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By L. Karr and D. Mouat

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Technical Note

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A BIOGEOCHEMICAL AND SPECTRAL ANALYSIS OF VEGETATION AFFECTED BY EXTERNAL ABIOTIC AGENTS: RESULTS OF AN INVESTIGATION FROM KITSAP COUNTY, WASHINGTON

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ABSTRACT Biogeochemical and ground-based remote sensing techniques were used in an investigation designed to detect, assess, and monitor hazardous waste disposal activities at several Navy facilities. The investigation was designed to develop a timely and cost-effective strategy for the study of hazardous waste activities. Tissue samples from two tree species (Douglas fir and red alder) were collected from an ordnance burn site and from an electroplating acid waste disposal site near Bangor, Washington. The samples were measured with a spectroradiometer employing Landsat Thematic Mapper bands as well as narrow bandpasses (10 nm) along the red edge. The samples were also analyzed for their elemental content. Control sites were also chosen and sampled. Results showed that red edge reflectance values were significantly different among samples collected at the hazardous waste sites than in samples collected at the control sites. Landsat TM bands 1, 3, and 5 readings were also significantly different. Elemental differences among the plant tissues were less informative. Zinc concentrations, however, were significantly lower on both sites.

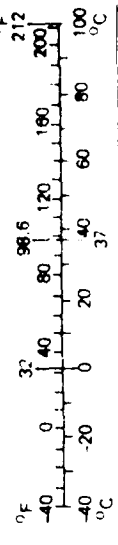
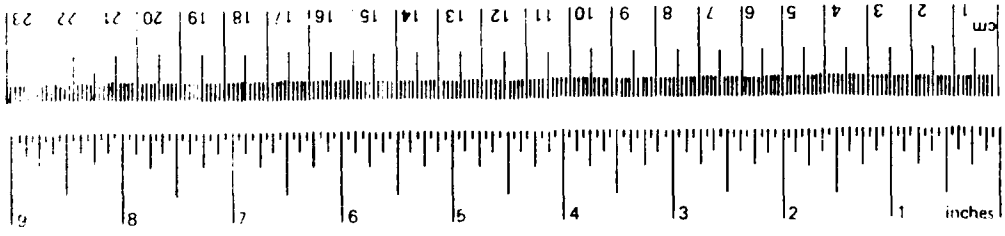
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METRIC CONVERSION TABLES

| Approximate Conversions to Metric Measures | | | | Approximate Conversions from Metric Measures | | | |
|--|------------------------|----------------------------|---------------------|--|-----------------------------------|-------------------|------------------------|
| Symbol | When You Know | Multiply by | To Find | Symbol | When You Know | Multiply by | To Find |
| in | inches | 2.5 | centimeters | cm | centimeters | 0.04 | inches |
| ft | feet | 30 | centimeters | cm | inches | 0.4 | inches |
| yd | yards | 0.9 | meters | m | feet | 3.3 | feet |
| m | miles | 1.6 | kilometers | km | meters | 1.1 | meters |
| | | | | | kilometers | 0.6 | miles |
| m ² | square inches | 6.5 | square centimeters | cm ² | square centimeters | 0.15 | square inches |
| ft ² | square feet | 3.09 | square meters | m ² | square meters | 1.2 | square yards |
| yd ² | square yards | 0.8 | square meters | m ² | square kilometers | 0.4 | square miles |
| mi ² | square miles | 2.6 | square kilometers | km ² | hectares (10,000 m ²) | 2.5 | acres |
| | acres | 0.4 | hectares | ha | | | |
| oz | ounces | 28 | grams | g | grams | 0.035 | ounces |
| lb | pounds | 0.45 | kilograms | kg | pounds | 2.2 | pounds |
| | short tons | 0.9 | tonnes | t | short tons | 1.1 | short tons |
| | 12,000 lb | | | | | | |
| tsp | teaspoons | 5 | milliliters | ml | milliliters | 0.03 | fluid ounces |
| Tbsp | tablespoons | 15 | milliliters | ml | liters | 2.1 | pints |
| fl oz | fluid ounces | 30 | milliliters | ml | liters | 1.06 | quarts |
| c | cups | 0.24 | liters | l | liters | 0.26 | gallons |
| pt | pints | 0.47 | liters | l | cubic meters | 35 | cubic feet |
| qt | quarts | 0.95 | liters | l | cubic meters | 1.3 | cubic yards |
| gal | gallons | 3.8 | liters | l | | | |
| ft ³ | cubic feet | 0.03 | cubic meters | m ³ | | | |
| yd ³ | cubic yards | 0.76 | cubic meters | m ³ | | | |
| °F | Fahrenheit temperature | 5/9 (after subtracting 32) | Celsius temperature | °C | Celsius temperature | 9/5 (then add 32) | Fahrenheit temperature |



* In 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weight and Measures, Price \$2.25, SD Catalog No. C13.10.286

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EXECUTIVE SUMMARY

The Navy must comply with numerous environmental regulations relating to the identification, assessment, monitoring, and cleanup of hazardous waste sites. Standard methods employed in all phases of compliance are labor intensive, time consuming, and costly at the very least. This study provides the ground basis for initiating development of a new protocol for environmental assessment that may be employed from airborne sensors, thus providing more data in a shorter period of time at a reduced cost.

This study shows that plants, being effective integrators of environmental conditions, can be used for deriving information. It was shown that vegetation (from known hazardous waste sites) does in fact respond spectrally to anomalous concentrations of environmental contaminants. The results show that red edge reflectance values are significantly different between samples from two contaminated sites and their respective controls. Further ground-based experiments need to be conducted concurrent with airborne sensor readings.



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INTRODUCTION

This report describes a project initiated in August 1988 by the Naval Civil Engineering Laboratory (NCEL). The project was designed to develop a strategy involving geobotanical, biogeochemical, and remote sensing techniques for the detection, assessment, and monitoring of environmentally contaminated areas at Navy facilities. This strategy was to be accomplished using techniques which could be repeated and would be rapid, efficient, and cost-effective. While the development of the techniques occurred at sites having known contamination, the techniques, if proven effective, could be used for the identification of unknown sites, as well as for the assessment and monitoring of known sites.

The Navy has long had the need to locate, assess, and monitor hazardous waste activities. At present, the Navy is using techniques that may not be adequately assessing the magnitude of hazardous waste impacts. Often the Navy responds to discoveries of hazardous waste made by other agencies. The techniques developed during this investigation should allow the Navy to discover the existence of toxic materials within its facilities and to monitor and prioritize hazardous disposal activities which are spreading both inside and outside its facilities. The techniques developed should allow the Navy itself to make determinations regarding the existence and extent of hazardous waste within its facilities and to remedy the problem.

Three study areas were chosen on the basis of stated need by the Naval Facilities Engineering Command (NAVFAC) and an ongoing Installation-Restoration Program. The areas also met criteria involving the composition and distribution of overlying vegetation as well as minimal apparent ancillary cultural disturbances which might have confused observations. These areas are located north of Bremerton, Washington, and include two sites on the Naval Submarine Base, Bangor (Figure 1) and one site at the Navy Undersea Warfare Engineering Station (NUWES) at Keyport. The Keyport site was dropped from the investigation because of cloudiness at the time of the field investigation which precluded the use of one of the techniques (the ground-based spectroradiometric measurements).

BACKGROUND

The Bangor sites included an electroplating acid waste disposal site (used between 1960 and 1973) that contained several toxic heavy metals that had been dissolved or suspended in electroplating solutions, and an ordnance (primarily trinitrotoluene - TNT) burn disposal site (used between 1946 and 1965). The Keyport site involved a landfill (now covered primarily by asphalt) which reportedly had high concentrations of trace metals, petroleum hydrocarbons (including Otto fuel), and unidentified halogenated organics incorporated into the fill.

The general region of the study area is located within the Puget Sound lowland of western Washington. This area was glaciated during the Pleistocene era. Consequently, the geomorphology of the region as well as the soils have been highly influenced by that action. The soils in most places are derived from glaciofluvial action as well as from till. The resultant topography in the immediate vicinity of the study areas clearly exhibits those characteristics (i.e., terraces, deltas, and bars resulting from the glaciofluvial action and gently undulating to hilly topography resulting from the glacial till). The soils of the study area region are quite gravelly due to the glacial activity (a typical soil is a gravelly sandy loam), and, as a result, tend to drain very rapidly. The vegetation is typical of the Puget Sound lowland, consisting of conifers including Douglas fir, western hemlock, and western red cedar. In addition, where Douglas fir (or other conifers) have fallen, been logged, removed, or burned, alder typically comes in. Numerous minor western hardwood species are also found intermingled within both the coniferous and broad-leaved forests.

Biogeochemical Effects of Heavy Metals and Organics on Vegetation

Extensive literature exists on the toxic effects of heavy metals on vegetation. Very limited literature exists on the effects of organics such as TNT or its secondary products. To understand the response of plants to heavy metal stress or to the effects of potentially toxic organic compounds, it would be helpful to review a plant's response to general environmental stress (Warren, 1980; Foy, 1973; Gates, 1980; Knipling, 1970; and Bunnik, 1978). A plant responds in many ways to the stress of abnormal situations (Treshow, 1970). There are four basic types of response: (1) growth response, (2) reproductive effects, (3) chlorosis, and (4) necrosis. Growth is influenced by two fundamental metabolic processes: photosynthesis and respiration. Photosynthesis is the conversion of radiant energy to chemical energy. Chemical energy is stored in the form of carbohydrates in the cell and is released through respiration. The process occurs only in illuminated green tissue, because chlorophyll plays an essential role in the conversion of light energy to chemical energy. While chlorophyll is found in many plant parts, most of the chlorophyll pigments are concentrated in the chloroplasts of leaf mesophyll cells. Although there are several kinds of chlorophylls, chlorophyll a and b are the only important ones in woody plants (Kramer and Kozlowski, 1979). Chlorophyll is fluorescent, absorbing certain wavelengths of visible light primarily in the red and blue part of the spectrum. Chlorophyll molecules are organized within the chloroplasts in photosynthetic units, each consisting of several hundred molecules. Failure to develop or maintain chlorophyll results in a yellowing of leaves or "chlorosis." The major environmental factors affecting chlorophyll formation are light, temperature, minerals, water, and oxygen; but chlorophyll formation is very sensitive to almost any factor which disturbs metabolic processes. Probably the most common cause of chlorosis is a result of a mineral deficiency or toxicity (the significance of this will be discussed later). The process of photosynthesis can be broken down into the following sequential events: (1) trapping of light energy by the chloroplasts, (2) splitting of water and release of high-energy electrons and oxygen (O₂), (3) electron transfer

leading to generation of chemical energy in the form of adenosine triphosphate (ATP) and reducing power as nicotinamide adenine dinucleotide phosphate (NADPH), and (4) terminal steps involving expenditure of energy of ATP and the reducing power of NADPH to fix carbon dioxide (CO₂) molecules in phosphoglyceric acid and subsequent conversion into more complex carbohydrates.

Photosynthesis includes a photochemical phase requiring a light phase as well as a dark phase. The photochemical phase of photosynthesis consists of two light reactions which are joined together by electron carriers. The systems operate through the use of different pigments. The operation of each light reaction or photosystem involves absorption of one quantum of light energy by each reaction center, which is then said to be in an "excited" state. In the first photosystem, the "excited" reaction center gives up an electron to an electron acceptor and the electron then moves down the energy scale to ferredoxin and is involved in the reduction of NADP⁺ to NADPH. In the second photosystem, the energy absorbed is used to bring about the excitation of electrons and the photolysis of water. The pigments of this photosystem include a species of chlorophyll a with an absorption maximum of about 680 nm, some additional chlorophyll a and b, and carotenoids. The importance of this sequence in this discussion is that disruptions in the rate of photosynthesis and the production of chlorophylls affects the spectral response of vegetation including absorptions in the 680 nm region (the beginning of the "red edge").

Mineral elements in the soil, whether required for normal nutrition or not, are all absorbed by the plant to some extent. Above essential nutrient needs, the plant may absorb and accumulate excessive toxic amounts. The ratio between many of these elements is also vital. Too much as well as too little of many mineral elements will upset the ratio and cause abnormal development or response. Figure 2 is a dose-yield response curve for hypothetical nutrients and nonessential elements.

The dose-yield response curve is comprised of three distinct phases or zones which define the nutrient status of the overall plant: (1) deficiency, (2) tolerance, and (3) toxicity. A depletion of an element may be just as useful an indicator as an enrichment, for both provide information about the geochemistry of an area. High unit toxicity elements such as copper will have a limited range between threshold and lethal toxicity, while low unit toxicity elements such as Cr and Mn will have a broader range.

While nutrient requirements are largely inherited, nutrient absorption and accumulation also depend on such physical factors of the soil as structure and acidity. About one-fourth of the earth's soils are considered to produce some kind of mineral stress (Hale and Orcutt, 1987). Most of this stress can be attributed to an overabundance or abnormal concentration of essential nutrients. Approximately 15 to 17 elements are considered to be essential to plant growth and reproduction. These include C, H, O (non-nutrients), N, P, K, S, Ca, Mg (macronutrients), Cu, Zn, B, Cl, Mo, Mn, and Fe (micronutrients). Numerous other elements including Se, Ni, Cr, Co, and Al, while not possibly being essential, are taken up into plant tissues and may affect photosynthesis.

There are many plants in which tissue metal concentration is well correlated with the soil metal concentration. A plant's response to a change in element concentration is concentration dependent; that is, the degree of response of a plant to a change in concentration of a specific element may not be the same when the concentration is high as where there is only a low background concentration of the same element.

Nutrients are absorbed from soil solutions in the ionic form: the common metals are taken up as cations, and the macronutrients N, P, and S as oxyanions. There are three main mechanisms whereby ions may be absorbed by plants (from Brooks, 1983). Two of these involve uptake at the root system and the third involves foliar absorption in the aerial parts of the plant. This latter mechanism is not common in our study area region. Uptake at the root system involves either diffusion into the plant from the soil solution or cation exchange at the surface of clay minerals. Some ion absorption also occurs by simple diffusion into the cells of the root tips. A surprising feature of the accumulation of ions by roots is that their concentration in the cell fluid is often many times greater than in the soil solution. This is known to be a metabolically mediated process requiring the expenditure of cellular energy. The ions absorbed at the roots of the plants usually are translocated in an upward direction toward the leaves. The xylem appears to be the chief medium of the movement. Plants vary greatly in their ability to accumulate elements from the soil. Levels of selenium in plants, for example, may vary by a factor of 4,000 (Brooks, 1983)!

A plant's response to soil nutrient concentration may be influenced by the amount of other elements present. For example, a number of plants will secrete chelating agents in response to an iron deficiency. The soil will become more acid and many metals in addition to iron will become available for absorption by the plant. Thus, changes in one nutrient can result in changes in tissue concentrations of many others. A classic example of effects on mineral uptake according to soil concentration can be found in the Josephine ophiolite of southwest Oregon. The peridotites of this area have much lower concentrations of calcium than most rock types. In fact, the magnesium/calcium ratios of the soil solutions are much greater than one (in "normal" soils, the ratio may be 1/10 or 1/20). It has been hypothesized that as the plant attempts to uptake the essential nutrient calcium, it takes up an abnormal and often toxic level of the nutrient magnesium (both are divalent ions).

When small localized areas of abnormally high metal concentration occurs, a plant's response is typically avoidance. When the metal is evenly distributed in the soil, all roots are affected in the same way and tissue analysis will reflect the soil concentration. However, when the high concentration areas are localized, root growth in the toxic areas will be inhibited while the root growth in the rest of the soil will continue at a normal rate. Plants adopt varying strategies to deal with anomalous elemental concentrations. These may include a biochemical avoidance, internal detoxification, or a biochemical tolerance. A linear relationship between total soil concentration and tissue concentration is rare. Most plants function as elemental accumulators at low background levels. Often soil concentration may remain static with tissue concentration increasing or decreasing. This may occur when pH changes, causing elements to mobilize or become less mobile, thereby resulting in tissue concentrations to increase or decrease.

Solubility and mobility factors determine the plant-available fraction of an element in the soil. In Carlisle et al. (1986), Nye and Tinker expressed the mean concentration of an element in a plant in relation to the simultaneous process of growth and uptake as:

$$X = (S/R_w)(M_r/M)$$

where X is the fraction of the element to dry matter governed by the specific nutrient absorbing power of the root (S); R_w is the relative growth rate of the plant; and M_r/M is the root/plant mass ratio.

An increase in the soil pH of one unit from, for example, pH 5 to pH 6, will decrease the availability of most cations by half and considerably increase the availability of anions.

Spectral Reflectance of Plants

One impact of differential cation distribution in soils may be a resulting impact on the spectral response of associated vegetation. The spectral reflectance of plants can be a very revealing indicator of the plant's response to geochemical conditions.

Plant spectral response depends upon a number of factors including leaf geometry, morphology, physiology, chemistry, soil site, and climate (Gates, 1970). A plant leaf reflects radiation in a manner that is uniquely characteristic of pigmented cells containing water solutions. Figure 3 illustrates a typical spectral (from 0.4 μm to 2.4 μm) response curve of a healthy green leaf. Reflectance patterns can be grouped into three distinct regions: 0.4 μm to 0.7 μm , 0.7 μm to 1.3 μm , and 1.3 μm to 2.4 μm . In the visible part of the spectrum (0.4 μm to 0.7 μm), plant spectral response is fairly low with lower blue and red reflectance than green. This is due to plant pigment absorption, chiefly chlorophyll and carotene, in blue and red. A lesser absorption in green results in higher green reflectance. Relatively slight changes in pigmentation will affect plant spectral response in this region. Pigmentation changes, such as chlorosis, can occur because of abnormal soil geochemistry. Pigment absorption is not especially significant between 0.7 and 2.4 μm . Instead, intercellular air spaces developed in the spongy mesophyll of the leaf increase the number of reflecting surfaces with abrupt changes in the index of refraction. The spectral result is a rapid increase in reflectance at approximately 0.7 μm . This is largely the result of the interaction of incident radiation with the mesophyll structure. Once the leaf mesophyll is fully developed, small external changes will probably not affect the reflectance. Large changes in water availability, however, probably would affect near infrared reflectance (Gates, 1970). Beyond 1.3 μm , plant spectral response is largely a function of internal leaf water content.

Most measurements of vegetation reflectance prior to 1983 by remote sensing techniques typically utilized broad spectral bands on the order of 100 nm. This low spectral resolution precludes the response of vegetation to more subtle features. In particular, the spectral region associated with the "red edge" requires narrow spectral bands to resolve subtle variations that may be associated with metal stress. The red edge is a unique feature of green vegetation because it results from two

special optical properties of plant tissue: high internal leaf scattering causing large near infrared reflectance, and chlorophyll absorption giving low red reflectance (Horler, 1983). Horler reports that as chlorophyll content increases, the red edge shifts progressively to longer wavelengths. He states that the position of the red edge may be a good measure of the amount of chlorophyll in the leaf. He further reported that there appears to be a link between the wavelength of the red edge and plant chlorophyll content. The red edge appears to shift to shorter wavelengths as a result of plant stress (Horler, 1983).

The previous discussion relates primarily to the effects of heavy metals on plants. In fact, other materials may affect vegetation with similar deleterious effects. A number of organics have devastating effects on plants (obviously herbicides). These materials affect the plants ability to metabolize and in fact may cause a total metabolic breakdown.

In studies involving plant growth and metabolism in soil solutions containing varying concentrations of TNT, Palazzo and Leggett (1986) found that plant growth and development were affected by TNT. The greatest changes in physiological activity occurred between concentrations of 0.5 and 5 mg/L of TNT. Results of their study showed that a breakdown in root cell structure was accompanied by a reduction of root and aboveground biomass growth.

METHODS

Statistical Evaluation

A methodology has been developed for this project which centers on a statistical evaluation of the effects of hazardous waste on the overlying vegetation. The methodology involved the analysis of paired sets of observations for each of the study areas. Of paramount importance in the establishment of each paired set was uniformity of observation. That is, vegetation species, site, geology, climate, sampling procedures, etc., all had to be as similar as possible. It might be hypothesized that relatively small differences in any one of those factors could greatly skew results.

The first step involved a reconnaissance of adjacent areas to the investigation site in order to locate areas having similar topography, geology, and vegetation composition. Those areas would be used as the second (control) of each of the paired sites for the three study areas. The reconnaissances for each area did, in fact, reveal appropriate adjacent areas which were evaluated for selection for use as the paired sites.

The second step of the methodology involved four principal stages. These included: (1) species observations and reconnaissance, (2) tissue sampling and analysis, (3) ground spectroradiometric measurements, and (4) data analysis.

It was important that species composition be carefully ascertained throughout each of the study areas. Homogeneous areas of highly specific composition might indicate a taxonomic response to the underlying geochemical conditions. Therefore, ground reconnaissance transects were

conducted through each of the study areas prior to sampling. Extreme taxonomic responses might preclude other types of sampling. That is, if certain major species did not occur within a significant part of a study area, it would obviously be impossible to biogeochemically or spectrally sample it.

The major perennial species were noted and recorded at each study area. These species were later evaluated and a decision was made to use them for tissue sampling and spectral analysis. The decisions were made on the basis of distribution of the more dominant species throughout each of the paired sites. As it turned out, only Douglas fir (Pseudotsuga menziesii) and red alder (Alnus rubra) were used in the subsequent analyses. The other species were either not plentiful enough for an adequate sample, or else had discontinuous distributions.

At each of the paired sites, tissues including the last years' twigs and leaves were clipped and stored from a number of individual trees for subsequent biogeochemical analysis. At one site (the ordnance burn site) two species grew ubiquitously and were sampled. At the other two sites, only one species (Douglas fir) was sampled. At least five samples of each species were collected from each paired site. Individual trees were randomly accessed but were sampled with careful criteria. These included distance above ground (4-1/2 feet above ground level) and the same side of the tree. Care was taken to ensure that the same ratio of needles or leaves to twigs was taken at each site. Approximately 100 grams (minimum) of leaf tissue was gathered and bagged (in Hubco bags) at each site. The location of the sample was determined via tape and compass and recorded. Careful documentation has been made of each sample site. A location number was recorded on the sample bag. The samples were sent to a preparation lab for washing and subsequent pulping. Those samples were then submitted for biogeochemical analysis involving elemental concentration through either an Inductively Coupled Plasma (ICP) emission spectroscopy device or through neutron activation (in which the sample is irradiated and emitted neutrons are measured spectroscopically). The two biogeochemical analytical techniques were used because of the importance of assessing different sets of elements. Lead, for example, is only measured through the use of the ICP. Both techniques are accurate to parts per billion (ppb) for some elements and parts per million (ppm) for others.

Coincident with the biogeochemical sampling was a spectroradiometric analysis conducted with a hand-held ratioing radiometer (HHRR). The HHRR is an electro-optical instrument with electronic readout designed primarily for use in environmental investigations. The HHRR measures the energy reflected by a target of interest through a set of ten filters of the operators choosing. Typically, the narrowest filter used is 10 nm with the widest over 100 nm. In the experiments conducted, five filters having 10 nm bandpasses centered on 680 nm, 700 nm, 720 nm, 740 nm, and 780 nm were used. These filters were used since they represent the entire range of the red edge of spectral reflectance. This region has been hypothesized (e.g., Milton, 1983) as being highly sensitive to vegetation affected by metal and moisture stress. In addition, filters for the first five Landsat Thematic Mapper (TM) bandpasses (that is, 420 nm to 500 nm, 520 nm to 600 nm, 630 nm to 690 nm, 760 nm to 900 nm, and 1.55 um to 1.75 um) were also employed. Landsat TM bands were

felt to be especially significant because of their widespread use not only in the Landsat satellite, but also in airborne sensors employing the same bandpass configuration. It was felt that if the techniques were found to be useful, a system having operational capability would be essential.

The HHRR signal is displayed in a liquid crystal display (LCD) after amplification and rectification. Although the instrument was initially built to display a ratio of two filters for the target, it can be used as a direct reading spectroradiometer. The footprint (or area viewed) is approximately 4 cm by 20 cm from a height of about 1 meter. The operator uses it mounted on a tripod and pointed vertically down at all times in order to ensure consistency in viewing angle. The instrument is pointed at a flat reflectance standard (fibrefrax and barium sulfate are two such materials) and a measurement is taken. The standard is then withdrawn, the target exposed, and a second measurement is taken. The target reflectance is the ratio of the target reading versus the standard reading. The LCD display is then recorded (for these samples, recording was done by hand). Three readings were taken of each target and the average was used for subsequent analysis. Targets consisted of five branchlets, approximately 1/2 meter long, superimposed on one another with the top side of the leaves exposed. The ends of the cut branches were wrapped with wet towels to minimize dessication and moisture stress. In all cases, readings were taken within 5 minutes of branch removal. Readings were always taken when the skies were cloud free. This was determined by analyzing the radiometer display. A shift in the readout of more than two or three counts meant that atmospheric interference was occurring and readings were suspended. No readings were taken at the Keyport site since atmospheric interference was extreme due to a continuous cloud cover.

Data Analysis

The Student's T-test was determined to be the most appropriate technique due to the number of samples taken and the nature of the hypothesis to be tested. Data were converted to reflectances, averaged, and then entered into a Student's T-test program for determination of statistical significance of the broad and narrow band spectral characteristics of vegetation growing on affected areas versus unaffected areas.

RESULTS AND DISCUSSION

Results show that some of the techniques tested were only partially successful. The NUWES Keyport site should be excluded from discussion at this point because spectral measurements were not acquired due to cloudy conditions. cursory examination of the biogeochemical data indicates high zinc and arsenic levels in vegetation growing on the landfill compared with the control site. This observation may indicate the value of ground-based spectral measurements.

Results for the electroplating acid waste disposal site and the ordnance burn site indicate that both biogeochemical analysis and ground spectral analysis might be appropriate for discriminating hazardous waste sites. Each of the techniques was found to be more useful for analyzing one of the sites than for the other.

Results of the ground spectral analysis have been most interesting. The narrow bandpass filters located along the red edge were more successful in discriminating hazardous waste disposal than were the wider Landsat TM bandpass filters.

Electroplating Acid Waste Disposal Site

Biogeochemical and spectral samples were collected along a series of transects at the site. Data were analyzed for a cluster of five samples collected in the immediate vicinity of the site and a cluster of four samples collected in the control area.

Ground spectral results are indicated in the Appendix to this report. Graphs of plant spectral response employing both the narrow band red edge filters and the Landsat TM filters are illustrated in Figures 4 and 5. An examination of the narrow band spectra shows that vegetation growing near the site have spectra which are displaced vertically upward and to the left than the vegetation growing in the control site. The data were subsequently examined statistically using Student's T-test with an a priori level of significance set at 5 percent in order to determine if the spectral responses of vegetation growing in the vicinity of the acid waste disposal site were significantly different from vegetation growing in a nearby control site. Results of the "T"-test, which are also included in the Appendix, show that vegetation spectral response in the five narrow band red edge channels indicates a highly significant difference between vegetation growing near the acid waste disposal site and vegetation growing on the control site. In fact, the three bandpasses situated along the red edge differed with a level of significance of less than 0.5 percent. TM bands 1, 2, 3, and 5 all differed significantly with the visible bands (TM 1, 2, and 3 differing with a level of significance of less than 0.1 percent). TM band 4, the near infrared band, had no significant difference. Biogeochemical results were quite inconclusive. Levels of arsenic were greater in trees growing near the disposal site and levels of zinc appeared to be lower near the site. Other elements showed little difference.

Ordnance Burn Site

Fifteen spectral and biogeochemical samples were collected in the vicinity of the ordnance burn site and within a control site located in the immediate vicinity. These samples were divided between two species, Douglas fir (*Pseudotsuga menziesii*) and red alder (*Alnus rubra*), as both of these species were ubiquitously present within both the burn site as well as within the control area.

Ground spectral results are summarized in the Appendix. The spectra depicted are illustrated in Figure 5. This figure shows results from the narrow band filters as well as from the TM band equivalents of both

Douglas fir and red alder; vertical bars representing one standard deviation from the mean are given. Figures 6, 7, 8, and 9 show the displacement of spectra of the burn site species (both the Douglas fir and the red alder) from the spectra of the control site species. While the displacement may not appear to be as great as for the acid waste spectra, the level of significance of the difference of the set involving the narrow band spectra is nevertheless as important. T-tests applied to the data set show that there were no significant spectral changes in red alder measured with the "red edge" narrow band filters, while Douglas fir had significant differences in the middle of the red edge at 720 nm. Surprisingly Landsat TM results were more significant, with red alder exhibiting significant differences in TM 1 and TM 3, and Douglas fir exhibiting significant differences in TM 1, TM 3, and TM 5. TM 4/3 ratios were highly significant for both red alder and Douglas fir.

Biogeochemical results were more significant for the ordnance burn site than for the acid waste disposal site. Zinc was the most significant element with considerably greater differences on the site as opposed to the control site.

RECOMMENDATIONS

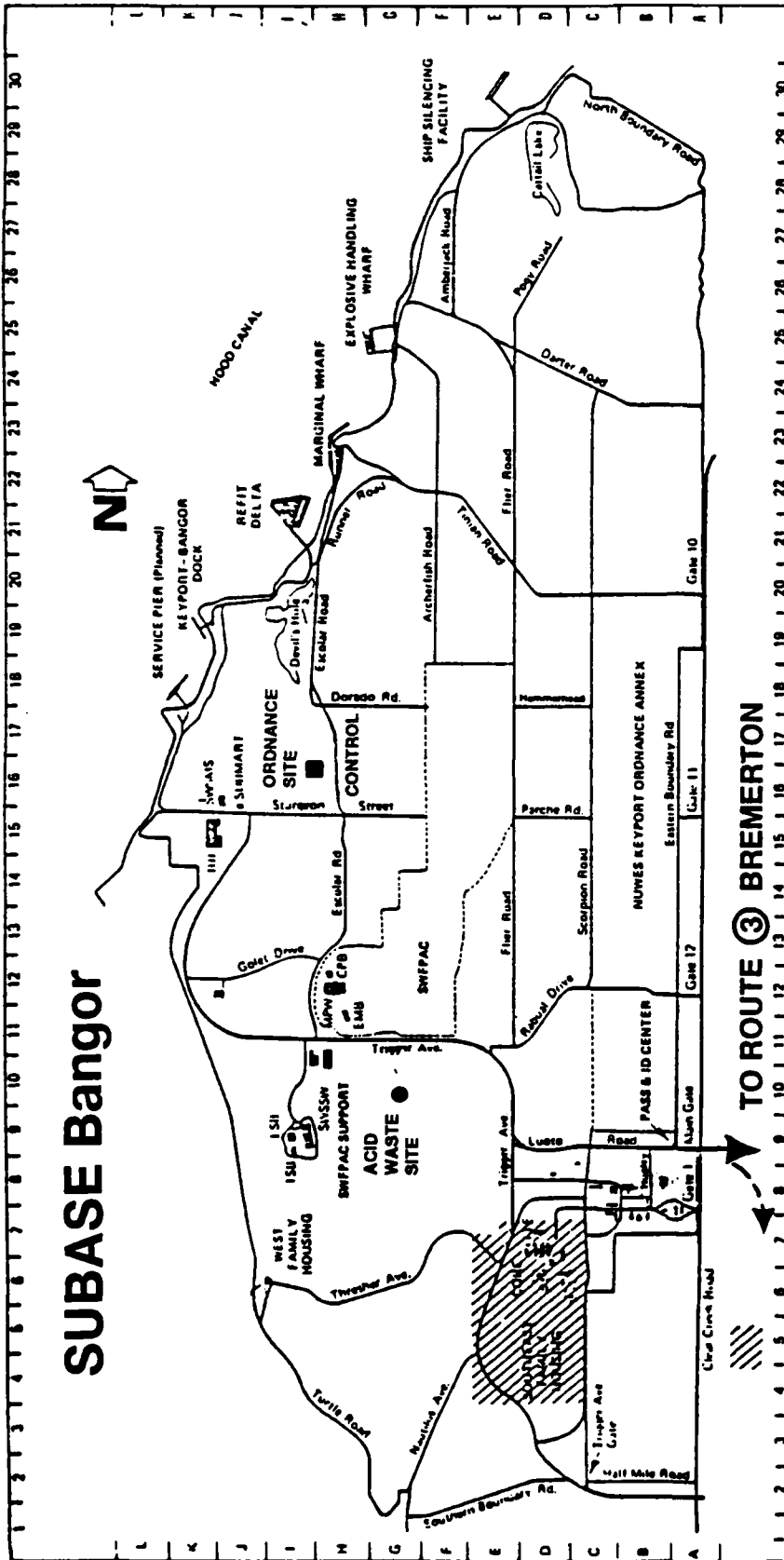
The results of the investigation indicate that discrimination between contaminated and uncontaminated sites is possible through the use of vegetative spectral reflectances. To further test this hypothesis, additional ground-truthing is recommended. In addition, it is recommended to conduct a fly-over of the test area using the bands that clearly discriminated between the sites to verify the procedure. Since the contaminated areas have been delineated to a degree using traditional methods, this second phase will test the accuracy of the remote procedure from an applications viewpoint.

If contaminated areas can be delineated using a remote sensing technique, as proposed, the method may provide a faster and more economic means for environmental assessments and for routine monitoring of facilities. Until further tests are completed to verify the applicability of this technique, cost and time savings cannot be calculated. It is estimated that sampling time and analysis will be reduced, but to what extent is unknown.

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| NAVY EXCHANGE GAS STATION | E-8 | |
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Figure 1. Acid waste site and ordnance waste site location, Subbase, Bangor.

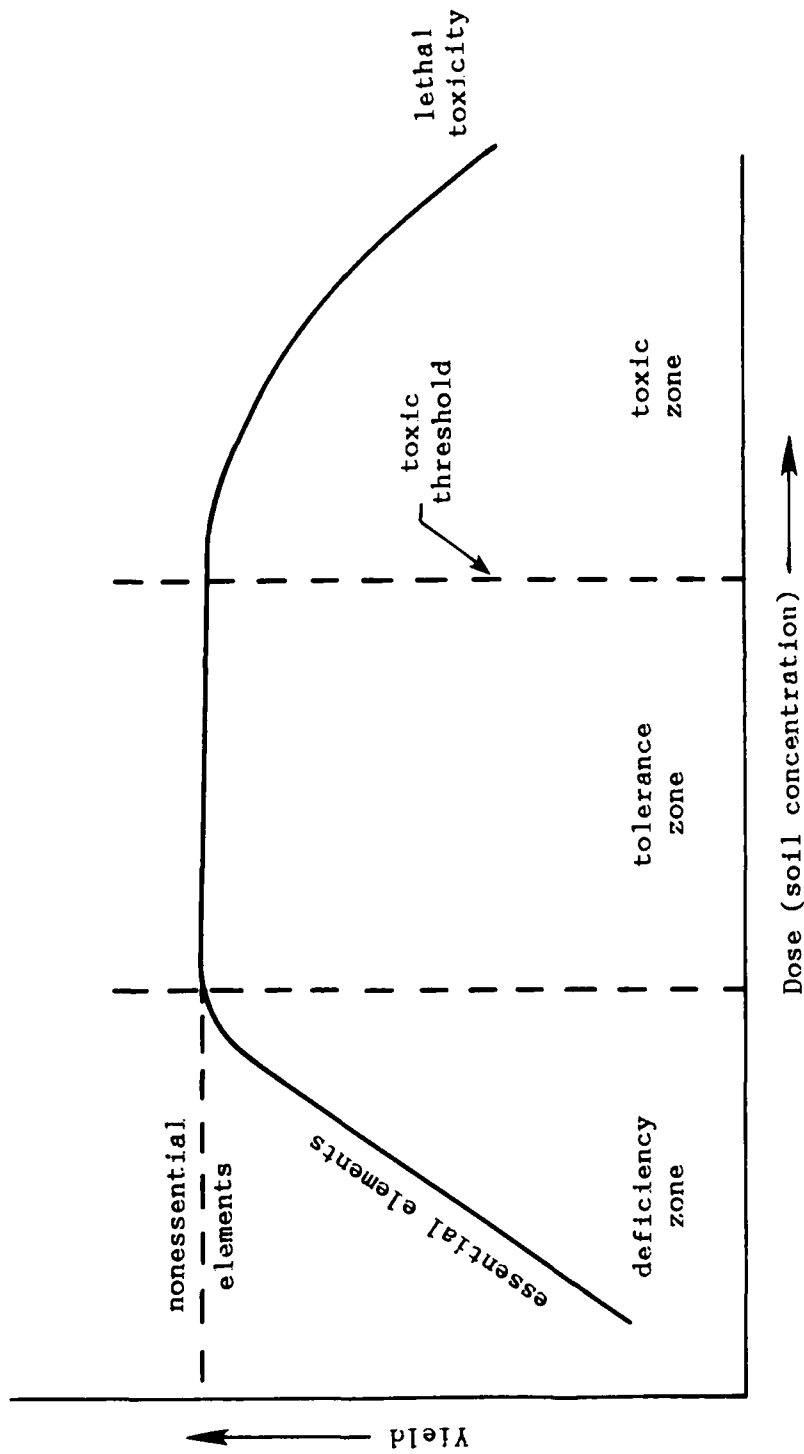


Figure 2. A dose-yield response curve for typical essential nutrients and nonessential elements (adapted from Carlisle et al., 1986).

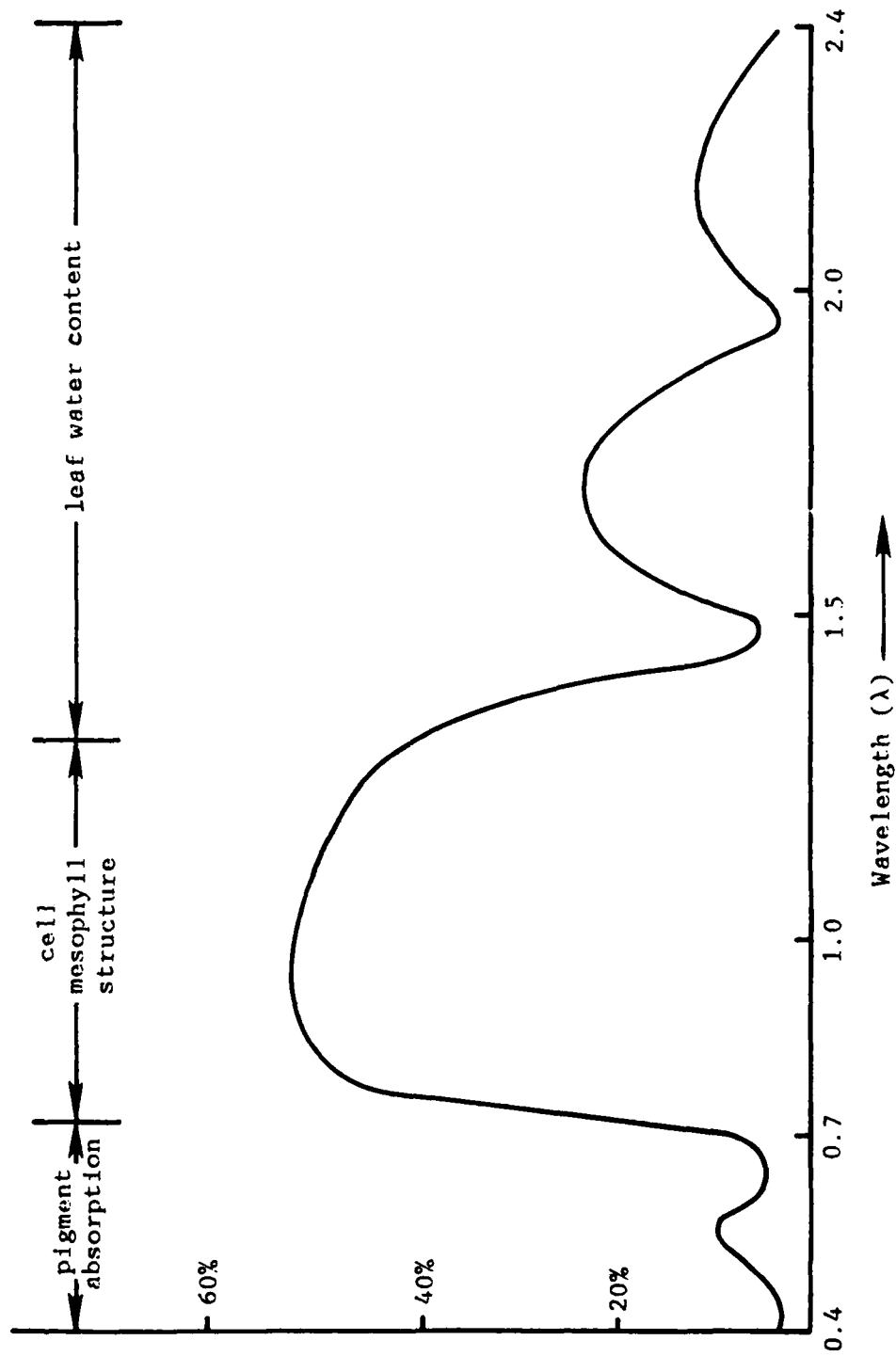


Figure 3. A spectral response curve of a typical healthy leaf between 0.4 μm and 2.4 μm .

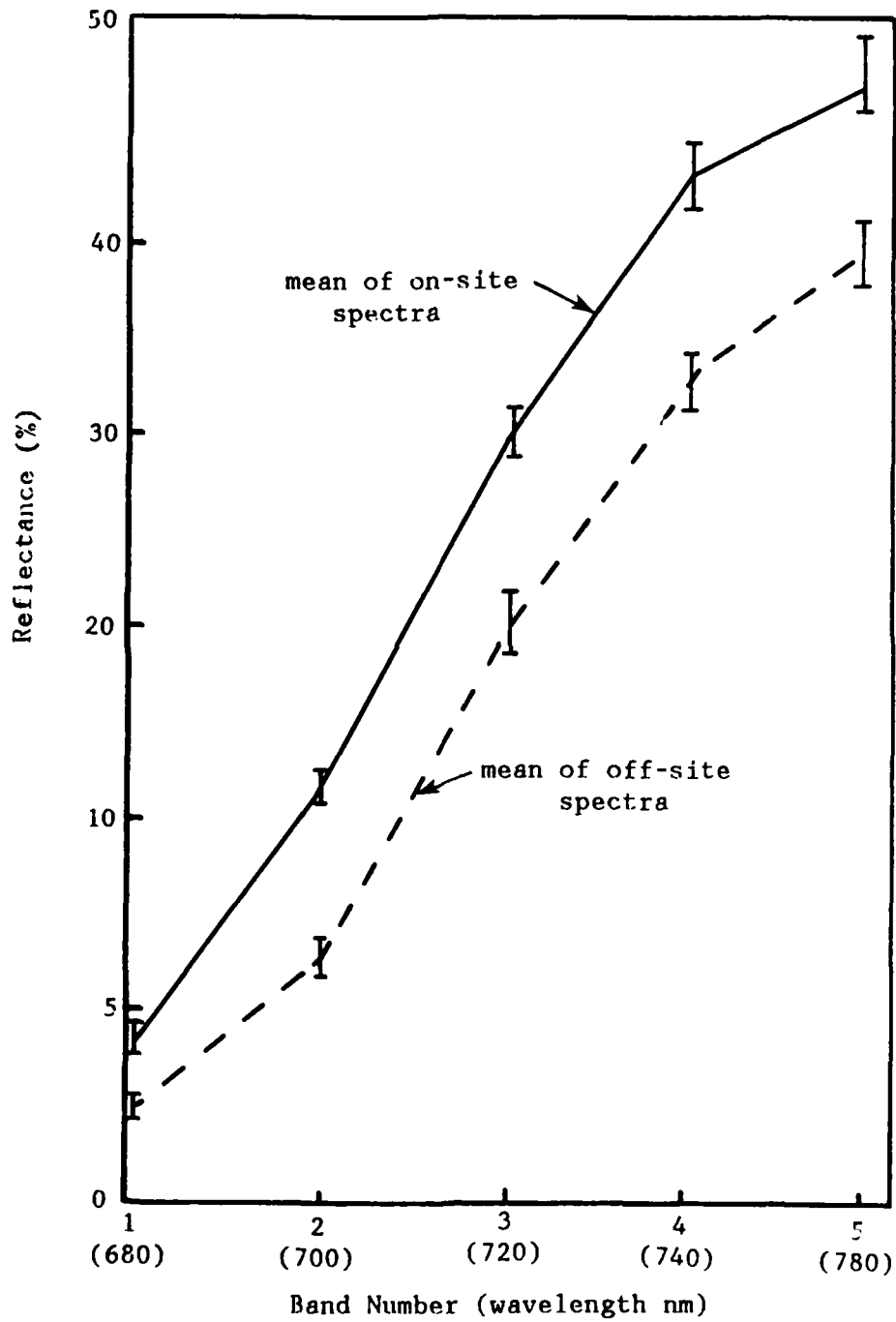


Figure 4. Reflectance spectra of Douglas fir growing on and off an acid waste disposal site, Bangor, WA.

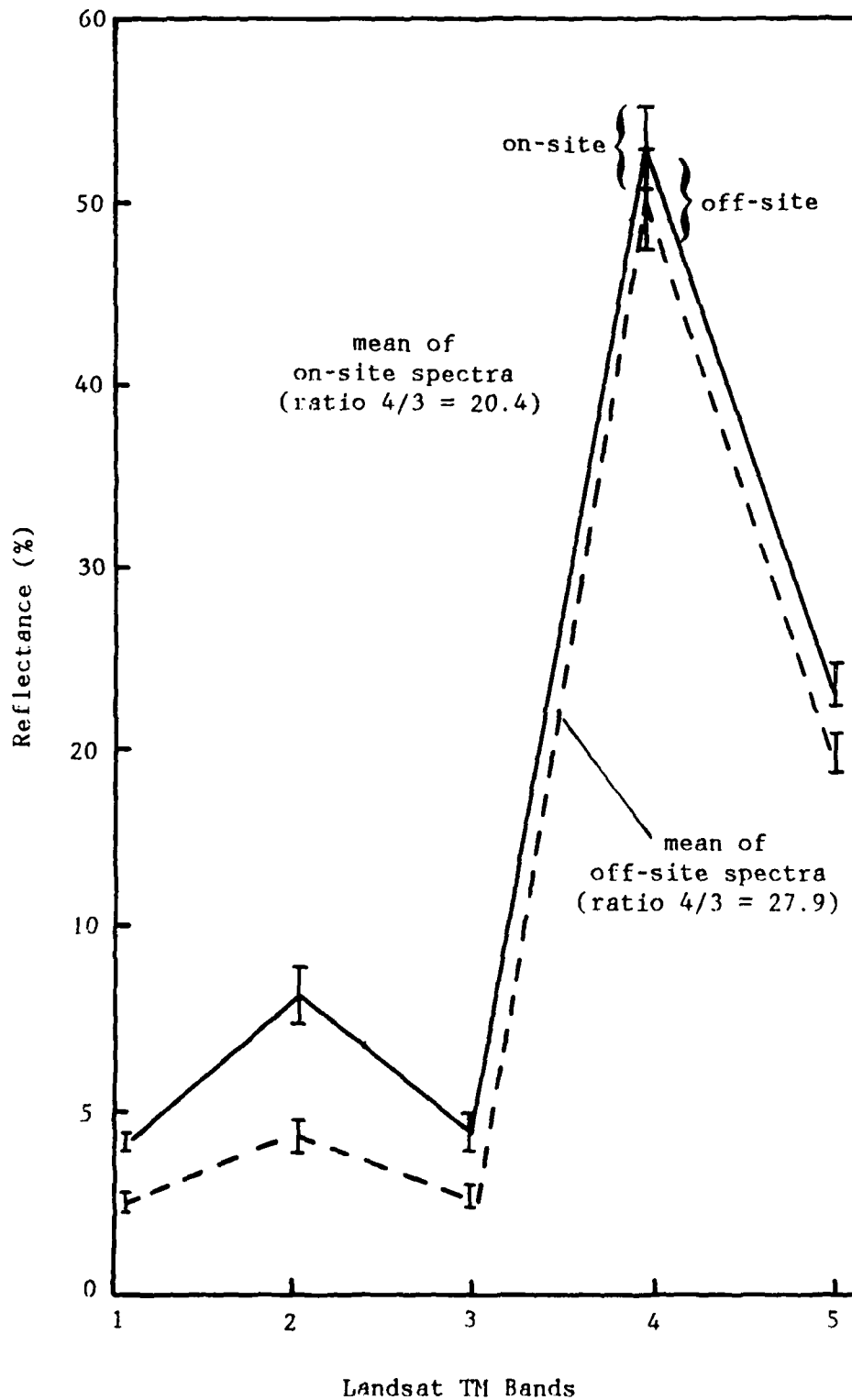


Figure 5. Landsat TM reflectance spectra of Douglas fir growing on and off an acid waste disposal site, Bangor, WA.

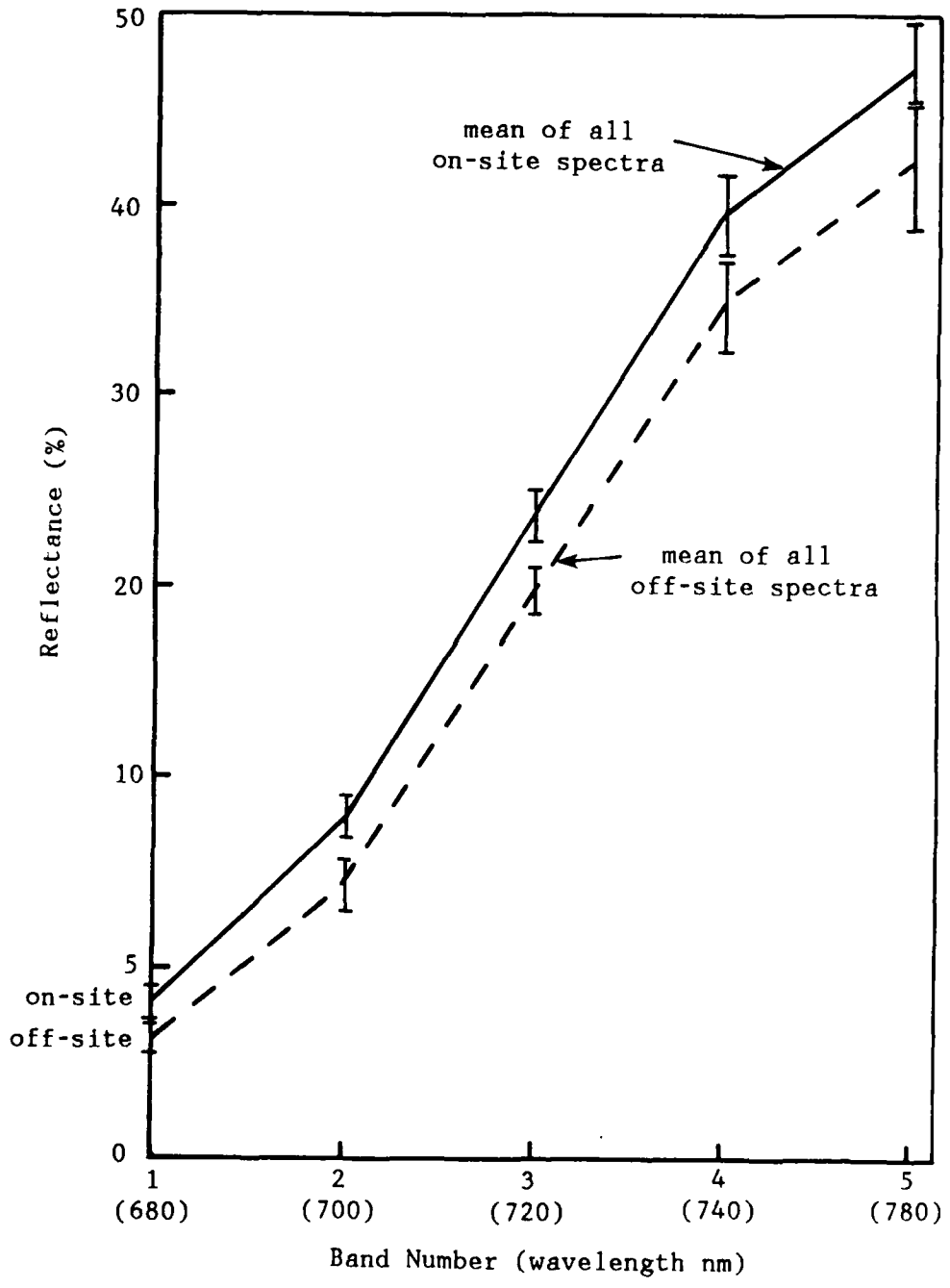


Figure 6. Reflectance spectra (10 nm bandpass) of Douglas fir growing on and off an ordnance burn site, Bangor, WA.

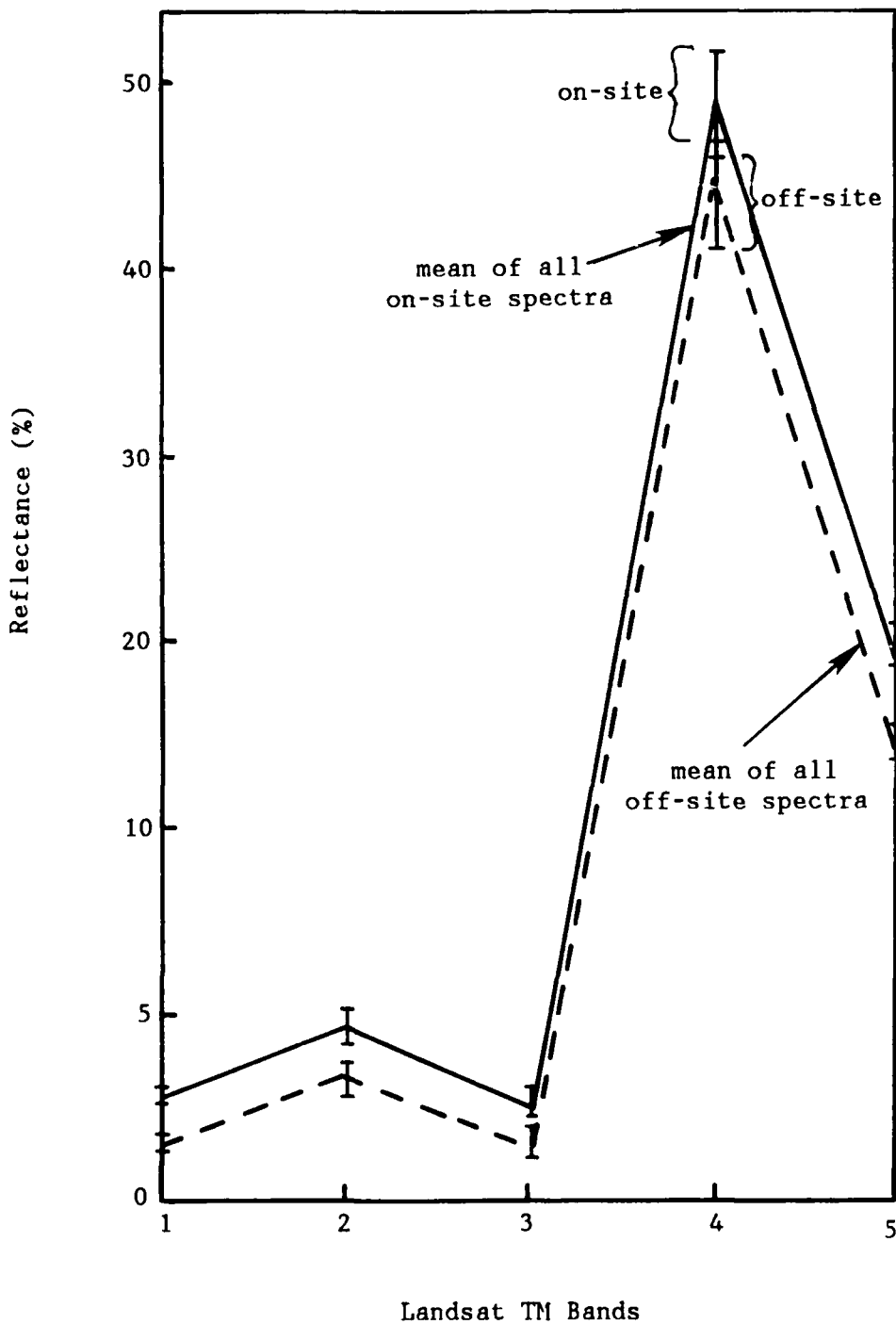


Figure 7. Landsat TM spectra of Douglas fir growing on and off an ordnance burn site, Bangor, WA.

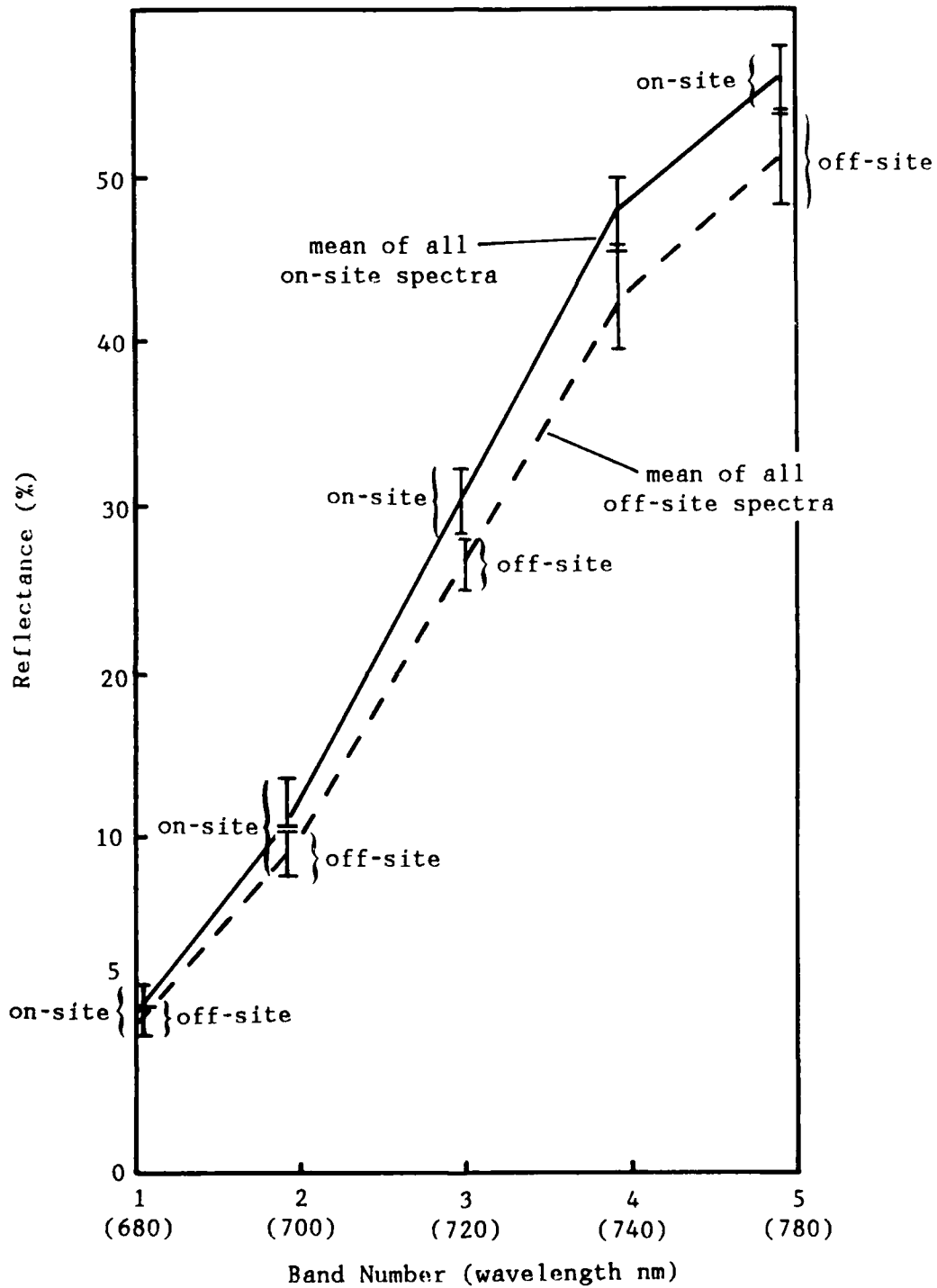


Figure 8. Reflectance spectra (10 nm bandpass) of red alder growing on and off an ordnance burn site, Bangor, WA.

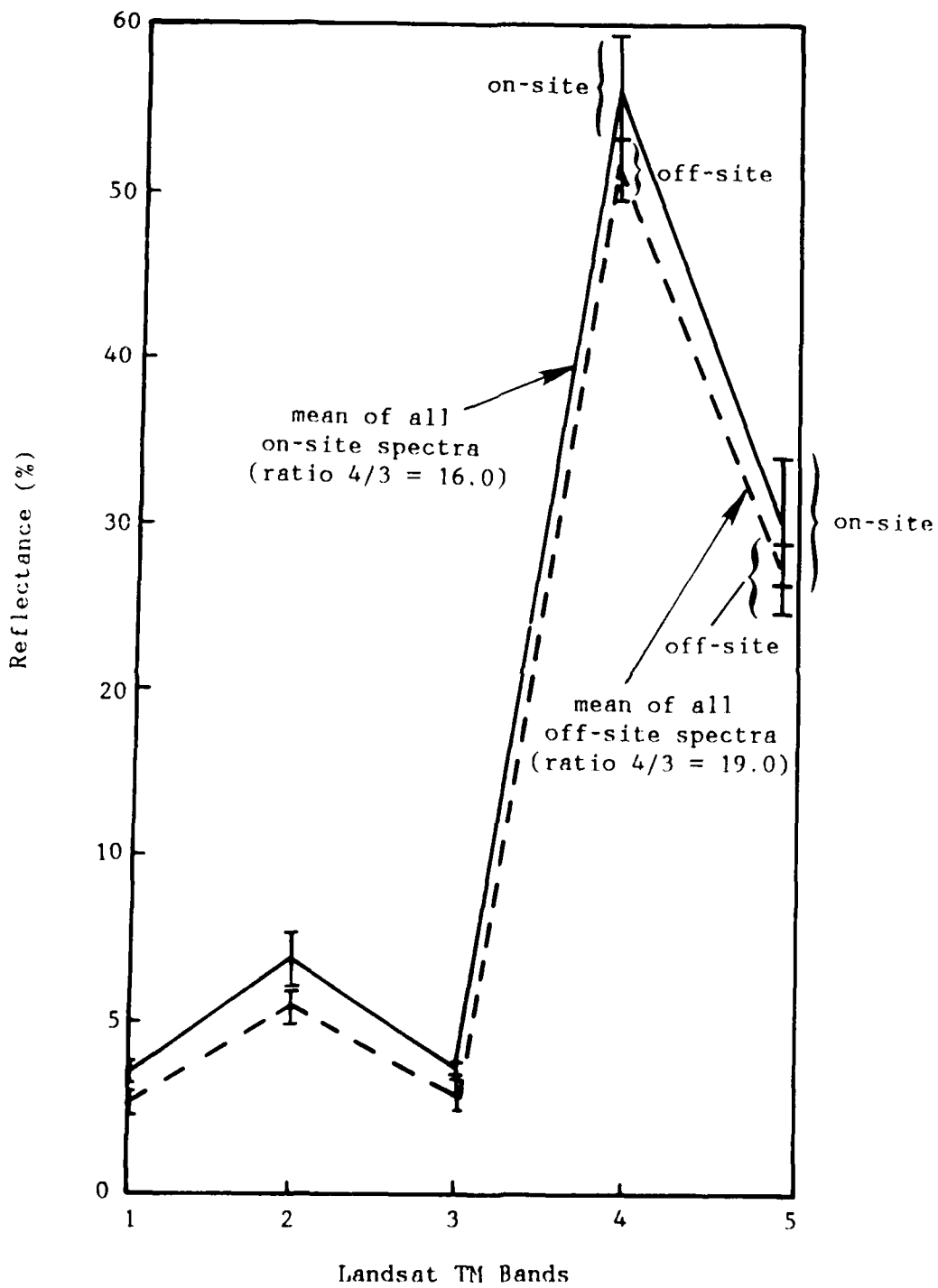


Figure 9. Landsat TM reflectance spectra of red alder growing on and off an ordnance burn site, Bangor, WA.

Appendix

REFLECTANCE SPECTRA

The reflectance spectra were derived by a Barringer Hand-Held Ratioing Radiometer. Spectra are from narrow-band filters (10 nm) located along the red edge and from the first five TM bands. Spectra are derived by dividing the target voltage response by a reflectance standard voltage response.

ORDNANCE BURN SITE

HHRR Channel (bandpass midpoint wavelength is given)

| Sample No. | 1 (680 nm) | 2 (700 nm) | 3 (720 nm) | 4 (740 nm) | 5 (780 nm) |
|------------------------|---------------|---------------|---------------|---------------|---------------|
| <u>On-Site/Species</u> | | | | | |
| D1 (Alru*) | 3.8% | 10.0% | 30.7% | 47.9% | 54.1% |
| D2 (Psme**) | 3.1% | 8.0% | 24.7% | 42.8% | 50.6% |
| D7 (Alru) | 3.7% | 7.9% | 25.7% | 46.1% | 57.4% |
| D8 (Alru) | 4.7% | 10.4% | 27.0% | 43.1% | 50.8% |
| D9 (Psme) | 4.7% | 8.7% | 23.1% | 38.3% | 45.7% |
| D10 (Alru) | 6.2% | 14.1% | 35.1% | 53.3% | 59.2% |
| D32 (Psme) | 4.4% | 10.0% | 24.9% | 42.5% | 50.1% |
| SD*** (Alru) | 1.16% | 3.16% | 4.22% | 4.28% | 3.71% |
| SD (Psme) | 0.71% | 1.06% | 2.22% | 3.98% | 4.01% |
| <u>Control Site</u> | | | | | |
| D12 (Alru) | 4.0% | 9.3% | 22.1% | 36.7% | 44.1% |
| D20 (Alru) | 5.8% | 10.4% | 29.2% | 49.8% | 59.3% |
| D21 (Alru) | 4.5% | 9.0% | 25.4% | 42.8% | 51.6% |
| D22 (Alru) | 4.6% | 10.1% | 26.4% | 42.0% | 49.3% |
| SD | 0.76% | 0.66% | 2.93% | 5.38% | 6.32% |
| D14 (Psme) | 2.2% | 6.2% | 21.6% | 39.6% | 48.5% |
| D15 (Psme) | 2.9% | 6.7% | 20.7% | 39.0% | 49.7% |
| D18 (Psme) | 4.3% | 9.3% | 21.3% | 33.2% | 39.1% |
| D19 (Psme) | 3.2% | 7.2% | 18.4% | 30.1% | 35.5% |
| SD | 0.87% | 1.36% | 1.45% | 4.60% | 6.99% |

*"Alru" is an alphameric designator for Alnus rubra or red alder.

**"Psme" is an alphameric designator for Pseudotsuga menziesii or Douglas fir.

***SD - Standard deviation.

ORDNANCE BURN SITE

TM Channel (midpoint wavelength is given)

| <u>Sample No.</u> | <u>1</u> <u>(485 nm)</u> | <u>2</u> <u>(560 nm)</u> | <u>3</u> <u>(660 nm)</u> | <u>4</u> <u>(830 nm)</u> | <u>5</u> <u>(1650 nm)</u> |
|------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|------------------------------|
| <u>On-Site/Species</u> | | | | | |
| D1 (Alru) | 3.9% | 8.7 | 3.8% | 58.4% | 38.1% |
| D7 (Alru) | 3.2% | 5.3% | 3.2% | 56.4% | 24.1% |
| D8 (Alru) | 2.9% | 5.8% | 3.2% | 47.1% | 20.6% |
| D10 (Alru) | 3.7% | 7.7% | 3.8% | 61.6% | 35.2% |
| SD | 0.46% | 1.60% | 0.35% | 6.32% | 8.46% |
| D2 (Psme) | 3.0% | 5.6% | 3.1% | 59.0% | 21.6% |
| D32 (Psme) | 3.1% | 5.6% | 2.6% | 49.5% | 15.7% |
| D9 (Psme) | 1.8% | 3.5% | 1.8% | 45.8% | 17.3% |
| SD | 0.63% | 1.30% | 0.57% | 7.39% | 2.53% |
| <u>Control Site</u> | | | | | |
| D12 (Alru) | 2.0% | 4.8% | 2.0% | 51.8% | 21.3% |
| D20 (Alru) | 4.2% | 6.6% | 3.8% | 55.8% | 29.2% |
| D21 (Alru) | 2.2% | 4.8% | 2.2% | 53.1% | 28.3% |
| D22 (Alru) | 3.0% | 5.7% | 3.1% | 51.8% | 28.7% |
| SD | 1.00% | 0.86% | 0.83% | 1.89% | 3.73% |
| D14 (Psme) | 2.3% | 4.5% | 2.4% | 52.1% | 15.7% |
| D15 (Psme) | 1.8% | 3.5% | 1.7% | 55.2% | 14.6% |
| D18 (Psme) | 1.1% | 3.0% | 1.1% | 36.2% | 11.6% |
| D19 (Psme) | 1.0% | 2.6% | 1.0% | 34.7% | 11.6% |
| SD | 0.61% | 0.82% | 0.64% | 10.6% | 2.10% |

ACID WASTE SITE

HHRR Channel (bandpass midpoint wavelength is given)

| <u>Sample No.</u> | <u>1</u> <u>(680 nm)</u> | <u>2</u> <u>(700 nm)</u> | <u>3</u> <u>(720 nm)</u> | <u>4</u> <u>(740 nm)</u> | <u>5</u> <u>(780 nm)</u> |
|------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| <u>On-Site/Species</u> | | | | | |
| 44 (Psme) | 2.7% | 10.6% | 29.2% | 42.4% | 47.6% |
| 45 (Psme) | 3.2% | 11.3% | 26.5% | 35.7% | 40.0% |
| 52 (Psme) | 4.0% | 10.1% | 28.6% | 44.4% | 50.9% |
| 53 (Psme) | 4.2% | 10.7% | 28.3% | 43.3% | 49.6% |
| 62 (Psme) | 2.8% | 11.0% | 29.7% | 42.6% | 47.0% |
| SD | 0.69% | 0.45% | 1.22% | 3.43% | 4.22% |
| <u>Control Site</u> | | | | | |
| 48 (Psme) | 1.6% | 4.3% | 16.0% | 29.9% | 36.2% |
| 59 (Psme) | 2.1% | 5.9% | 20.4% | 36.7% | 44.0% |
| 60 (Psme) | 2.6% | 5.9% | 19.5% | 34.4% | 41.2% |
| 61 (Psme) | 1.9% | 6.2% | 20.8% | 35.0% | 40.7% |
| SD | 0.42% | 0.86% | 2.19% | 2.90% | 3.22% |

ACID WASTE SITE

TM Channel (midpoint wavelength is given)

| <u>Sample No.</u> | <u>1</u> <u>(485 nm)</u> | <u>2</u> <u>(560 nm)</u> | <u>3</u> <u>(660 nm)</u> | <u>4</u> <u>(830 nm)</u> | <u>5</u> <u>(1650 nm)</u> |
|------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|------------------------------|
| <u>On-Site/Species</u> | | | | | |
| 44 (Psme) | 3.4% | 7.5% | 4.2% | 51.2% | 19.9% |
| 45 (Psme) | 3.7% | 9.0% | 5.4% | 46.0% | 21.2% |
| 52 (Psme) | 3.8% | 7.7% | 4.5% | 59.4% | 25.1% |
| 53 (Psme) | 3.5% | 6.9% | 4.0% | 48.0% | 21.4% |
| 62 (Psme) | 3.8% | 9.6% | 4.4% | 54.6% | 21.2% |
| SD | 0.18% | 1.12% | 0.54% | 5.34% | 1.96% |
| <u>Control Site</u> | | | | | |
| 48 (Psme) | 2.0% | 3.2% | 2.0% | 38.3% | 14.4% |
| 59 (Psme) | 2.2% | 4.1% | 2.4% | 46.5% | 18.7% |
| 60 (Psme) | 2.1% | 4.4% | 2.9% | 51.5% | 19.0% |
| 61 (Psme) | 2.3% | 5.2% | 2.7% | 49.9% | 21.2% |
| SD | 0.13% | 0.83% | 0.42% | 5.88% | 2.12% |

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