	NR	NR	yes	heavy chlorosis needle loss damage percent foliar loss	spectral assessment	general trends reported
Vogelmann 1990	Landsat TM	30 m	NR	yes	Landsat pictures	percent foliar loss	5/4	$R^2 = 0.82$
Vogelmann and Rock 1980	Landsat TM	30 m	7 to 45	yes	Landsat pictures	percent foliar loss	5/4 7/4	$R^2 = 0.94$ $R^2 = 0.84$
Vogelmann and Rock 1990	Landsat TM	30 m		yes	Landsat picture aerial	defoliated vs. non-defoliated	5/4 3 4	significant difference between 1984 and 1988 difference images
Ekstrand 1989	Landsat TM	30 m	10 to 12	yes	yes	percent foliar loss	1+3 1/4 4/2+4+7	$r = 0.80$ $r = 0.76$ $r = 0.76$

1 = number of pixels covering sample or site; for Leckie et al. 1992 there were up to 55 pixels

2 = indicates whether data were corrected for some or all of atmospheric, canopy, and illumination geometry effects

3 = numbers are for bands used to assess spectral detection of damage classes

on detection of wavelength positional shifts between stress and control samples/sites. Collins et al. (1978) noted that blue shifts in the red edge inflection point (λ_{re}) should also be evident as depressed NIR/red ratios. This is intuitive when examining the red edge feature as presented in Figure 1.3. Blue shifts can cause increases in reflectance in the red absorption region. Increases in reflectance in the red absorption region would depress the magnitude of NIR/red ratios. How much of a blue shift is required before depressed NIR/red ratios can be detected, and what are the minimum spatial and spectral resolutions needed to connect a wavelength shift to a depressed NIR/red ratio are areas of active research. Developing more fully the connection between ratio techniques and wavelength shifts represents one approach to linking the detection to mapping of vegetation stress with more widely available low resolution sensing data.

As noted earlier, ratio techniques were developed primarily for application to spectral data acquired from satellite platforms. Applying ratio techniques, particularly combinations of red or visible and infrared, in arid environments has shown limited success in detecting vegetation stress (Tueller, 1987). Vegetation in arid regions usually comprises less than 30 percent of the ground cover, with the vegetation structure presenting small leaf area (e.g., vertically oriented and microphyllous leaves) for aerial and satellite measurements. Thus, the lack of greenness presented to the satellite or other vertically oriented remote sensing instrument hinders the ability of NIR/red ratios to distinguish subtle changes in vegetation.

The perpendicular vegetation index (PVI) (Richardson and Wiegand, 1977) and the other vegetation indices presented in Table 4-1 have attempted to remove the influence of soil for application in arid environments (e.g., Huete, 1988). Since the relationship between red edge shifts and the more sophisticated ratio techniques developed for use in arid environments has not yet been established, application of remote sensing in arid environments would favor the use of red edge shift techniques, especially as Horler et al. (1983) and Miller et al. (1990) have shown that the red edge position is not sensitive to mixed pixel problems.

Moisture Stress Detection

Gates et al. (1965), Allen and Richardson (1968), and Knipling (1970) have established that the decrease in plant reflectance beyond 1,300 nm (see Figure 1.3) is the result of water absorption. Tucker (1980) developed a stochastic model relating changing leaf spectral reflectance to changing leaf water content, and concluded that the 1,550 to 1,750 nm region was best suited for monitoring plant canopy water status. This conclusion no doubt contributed to the positioning of Landsat TM band 5 at this region of the EM spectrum.

Still, there have been relatively few investigations utilizing this spectral region to detect moisture stress. Using a hand-held radiometer (configured to replicate TM bands 3 (630 to 690 nm), 4 (760 to 900 nm), and 5 (1,550 to 1,750 nm)) placed slightly more than three inches above a salt marsh canopy, Hardisky et al. (1983) demonstrated that an infrared index $(4-5/4+5)$ successfully detected decreasing soil moisture content as a result of increasing salinity. Hunt et al. (1983) developed an equation to determine relative water content (RWC):

$$LWCI = \frac{-\log [1 - (TM4 - TM5)]}{-\log [1 - (TM4_{FT} - TM5_{FT})]}$$

where LWCI is the leaf water content index, TM4 and TM5 are leaf spectral reflectance in those channels, and TM4_{FT} and TM5_{FT} are the leaf spectral reflectance at full turgor (the amount of water in a leaf when it can hold no more). The authors showed that LWCI is effectively identical to RWC, which is measured as the ratio of the difference between fresh weight (FW) and dry weight (DW) divided by the difference between saturated or full turgor weight (SW) minus dry weight times 100 (e.g., ((FW-DW)/(SW-DW) * 100)).

The principal limitation with moisture stress detection is that it requires ground sampling to determine spectral reflectance at a known RWC. Ambrosia et al. (1991) found mixed results in detecting moisture stress in ponderosa pine stands (*Pinus ponderosa*) using a TM-like 5/4 ratio. The authors did not indicate that prior ground sampling of water status in the respective stands was done. Furthermore, the equation developed by Hunt et al. (1983) is specific to leaf water status (i.e., LWCI). At a minimum, water status would have to be sampled throughout the entire canopy (both vertically and horizontally). The cost associated with such a sampling effort is presently prohibitive for regional applications of this technique.

Finally, it should also be noted that NIR/red ratios have been applied to detect moisture stress indirectly. As part of the Large Area Crop Inventory (LACIE) undertaken by the USDA in the 1970s, Thompson and Wehmanen (1979) developed a Greenness Index Number (GIN) using Landsat MSS data. GIN was used to monitor the vigor of large agricultural fields devoted to wheat cultivation in the Great Plains. Tucker (1980) stated that GIN is an indirect measure of moisture stress, based on the assumption that moisture stress will retard plant development, resulting in lower overall chlorophyll concentrations. Landsat MSS data do not contain spectral measurements in the water absorption region (beyond 1,300 nm).

Summary and Conclusions

Studies utilizing ratio techniques to map forest decline were examined specifically to compare critical aspects of these studies with those using higher resolution data and red edge shift techniques (discussed in Chapter 2). The principal difference found in comparing these studies is the magnitude of detectable stress. The forest decline studies were successful in quantifying stress as percent foliar loss with instruments of low spectral resolution on a regional scale. The magnitude of stress present in these studies was much greater than those discussed in Chapter 2. It is clear that extensive vegetation injury due to extreme contamination may be mapped using ratio techniques with low resolution instrumentation, while areas of lower contamination may require high resolution instruments and more complex methods of analysis for successful detection of associated stress.

The natural connection between wavelength shift and ratio techniques shows that blue shifts in the red edge can be evident as depressed NIR/red ratios, although simple ratio techniques (e.g., NIR/red) may have limited application in arid environments because of their

sparse vegetation. Detection of moisture stress using spectral data beyond 1,300 nm was also discussed. While the spectral absorption feature of plants at wavelengths between 1,300 and 2,500 nm has long been recognized, it has seen little regional application due partly to the prohibitive cost of collecting the necessary ground data.

Finally, many of the techniques discussed have been developed in response to the limitations, characteristics, and availability of remote sensing data. This would suggest that many more techniques will become available for the application of vegetation stress detection and mapping as improvements in instrumentation occur and associated data become available.

5.0 RESULTS OF SACRAMENTO RIVER STUDY

As previously stated, DRI is examining remote sensing techniques useful in the detection of vegetation stress associated with contamination. During this review process, DRI had the opportunity to apply some of these techniques at a surrogate location for DOE, following a contamination event along the Sacramento River in northern California.

DRI researchers contacted the California Department of Fish and Game (CDFG) to offer a research program designed to determine if the spectral response of vegetation could be used to identify and separate areas affected by the contamination from areas unaffected in conjunction with CDFG's existing efforts. CDFG personnel were already performing qualitative observations as part of a damage assessment plan required under two federal laws, the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and the Federal Water Pollution Control Act, commonly known as the Clean Water Act. With the acquisition of a recently developed field portable, high resolution spectroradiometer, DRI made an initial investigation on July 26, 1991. Upon examination of the data, it was decided that a more thorough investigation deserved merit and researchers returned on August 13, 1991. Numerous vegetation reflectance spectra were collected along with observational data provided by CDFG. Logistical support from CDFG personnel was critical in obtaining these measurements. The results of applying remote sensing techniques to detect stressed vegetation resulting from contamination along the Sacramento River are presented below.

Background

On July 14, 1991, several train cars from a Southern Pacific train derailed along a section of track known as the "Cantara Loop" just north of the town of Dunsmuir, California. The loop is located directly over the Sacramento River approximately 36 miles upstream from its inlet to Shasta Reservoir. One of the derailed train cars was carrying the chemical sodium methylthiocarbamate (metam sodium), and leaked approximately 19,000 gallons of its contents into the Sacramento River. Upon mixing with the river water, metam sodium, a pesticide used to control soil fungi, bacteria, insects, and unwanted vascular plants, began to break down into several toxic compounds, including methylisothiocyanate (MITC) and hydrogen sulfide. Some of the breakdown products remained in the river as a visible plume, while others were volatilized into the atmosphere. Over the next few days, the plume was observed to travel downstream approximately 36 miles until slowing in the upper reaches of Shasta Reservoir. Damage to animal and plant life in and along the river was evident after the spill.

Methodology

Officials at the CDFG had selected numerous sites for vegetation transects where visual observations were recorded, along with the collection of plant tissue for herbarium samples and chemical analysis of MITC. For the purposes of the study, six species were chosen as sentinel

species and selected for spectral analysis. With the spill site located approximately 36 river miles above Shasta Reservoir, termed river mile 36 (RM36), three transect sites were selected downstream at river mile 27 (RM27), river mile 7 (RM07) and river mile 1 (RM01), and two sites upstream as control points located at river mile 37 (RM37) and several miles further upstream above Box Canyon Dam along South Fork Creek (RMSF). As not all six species could be located at the two control sites, two additional sites were selected for control along tributaries downstream from the spill; one along Dog Creek (RMDC), and one along Soda Creek (RMSC). This allowed four of the six species to have two control sites, while two had just one control. The six sentinel species selected for observation are listed in Table 5-1 and their relative locations in Table 5-2.

TABLE 5-1: Sentinel species selected for observation and analysis along the Sacramento River.

GENUS	COMMON NAME	ABBREVIATION
<i>Alnus rhombifolia</i>	Alder	ALRH
<i>Carex nudata</i>	Sedge	CANU
<i>Fraxinus latifolia</i>	Ash	FRLA
<i>Peltiphyllum peltatum</i>	Indian Rhubarb	PEPE
<i>Populus trichocarpa</i>	Cottonwood	POTR
<i>Salix melanopsis</i>	Willow	SAME

TABLE 5-2: Location of measured species.

SPECIES	AFFECTED SITES			CONTROL SITES			
	RM01	RM07	RM26	RM37	RMSF	RMDC	RMSC
ALRH	X	X	X	X	X		
CANU	X	X	X	X			
FRLA	X	X	X				X
PEPE	X	X		X		X	
POTR	X		X	X	X		
SAME	X	X	X	X	X		

Leaf samples were collected from the identified species and arranged to cover an approximate 15-inch-diameter circle. Ten spectra were collected for each sample with a 25 degree field of view using an Analytical Spectral Devices, PS-II. The PS-II records information

between 335 nm and 1,065 nm in 512 channels averaging approximately 1.4 nm in width. This provided the basis for spectral analysis and statistical tests. All spectra were collected within one minute after calibrating the spectrometer against a spectralon white reference standard at integration times of either 175 ms or 350 ms.

For this study, the position of the red edge was determined by calculating the first derivative of the individual spectral curves and having a computer program pick the maximum inflection point (MIP) on each first derivative curve (Figure 5.1). The associated wavelength of each MIP was averaged to determine the position of the red edge for each specimen at each location. First derivative curves were smoothed to eliminate the possibility of picking a MIP created by noise in the signal. The smoothing algorithm is that used by Milton et al. (1991), and was applied 10 times to each curve and is presented here:

$$a'(i) = \frac{a(i-1) + 2a(i) + a(i+1)}{4}$$

The first derivative calculation and smoothing operation was applied to each spectral curve between 400 and 800 nm. Student's t-tests were applied between each set of 10 MIP values for each species at each site to determine the significance of relative differences between calculated red edge positions. All red edge positions compared were statistically significantly different ($P < 0.001$) unless otherwise stated. (If $P < 0.001$, the likelihood that these are chance variations is less than 0.1 percent.)

Complications

It should be noted that unlike laboratory studies, many factors such as homogeneous sample availability for both control and affected species, uniform dose exposure, and a constant energy flux were uncontrollable; however, since that is the environment to which these techniques would be applied, it was a suitable environment for real world applications. Further confounding this study were observations that one or more of the toxic byproducts of the contaminant metam sodium was in a gaseous state that allowed both air currents and river hydraulics to play a role in the potential exposure at the leaf and root level, respectively. In fact, wind measurements supported observations of toxic gas moving upstream past one of the control sites at RM37. At several locations immediately upstream from trestles, large pockets of extensive injury to vegetation were observed. These areas are believed to be the result of the trestle shielding canyon winds, allowing a greater exposure dose and duration. This artifact became known as the "trestle effect." However, even with these complexities, it was hypothesized that due to contaminant-induced stress, the red edge might be observed to shift from the longest wavelengths at control sites to the shortest wavelengths immediately downstream of the spill site, with the red edge returning towards control site positions as one moved farther away from the spill site. This shift towards shorter wavelengths, or blue shift, would be consistent with the majority observations associated with stressed vegetation recorded in the literature.

Figure 5.1: Spectral reflectance and first derivative curves for two sites on the Sacramento River showing selection of the maximum inflection point for determining relative positions of the red edge.

Results

Generally, the evidence strongly supports this hypothesis. The average spectral curve from each set of measurements is plotted for all six species at their respective locations in Figures 5.2 through 5.7. Table 5-3 lists the computed red edge position (labeled MIP), the normalized difference vegetation index (NDVI), based on simulating Thematic Mapper (TM) bands 3 and 4, the standard deviation in MIP values, and the measured amount of MITC in parts per billion

Figure 5.2: Average spectral reflectance curves of *Alnus rhombifolia* (ALRH) at selected sampling sites along the Sacramento drainage, 8/13/91.

Figure 5.3: Average spectral reflectance curves of *Carex nudata* (CANU) at selected sampling sites along the Sacramento drainage, 8/13/91.

Figure 5.4: Average spectral reflectance curves of *Fraxinus latifolia* (FRLA) at selected sampling sites along Sacramento drainage, 8/13/91.

Figure 5.5: Average spectral reflectance curves of *Pelitiphyllum pelatum* (PEPE) at selected sampling sites along the Sacramento drainage, 8/13/91.

Figure 5.6: Average spectral reflectance curves of *Populus trichocarpa* (POTR) at selected sampling sites along the Sacramento drainage, 8/13/91.

Figure 5.7: Average spectral reflectance curves of *Salix melanopsis* (SAME) at selected sampling sites along the Sacramento drainage, 8/13/91.

TABLE 5-3: Results of analyses conducted for the Sacramento River study.

	Location	Maximum Inflection Point (MIP)	Standard Deviation	NDVI	Laboratory Results ppb of MITC*
ALRII					
Alder –	RMSF	722.6	0.791	0.772	5
<i>Alnus rhombifolia</i>	RM37	709.3	0.917	0.522	0
	RM26	707.9	3.935	0.521	11
	RM07	709.4	0.945	0.618	0
	RM01	715.4	0.738	0.750	11
CANU					
Sedge –	RM37	724.8	1.226	0.944	6
<i>Carex nudata</i>	RM26	706.4	2.018	0.626	1377
	RM07	714.2	4.044	0.741	233
	RM01	719.9	0.676	0.864	77
FRLA					
Ash –	RMSC	715.0	1.538	0.845	0
<i>Fraxinus latifolia</i>	RM26	712.7	4.120	0.339	0
	RM07	699.0	0	0.569	105
	RM01	705.0	0.590	0.823	0
PEPE					
Indian rhubarb –	RMDC	711.7	0.612	0.744	0
<i>Pettiphyllum peltatum</i>	RM37	705.0	0.590	0.746	0
	RM07	708.7	1.104	0.685	53
	RM01	704.3	0.676	0.667	0
POTR					
Cottonwood –	RMSF	718.6	0.676	0.758	0
<i>Populus trichocarpa</i>	RM37	714.1	0.979	0.621	12
	RM26	705.7	0.676	0.557	116
	RM01	712.3	0.945	0.658	35
SAME					
Willow –	RMSF	724.4	0.590	0.571	0
<i>Salix melanopsis</i>	RM37	716.6	0.725	0.849	0
	RM26	718.3	1.933	0.647	55
	RM07	706.1	0	0.638	0
	RM01	608.0	129.756	0.218	174

*detection limit of instrument is 5 to 10 ppb

(ppb) in each respective sample. MITC levels were determined using gas chromatography with a nitrogen-phosphorus detector with 5 to 10 ppb being the approximate detection limit of the instrument.

For all six species, the red edge position or MIP is at a maximum wavelength at one or both of the control sites (Table 5-3). For three of the five species located at RM26 (the closest site downstream of the spill site), the MIP has shifted to its measured minimum, averaging a shift of over 15 nm from the maximum control MIPs. The other two species display minimum MIPs at RM07, where the shift is 16.0 and 18.3 nm for ash and willow, respectively. RM07 is located just upstream from a train trestle which may be a contributing factor to the observed shifts. This also suggests the importance of specific plant locations within a site due to river and air current dynamics and their role in providing contact with the contaminant. These statements exclude the the calculated MIP of 608 nm for sample SAME at RM01, since no red edge is apparent in the averaged spectrum (Figure 5.7), and the specimen had died prior to spectral measurements. Significantly, all species at control site RM37 display a blue shift in the red edge as compared to duplicate controls, lending support to observations of gaseous byproducts moving upstream from the spill site at RM36 past RM37. This helps to explain the three instances where RM37 MIP values are not greater than all corresponding species downstream.

Two of the species, cottonwood and sedge, show unusually high correspondence at a number of levels. As seen in Table 5-3, cottonwood displays a shift from 718.6 nm at our "safe" control site RMSF, to 714.1 nm at RM37. Downstream of the spill, the red edge shifts to 705.7 nm at RM26 and then back up to 712.3 nm at RM01. These red edge positions are all significantly different with $p < 0.001$. Sedge (Table 5-3) exhibits similar behavior with a red edge maximum position of 724.8 nm at RMSF, and a minimum of 706.4 nm at RM26. The red edge shifts back towards the control at 714.2 nm and 719.9 nm at RM07 and RM01 sites, respectively. NDVI values also correspond well as control sites have the highest NDVI values and RM26 the lowest. This behavior corresponds exactly with what might be expected considering the conditions of the event. Even more significant is the direct correspondence these two species display with respect to measured amounts of MITC (Table 5-3). Control site samples had zero or detection limit amounts of MITC, while RM26 samples had the maximum recorded levels of 1377 ppb and 116 ppb for both species, sedge and cottonwood, respectively. Two other species, ash and willow, display a similar inverse relationship. At RM07, ash displays its minimum MIP value coincident with a measured value of MITC of 105 ppb, while the maximum MITC value in willow was 174 ppb, which was dead prior to the time of observation.

NDVI values generally behave proportionally to MIP values, and can draw attention to areas in the data where results of using the red edge technique are less clear. Its use clearly identifies the dead willow sample at RM01 and may help explain the seemingly inconsistent MIP values for willow at RM37 and RM26. NDVI values are computed by averaging the instrument response between 616 to 697 and 789 to 911 nm to simulate the response in channels 3 and 4, respectively, of the broad band TM instrument. The band response is then used to calculate NDVI as presented below:

$$NDVI = (tm4 - tm3) / (tm4 + tm3)$$

While averaging the response over the range covered by channels 3 and 4 deletes information contained in the those areas, calculating NDVI is an accepted method of providing a parameter that helps quantify the vigor or health of vegetation (Richardson and Everitt, 1992). As NDVI is somewhat sensitive to the strength of the energy flux during measurement, its use with high spectral resolution data may decrease as other techniques become available.

Summary and Conclusions

The evidence presented here strongly supports the hypothesis that shifts in the red edge of vegetation would occur due to stress caused by contamination and would correspond with distance from the spill site. While the mechanism of MITC uptake is not well understood, it appears that vegetation along the Sacramento River may have been exposed to toxins through contact at both the root and leaf level. Spectral measurements have provided a method of stress detection that corresponds extremely well with chemical analysis results of plant tissue. The fact that one-third of the species studied displays this correspondence in an uncontrolled field experiment lends great support for spectral applications at other contaminated sites. Furthermore, the spectral measurements seem to be sensitive enough to detect departures from normal even when toxin uptake does not occur. This has significant implications for many contaminants of concern at DOE sites, such as PCBs, that are typically bound in the soil and not incorporated into plant tissue. In addition, the magnitude of the observed shifts potentially allows for current airborne systems to detect these kind of spectral changes.

In retrospect, if this were a designed experiment, the greatest change in methodology would be for data collection efforts to have occurred prior to the spill. It is suspected this effort would further confirm the results and clarify any ambiguities in the data. This is significant in that it sets a precedent for DOE to obtain high resolution spectral data to establish baseline conditions specifically for monitoring and evaluating efforts undertaken during remediation activities.

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6.0 PHYSIOLOGICAL RESPONSE OF PLANTS TO STRESS⁵

The preceding chapters have discussed various remote sensing techniques used to detect vegetation stress, which has been linked to changes in chlorophyll. This chapter reviews three important physiological functions that can all be affected by the presence of contaminants. These three physiological functions (chlorophyll/chloroplast development, photosynthesis, and nutrient uptake) rely either directly or indirectly on the presence of chlorophyll. Each is reviewed below.

Chlorophyll/Chloroplast Development

In angiosperms (flowering plants), chlorophyll forms only in the presence of light. (Conifers and less structurally complex plants can form chlorophyll in the absence of light, although light stimulates the process.) It has been shown that chlorophyll concentrations increase tenfold in spinach leaves as they grow from immaturity to full size. The light-stimulated chemical reactions use a precursor chlorophyll molecule, protochlorophyllide a, to form chlorophyll a, which is then used to form chlorophyll b.

The series of light-stimulated reactions that result in the formation of chlorophyll is shown in Figure 6.1. While numerous chemical compounds are shown in this figure, the important

Figure 6.1: Light-stimulated reactions of chlorophyll synthesis (reproduced from Salisbury and Ross, 1979).

components to notice are NADH/NAD⁺ (nicotinamide adenine dinucleotide, a chemical cousin of NADPH/NADP⁺ critical in photosynthesis) and the amino group NH₂. NH₂, the building block of proteins, is an essential component of NADH/NAD⁺, as is the phosphate compound PO₄³⁻. These chemical compounds are highlighted because reduction in uptake of nitrogen (N),

⁵Adapted primarily from Salisbury and Ross (1979) and Rost et al. (1979).

phosphorous (P), iron (Fe), and magnesium (Mg) or interruption in the metabolism of any of these elements (for example, incorporation of H_2PO_4^- into NADH/NAD^+) can cause a reduction in chlorophyll concentration.

A second important characteristic of chlorophyll development is that it precedes and stimulates the development of the fine structures in the chloroplast organelle.⁶ The basic structure of the chloroplast organelle is shown in Figure 6.2. The label G marks a granum, which

Figure 6.2: Anatomical structure of chloroplast organelle (reproduced from Salisbury and Ross, 1979).

is a stack of thylakoids. Thylakoids are “sacs” which contain chlorophyll, and are where many photosynthetic reactions take place. Individual granum (G) stacks are sometimes connected by stroma lamellae (SL). The granum stacks and stroma lamellae are suspended in a colloidal matrix called the stroma (S). SG depicts a starch grain, the ultimate product of photosynthesis. Thus, physical structures may be changed by processes that affect chlorophyll development.

⁶An organelle is a membrane-bound special region within a cell in which particular functions are carried out. Photosynthesis is carried out in chloroplasts, and respiration is carried out in mitochondria.

Photosynthesis

Photosynthesis is simplified and summarized by the equation below:

The details of the reactions that this equation summarizes are complex; however, an attempt is made to present a clear and understandable review of photosynthesis using the following three diagrams.

Figure 6.3 shows how light absorbed by chlorophyll molecules is used to initiate a series of reactions that encompass photosynthesis. Upon absorbing light, chlorophyll molecules are converted from a stable or ground state to an excited state. Light accomplishes this by driving electrons away from the positively charged nucleus of a chlorophyll molecule a distance corresponding to the energy absorbed.⁷ The electronic energy of chlorophyll molecules is then transferred to an energy collection center, as shown in Figure 6.3 by the arcing arrows.

The “horizontal” energy transfer shown in Figure 6.3 is again represented in Figure 6.4 as the black lines that begin with a dot and end with an arrow. Figure 6.4 is read from bottom right to upper left. There are two energy collection centers, labeled P680 and P700. The transfer of electronic energy from chlorophyll molecules to P680 and P700 has been compared to a “bucket brigade.” Each of the smaller circles in Figure 6.4 represents a chlorophyll molecule within the thylakoid.

After receiving energy from excited chlorophyll molecules, P680 is able to remove electrons from water, splitting it into H^+ and OH^- . The electrons taken from water are then passed through a series of electron acceptors, and are eventually used to reduce $NADP^+$ to NADPH (top left-hand corner of Figure 6.4). Thus, water is critical in photosynthesis in that it provides a source of electrons necessary for electron transport reactions as well as the reduction of $NADP^+$.

Figure 6.4 is commonly referred to as the Z-scheme, and the series of reactions shown are known as the electron-transport or light reactions of photosynthesis. The rationale for presenting the Z-scheme is to highlight the importance of several nutrients (e.g., manganese, Mn; iron, Fe; Copper, Cu) involved in photosynthesis.

Ultimately, the NADPH and ATP created by light reactions of photosynthesis are used to produce 6-carbon carbohydrates. The production of these sugars in photosynthesis is referred to

⁷The five sets of five horizontal lines in Figure 6.3 represent the excited state of a chlorophyll molecule. In addition to being used for photosynthesis, the energy gained from light can be lost through release of heat or fluorescence (light production accompanying rapid decay of electronic energy). Blue light causes the chlorophyll molecule to take on a higher energy state (an electron is driven further from the nucleus of the chlorophyll molecule) than red light. This happens because blue light is of a shorter wavelength than red light and therefore contains more energy (refer to Introduction). Ultraviolet (UV) light is of shorter wavelength than blue light (less than ≈ 400 nm), containing even more energy. If UV light were absorbed by chlorophyll molecules, the heat produced through electronic decay would be potentially harmful to plants. Figure 6.3 shows why UV, IR, and visible light is referred to as “too hot,” “too cold,” and “just right,” respectively, in the Introduction.

Figure 6.3: Model simplification of how light energy striking a chlorophyll molecule is utilized for photosynthetic reactions (reproduced from Salisbury and Ross, 1979).

as the Calvin-Benson or dark cycle reactions and is shown in Figure 6.5. Starting near the upper left-hand portion of the diagram, carbon dioxide and water are added to ribulose diphosphate to form 3-PGA (3-phosphoglyceric acid). NADPH and ATP are then added and 3-PGA is converted to 3-phosphoglyceraldehyde (3-PGAldehyde), which can be transported outside the chloroplast envelope, for the production of 6-carbon carbohydrates in the presence of ATP. Alternately, some the 3-PGAldehyde produced remains in the chloroplast and is converted to ribulose-5-phosphate, which is then phosphorylated (PO_4^{3-} is added) to create ribulose diphosphate and the reaction can be repeated.

Figure 6.4: Z-scheme representation of electron-transport (light) reactions of photosynthesis. NADPH and ATP are produced for use in synthesis of six-carbon molecules (Calvin-Benson cycle) (reproduced from Salisbury and Ross, 1979).

Figure 6.5: Graphic summary of Calvin-Benson (dark) reactions of photosynthesis. The Calvin-Benson reactions use the NADPH and ATP produced in the light reactions to produce 6-carbon "sugars," which are the fuel for respiration (reproduced from Salisbury and Ross, 1979).

Nutrient Uptake

Water and nutrients are absorbed by plants through root uptake in the soil. Absorption of nutrients is an energy requiring process known as accumulation. In accumulation, nutrients must overcome electrostatic forces that bind nutrients to water and soil particles and a concentration gradient that exists since most nutrients are in greater concentration in plant tissues than in soil. The forces overcome are referred to as the electrochemical potential gradient. The energy required to transport these nutrients, essentially "upstream," is provided by ATP (not respiration); however ATP is produced by respiration, which is the catabolic process by which sugars produced in photosynthesis are translocated to the roots and broken down. Thus, nutrient uptake and photosynthesis work together in a positive feedback loop. Essential nutrients are taken up through the roots and transported to the leaf tissue. These nutrients perform essential functions in photosynthetic reactions that ultimately result in the production of sugar. Sugar is then transported back to the roots and respired to produce ATP, which supplies the energy necessary to take up nutrients against the electrochemical potential gradient.

Table 6-1 highlights essential functions of nutrients and their important role in aspects of photosynthesis and chlorophyll development. Nitrogen (N), as one of the two elemental components that comprise the amino group (NH_2), is found in all proteins as well as all plant tissues. It comprises nearly 50 percent of dry plant matter. Phosphorous (P) is part of ATP, and sulfur (S) is contained in two amino acids (there are 20 in all) that are found in nearly every protein. Iron (Fe), chlorine (Cl), manganese (Mn), and copper (Cu) are all directly involved in the light reactions of photosynthesis, three of which are shown in Figure 6.4. Potassium (K^+) acts as the primary charge-balancing cation during anion transport and controls stomatal opening. Stomates are the "pores" of the leaf, permitting gas exchange and potentially providing another pathway for contaminant uptake.

One of the ways contaminants can "stress" plants is to replace essential nutrients with part or all of the toxic compound itself. Replacement can occur as a result of the toxin having an equal or higher electronic affinity than the nutrient just as carbon monoxide (CO) is preferentially absorbed by humans over oxygen when present. Toxins may enter plant tissues below ground at the root zone or aboveground surface through the leaf stomates. Contaminants can also stress plants by binding essential nutrients through chemical reactions, creating a nutrient deficiency in vegetation. While this may be the less common mechanism of stress, it is worth consideration since spectral indications of stress may lack corresponding biogeochemical measurements as the contaminant was not actually incorporated into the plant tissue.

Summary and Conclusions

Spectral detection of vegetation stress is most typically the result of changes in chlorophyll. The essential plant functions involving chlorophyll (photosynthesis, nutrient uptake, and chlorophyll/chloroplast development) have been reviewed to highlight the numerous avenues that pollutants have to inhibit or interfere with these plant functions. Nearly every nutrient outlined is essential in physiological processes involving chlorophyll. By replacing any one of these nutrients, or causing a nutrient deficiency, pollutants can cause a reduction in chlorophyll concentration through involvement in photosynthetic reactions, nutrient uptake, or chlorophyll development. As discussed in earlier chapters, mild effects on these processes may be detectable through slight shifts in the red edge, while major effects causing foliar damage may be mapped using ratio techniques with existing instrumentation.

TABLE 6-1: Metabolic roles of essential elements (adapted from Salisbury and Ross, 1979).

Nitrogen: An essential part of all amino acids, proteins (including enzymes), coenzymes, chlorophyll molecules, nucleotides and nucleic acids, and many other plant components.

Phosphorus: Part of ATP and other nucleotides, nucleic acids, certain proteins, several coenzymes, membrane phospholipids, and attached to many different sugars that are important in photosynthesis and respiration.

Sulfur: Present in the essential amino acids cysteine and methionine and thus a part of nearly all proteins; part of a membrane sulfolipid and the vitamin coenzymes thiamine and biotin.

Potassium (K^+): Important in stomate movements (Ch. 3) and activates many enzymes. K^+ activates protein synthesis in plants and other organisms. In many cases (e.g., starch and protein synthesis), high concentrations (0.05M) of K^+ are required for full enzyme activation. It apparently acts as the primary charge-balancing cation during transport of anions (primarily NO_3^- , but also SO_4^{2-} , phosphates, and organic acid anions) from one plant part to another. K^+ moves readily through xylem phloem, whereas Ca^{+2} and Mg^{+2} move readily in xylem, but hardly at all in phloem. Considerable K^+ is probably required for this translocation function and for maintaining turgor and activating enzymes; hence, plants require much potassium (ca. 1 percent of dry weight).

Magnesium (Mg^{+2}): Chelated in and essential to activity of all chlorophyll molecules; also essential for maximum rates of most and perhaps all of hundreds of enzymatic reactions involving ATP. Most Mg^{+2} is apparently bound to ATP, ADP, other nucleotides, or organic acids. Mg^{+2} also enhances activity of several other respiratory enzymes and is essential for full activity of the two principal CO_2 -fixing enzymes, ribulose diphosphate carboxylase and phosphoenolpyruvate carboxylase. Mg^{+2} is also crucial to protein synthesis (holds two ribosome subunits together and facilitates peptide bond synthesis).

Calcium (Ca^{+2}): Exists to a great extent in central vacuoles in insoluble crystals of calcium oxalate and $CaCO_3$ (sometimes $CaSO_4$ and $Ca_3(PO_4)_2$), thus keeping possibly toxic oxalates out of the cytoplasm (yet we lack good evidence that failure to do so would harm plants). Some Ca^{+2} also occurs in the middle lamella between adjacent cell walls, where it is bound to carboxyl groups of pectins; hence, may be important in "cementing" walls together, although more evidence is needed.

Iron: Exists in divalent or trivalent forms in cytochromes and ferredoxin (proteins essential to light-driven reactions of photosynthesis), in cytochromes involved in the mitochondrial electron transport system of respiration, in catalase and peroxidase (enzymes that catalyze the breakdown of toxic H_2O_2 into H_2O and O_2), and in nitrite reductase and nitrate reductase (essential to nitrogen metabolism).

Chlorine(Cl^-): Clearly important, but only one function presently well recognized, the stimulation of photosynthesis by somehow enhancing electron transfer from H_2O to chlorophyll in photosystem II. The club-shaped root tips of chloride-deficient plants suggest other undiscovered role(s).

Zinc: Few known important functions in higher plants, one a possible role in synthesis of the amino acid tryptophan and of the hormone auxin. Zinc is also a part of carbonic anhydrase, a chloroplast enzyme that catalyzes the reaction between CO_2 and H_2O to form H_2CO_3 .

Copper: Essential to photosynthesis, existing in the protein plastocyanin, an electron carrier in the light reactions; essential to respiration (part of cytochrome oxidase).

Molybdenum: Required in the smallest quantities by plants, its only known functions being in nitrate reduction. Plants can be grown in the absence of molybdenum if they are provided with reduced nitrogen(NH_4^+); hence, no other functions may exist.

Manganese: Exists primarily as Mn^{+2} in plants but can apparently undergo oxidation (during photosynthesis) to the Mn^{+3} valence state; like Cl^- , enhances electron transfer from H_2O to chlorophyll; also activates certain enzymes involved in fatty acid synthesis, nucleotide synthesis (i.e., orotidine-5'-phosphate decarboxylase), respiration, and others. Often activation by Mn^{+2} is also accomplished by the more abundant Mg^{+2} ; Mn^{+2} chelates with phosphate groups in such nucleotides as ADP and ATP, as does Mg^{+2} .

Boron: Essential for higher plants, which grow slowly and will not complete their life cycles without it; but its biochemical roles are uncertain. Monocots so far investigated generally need less than half as much boron as dicots. Suggested essential roles include: in translocation of sugar (via the phloem), in synthesis of pyrimidine bases (thus, RNA and DNA).

7.0 SUMMARY AND CONCLUSIONS

This document has examined several aspects of remote sensing that may be used to assess contamination on DOE sites in support of Environmental Restoration and Waste Management (ERWM) activities. The remote sensing techniques reviewed have focused on detecting spectral changes in vegetation as a result of anthropogenic and natural environmental conditions. Vegetation was examined for several reasons including its ability to indicate characteristics of both surface and subsurface conditions and its unique spectral signature. If the studies reviewed herein are accepted as evidence of the capability to detect contaminant-induced changes in vegetation using remote sensing, then it seems probable that remote sensing techniques can be more fully developed for successful application with respect to detecting, mapping, and monitoring areas of contamination on DOE sites, and may prove to be a cost-effective method relative to traditional techniques, such as drilling for soil and groundwater analysis. This review reveals a few themes that can either be categorized as fundamental, recurrent, and/or significant and are therefore worthy of recapitulation.

The importance of understanding expected magnitudes of stress has been emphasized at several points throughout this review. The significance of quantifying the magnitude of vegetation stress is illustrated in Figure 7.1. The center (gray-shaded) circle may be considered as ideal conditions, and all points beyond as representing some degree of stress. It may be that the magnitude of stress that typifies geobotanical exploration (the majority of studies discussed in Chapter 2) is so small that it only slightly juxtaposes the population. The forest decline studies in Chapter 4, on the other hand, would appear to represent the other extreme, where environmental conditions have pushed the vegetation to the outer edges of the gray area in Figure 7.1. While there have been attempts to quantify magnitudes of stress (e.g., Yuan et al., 1989), most have not been conducted in consideration of spectral measurements.

In regards to specific techniques reviewed, it is clear that spectral shifts, either in wavelength positions (horizontal) or percent reflectance (vertical), may be small compared to the signal variation caused by atmospheric and other environmental constraints. Radiometric correction of the "raw" spectral data would appear to be a necessary prerequisite for the detection of vegetation stress when the spectral data are acquired above the canopy. Corrections may range from the relatively simple, such as dark pixel subtraction (e.g., Ahern et al., 1977), to the more sophisticated that account for sun/sensor/target and atmospheric conditions (e.g., Suits, 1972; Leprieur et al., 1988), and beyond. It is highly recommended that some level of correction be applied to raw spectral data collected for purposes of mapping vegetation stress on DOE sites.

Red edge shift detection techniques have received considerable attention in the remote sensing literature in part due to their success in identifying characteristics associated with environmentally stressful conditions that were undetectable by human observation. Another principal advantage of this technique is its apparent insensitivity to mixed pixel problems. Its principal disadvantage is a lack of airborne instrumentation of a resolution necessary to detect the relatively small but consistent findings of red edge shifts towards shorter wavelengths in stressed relative to control samples, especially in laboratory studies.

Figure 7.1: Response of population density to changing environmental gradients (reprinted from Whittaker, 1975).

The introduction of wave-form analysis (Collins et al., 1983) and the inverted Gaussian (IG) function (Hare et al., 1984; Miller et al., 1985) represent a fruitful expansion of red edge shift detection techniques, and have stimulated the recognition that the entire spectral profile may be useful for spectral detection of vegetation stress. This has led to the term "full spectral matching," and may become a much more utilized technique as more advanced instrumentation is applied to spectral studies in conjunction with well-characterized spectral curves representing normal and stressed vegetation in relation to specific contaminants. The principal advantage of full spectral matching is that it may allow all of the data collected by a sensor to be used as evidence for determining vegetation stress. A red edge shift may be inconclusive, but several other points along the vegetation spectral profile may indicate vegetation stress. Full spectral matching allows the interpreter to throw away an inconclusive point without loss of confidence. In addition, the IG function allowed the red edge to be modeled with relatively few data points, permitting application of this technique to both coarse and fine resolution instrumentation.

Comparison of the characteristics of ratio and red edge shift techniques reveals a functional similarity but for different degrees of stress. Greater understanding of spectral responses

attributable to environmental contamination may allow red edge shift techniques to be operationally applied to mapping and monitoring as opposed to simple detection.

Arid environments may present unique problems regarding mapping and monitoring of vegetation stress. Tueller (1987) has pointed out that ratio techniques, in particular those involving combinations of red and NIR, may be limited in arid environments because of a characteristic lack of greenness. Alternatively, ratio techniques have been successfully used to separate soil from vegetation and technical advances in instrumentation may be necessary for the more subtle distinction between healthy from unhealthy vegetation using these same techniques.

It is implicitly assumed that contamination of a magnitude to affect vegetation would be of interest to DOE. More than likely, there are areas of contamination, known and unknown, that may not sufficiently affect vegetation to a degree that allows for its detection with current remote sensing technology. Therefore, it is recommended that contamination thresholds for spectral detection be established for contaminants and vegetation species of concern to efficiently apply remote sensing technologies where warranted. In establishing these thresholds, changes in vegetation spectral properties should also be characterized to allow regional remote sensing investigations to search for unique spectral signatures in context of existing site information such as contaminant concentrations established by previous drilling methods. While airborne and satellite collected data offer some excellent characteristics in terms of uniform spatial sampling, the quantity of data can be immense. This emphasizes the necessity of knowing where and what to look for in terms of spectral characteristics for efficient application of this technology.

While many investigators have reported successful regional application of remote sensing techniques for mapping and quantifying vegetation damage as a result of air pollution and pest infestations, these studies have largely examined changes in vegetation of a greater magnitude than expected in many areas of contamination. However, their success should not be diminished in that most of these studies succeeded with data of low spectral resolution in a small number of bands. With the recent development of new technology allowing high spectral and spatial resolution from aerial and satellite platforms, there exists the possibility of regionally detecting more subtle changes in vegetation that have generally only been detectable in laboratory and ground-based field studies. In any case, practical application of remote sensing technology should establish baseline conditions over all areas of interest with the best technology available (AVIRIS is suggested). In this manner, temporal effects including changes over time can be more easily detected through subsequent remote sensing investigations. Furthermore, those areas of stressed vegetation identified can be pursued through historically successful ground-based spectral methods as well as more conventional techniques such as drilling.

As many of the techniques reviewed have developed concomitantly with advances in instrumentation that provided data of a quality suitable for their application, it is proposed that aerial surveys with the most advanced sensors available and subsequent distribution of the data will allow many more sensitive techniques to be developed for the detection of contaminant-induced stress in vegetation. It is clear that as instrumentation is developed that can record data of a quality more similar to that of laboratory instruments, successful techniques presently in use in these environments will be applied to remote sensing investigations.

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APPENDIX 1

Summary of Studies Examining Plant Responses to Certain Chemical Compounds

SUMMARY OF STUDIES EXAMINING PLANT RESPONSES TO CERTAIN CHEMICAL COMPOUNDS.

Metal/ Compounds	Plant Studied	Affected Process	Reference
Aluminum (Al)	Pine	reduced needle length; seedling height; biomass of needles, stems, and roots	Schier et al., 1985
	Onion	root elongation reduced	Clarkson and Sanderson, 1971
	Barley	DNA composition	Sampson et al., 1965
AlCl ₃	Red spruce <i>Picea rubens</i>	decreased fine root formation; interfered with essential nutrient uptake; decreased water absorption from soil	Pinder and McLoed, 1988
Cadmium (Cd)	Corn	reduced photosynthesis	Bazzaz et al., 1974
	Sunflower	respiration and CO ₂ fixation	Carlson et al., 1975 Weigel, 1985
	Silver maple	water conductivity	Lamoreaux and Chaney, 1977
	Barley	chlorophyll production	Stobard et al., 1985
CdCl ₂	Sudan-sorghum hay	biomass accumulated Cd, with no visible signs of injury	Brams et al., 1989
	<i>Brol</i>	in silver mining, Cd is highest in leafy tissue than roots	Boon and Soltanpour, 1992
	<i>Prunus persica domestica</i> <i>Pyrus communis</i>	fruiting was decreased and fruit flesh was decreased	Korcak, 1989
CdCl ₂ (cont.)	Nicotiana tabacum L.	bioaccumulation in leaves, levels of Cd in leaves to indicate Cd availability in soil	King, 1988

SUMMARY OF STUDIES EXAMINING PLANT RESPONSES TO CERTAIN CHEMICAL COMPOUNDS (continued).

Metal/ Compounds	Plant Studied	Affected Process	Reference
Chromium (Cr IV)	Oak/Pasture grasses	bioaccumulation in leaves and stems	Schroeder et al., 1962
	Beet roots	accumulator of Cr IV	Cary and Kubota, 1990
	Vegetables	leaf necrosis and foliar concentration	
	Barley	bioaccumulation	Dowdy and Larson, 1975
Copper	Rice	reduced nucleic acid content	Das Gupta and Mukherji, 1977
	Barley	loss of oxidase activity	Coombes et al., 1976
	Grass	reduced protein synthesis	Wu et al., 1975
	Chlorella (alga)	inhibited photosynthesis; noticeable change in the absorption spectrum of the algal chlorophyll	Gross et al., 1970 Gross et al., 1970
Cu(OH) ₂	Tomatoes	reduction of biomass production	Rhoads et al., 1989
	Lyes		
SO ₄ , NH ₄ , NO ₃	Lilac – <i>Cecr</i> Pines – <i>Pico, Pipo</i>	levels of bioaccumulation	Bytnerowicz et al., 1989
DEHP (di-2ethylhexyl- phthalate)	Vegetables	intact DEHP was not detected in any plants	
H ₂ O ₂	Red spruce	no foliar injury	Hanson and McLaughlin, 1989
Ozone	<i>Pinus</i> sp.	root starch reduction before visible injury	Scherzer and McClenahan, 1989

SUMMARY OF STUDIES EXAMINING PLANT RESPONSES TO CERTAIN CHEMICAL COMPOUNDS (continued).

Metal/ Compounds	Plant Studied	Affected Process	Reference
Zinc	Wheat/Maize	leaf turns blue-green at tips and dries out	Takkar and Mann, 1978
	Barley	bioaccumulation in all plant parts	Chang et al., 1983 & 1984
	Beans	xylem vessel alterations	Robb et al., 1980
	<i>Brol</i>	in silver mining, leafy tissue concentrations were highest	Boon and Soltanpour, 1992
Mercury (Hg)	Rice	root growth, germination	Beauford et al., 1977 Prasad and Prasad, 1987
	Most plants	inhibits water uptake synthesis of protein chlorophyll production	
71 CH ₃ HgCl	Spruce	seedling root elongation reduction within one day	Godgold and Hutterman, 1986
Lead (Pb) aerosol	Microflora on leaf surface	potential toxin in the food chain when ingested when on plant surfaces, but not toxic to plants	Koepppe, 1991
	<i>Brassica oleracea</i>	Pb not accumulated in leaves	Boon and Soltanpour, 1992
Pb(NO ₃) ₂	Sudan-sorgham hay	biomass did not accumulate Pb, no visible signs of effected tissue	Brams et al., 1989
PCBs	Fescue	no detectable levels >20 ug/Kg	O'Connor et al., 1990
PCBs (cont.)	Carrot	detectable in peels; peels are rich in lipid rich epidermal layer	
	Lettuce	not detectable	

SUMMARY OF STUDIES EXAMINING PLANT RESPONSES TO CERTAIN CHEMICAL COMPOUNDS (continued).

Metal/ Compounds	Plant Studied	Affected Process	Reference
Radium-226	Grasses – <i>Pepu</i> , <i>Lele Lam.</i> , <i>Ecpo</i> , <i>Erar</i> , <i>Deci</i> , <i>Sobi</i>	bioaccumulation – ^{226}Ra concentration is 6 times higher in plant tissue when grown on tailings from phosphate mines	Mislevy et al., 1989
Se (IV)	Alfalfa	plant dry weights decreased from 37 → 29.6 g; Se accumulated in plant proportional to solution Se (VI) concentration	Mikkelsen et al., 1988
SO ₂	Loblolly pine	distributed in the chloroplast; chlorophyll material	Gay and Murphy, 1989
Tritium & other water radionuclides ^{60}Co ^{238}Pu	<i>Quercus alba</i>	monitors ^3H in soil because of deep roots; ^3H activities in foliage reflect ^3H activities in the soil water	Kalisz et al., 1988

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APPENDIX 2

Contaminants of Interest to DOE and Other Agencies

Contaminants of Interest to DOE and Other Agencies

The following individual contaminants and mixtures were identified in the ground at 91 waste sites at 18 DOE facilities within the weapons complex. These data come from the report by R. G. Riley and J. M. Zachara (1992) entitled "Nature of Chemical Contaminants on DOE Lands and Identification of Representative Contaminant Mixtures For Basic Subsurface Science Research."

Fuel hydrocarbons, chlorinated hydrocarbons, radionuclides, metals, inorganic anions, and ketones were the contaminant classes most frequently measured in the ground at DOE facilities.

The chlorinated hydrocarbon, fuel hydrocarbon, radionuclide(s), metal(s), and ketone reported in groundwater most frequently were trichloroethylene, toluene, tritium/uranium, lead/chromium, and acetone, respectively.

Binary contaminant mixtures were reported at 64 percent of the waste sites and ternary mixtures were observed at 49 percent of the sites. Information on the contaminants and their in-ground combinations was used to generate generic mixtures for future research. These mixtures include:

- Chlorinated hydrocarbons and fuel hydrocarbons.
- Metals/anions and radionuclides.
- Organic solvents and PCBs.
- Metals/radionuclides and organic acids.
- Metals/radionuclides and complexing agents.
- Metals/radionuclides and ketones.
- Metals/radionuclides, organic acids/complexing agents, and organic solvents.
- Metals/radionuclides and natural organic substances.

The above mixtures all have equal priority for research, based on the frequency of their occurrence, their likelihood to influence contaminant dynamics, and the extent of research knowledge.

The following are the 25 most frequently identified substances at 546 Superfund sites (adapted from McCoy & Assoc. "Haz. Waste. Consult." 3:2(1985):

<u>Substance</u>	<u>Percent of Sites</u>
Trichloroethylene	33
Lead and compounds	30
Toluene	28
Benzene	26
Polychlorinated biphenyls	22
Chloroform	20

Tetrachloroethylene	16
Phenol	15
Arsenic and compounds	15
Cadmium and compounds	15
Chromium and compounds	15
1,1,1-Trichloroethane	14
Zinc and compounds	14
Ethylbenzene	13
Xylene	13
Methylene chloride	12
trans-1,2-Dichloroethylene	11
Mercury	10
Copper and compounds	9
Cyanides (soluble salts)	8
Vinyl chloride	8
1,2-Dichloroethane	8
Chlorobenzene	8
1,1-Dichloroethane	8
Carbon tetrachloride	8

The following are the frequency of substances reported at final National Priorities List Sites as of March 14, 1991:

<u>Chemical Name</u>	<u>Frequency</u>
1,1,2-Trichloroethylene (TCE)	401
Lead	395
Chromium and compounds, NOS (CR)	310
Toluene	281
Benzene	249
Tetrachloroethene	210
1,1,1-Trichloroethane	202
Chloroform	196
Arsenic	187
Polychlorinated Biphenyls, NOS	185
Cadmium (CD)	179
Zinc and compounds, NOS (ZN)	159
Copper and compounds, NOS (CU)	150
Xylene	136
1,2-Trans-Dichloroethylene	134
Ethylbenzene	130
Phenol	126
1,1-Dichloroethane	124
Methylene Chloride	107

1,1-Dichloroethene	106
Mercury	97
Vinyl Chloride	92
Cyanides (soluble salts), NOS	90
Nickel and compounds, NOS (NI)	83
Carbon Tetrachloride	81
1,2-Dichloroethane	77
Chlorobenzene	65

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Nevada Operations Office
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Las Vegas, NV 89193-8518

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Environmental Restoration Division
Nevada Operations Office
U.S. Department of Energy
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Las Vegas, NV 89193-8518

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EM-542
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Nuclear Chemistry Division
Lawrence Livermore National Laboratory
P.O. Box 808
L-237
Livermore, CA 94550

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Lawrence Livermore National Laboratory
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Virginia Glanzman
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Denver, CO 80225

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U.S. Geological Survey
Water Resources Division
6770 S. Paradise Rd.
Las Vegas, NV 89119

Paul Orkild
U.S. Geological Survey
Box 2506, MS 913
Denver Federal Center
Denver, CO 80225

Doug Trudeau
U.S. Geological Survey
Water Resources Division
6770 S. Paradise Rd.
Las Vegas, NV 89119

Desert Research Institute

Roger Jacobson
Desert Research Institute
Water Resources Center
P.O. Box 19040
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Marjory Jones
Desert Research Institute
Water Resources Center
P.O. Box 60220
Reno, NV 89506-0220

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Water Resources Center
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Germantown, MD 20874

David J. Roelant
BDM Federal
12850 Middlebrook Road
Trevion I, Suite 300
Germantown, MD 20874

International Technology Corp.

Rick Waddell
Geotrans
c/o IT
4330 Valley View
Suite 112
MS-439
Las Vegas, NV 89103

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International Technology Corp.
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