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Visible near-infrared diffuse reflectance spectroscopy and portable X-ray fluorescence spectroscopy for rapid compost analysis

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VISIBLE NEAR-INFRARED DIFFUSE REFLECTANCE SPECTROSCOPY AND PORTABLE X-RAY FLUORESCENCE SPECTROSCOPY FOR RAPID COMPOST ANALYSIS

A Thesis

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by
Amanda Lynne McWhirt
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ABSTRACT

Quantitative and qualitative evaluation of compost is necessary in order to provide consumers with basic knowledge about the product's composition, and to protect public health and the environment by preventing the spread of contaminated material. Current methods for analysis of basic compost properties give accurate results but are time consuming and require numerous laboratory procedures. This study evaluated the use of visible near-infrared diffuse reflectance spectroscopy (VisNIR DRS) for organic matter (OM) determination and field portable X-ray fluorescence (PXRF) spectroscopy for determination of elemental composition of composted materials. These technologies were evaluated as alternatives to standard laboratory methods for their use in rapid *in situ* analysis. Thirty-six compost samples from a wide range of feedstocks were gathered and tested with VisNIR DRS and PXRF. For VisNIR DRS, the influence of sample moisture on scanning results was evaluated and the use of raw reflectance, first-derivatives, and second-derivatives of the reflectance spectra were compared. Partial least squares regression (PLS) and principal component regression (PCR) were used to build regression models of VisNIR DRS scans and lab measured OM. For PXRF, the influences of sample moisture, particle size, inter-elemental interactions, and OM on PXRF scanning results were investigated. Results from the VisNIR DRS study produced a promising r^2 value of 0.82 and residual prediction deviation (RPD) value of 1.72 for the oven–dried first-derivative PLS model. Results indicate that VisNIR DRS shows great promise as a technique for analysis of OM content of dried compost samples, however further investigation with a larger sample set is necessary before VisNIR DRS can replace laboratory methods. Results of PXRF for elemental analysis were most promising for dried samples and for determining the elements Ca, Cr, Cu, Fe, K, Mn, P, and Zn. Arsenic detection was found to be greatly limited due to the influence of elevated Pb concentrations in the samples. Additionally, sample moisture, particle size, and

OM was found to have varying influences on PXRF scan results for different elements. Compost elemental screening and definitive quantification of certain elements via PXRF is recommended by this study.

CHAPTER 1: INTRODUCTION

Compost is an organic substance which results from the decomposition of previously living matter (e.g. grass, leaves, wood, manure, animal carcasses). Compost is often utilized as a mulch, soil amendment, or soil conditioner. Moisture, aeration, temperature, carbon to nitrogen ratio, and material inputs are all managed in order to control the speed of the decomposition, and ultimately the attributes of the final product (Martin and Gershuny 1992).

The managed aerobic decomposition process involves physical, chemical, and biological processes, including a succession of different organism's consumption and degradation of complex biodegradable material, into simpler and more stable molecular compounds (Martin and Gershuny 1992, Berg and McClaugherty 2008). Different organisms are responsible for the decomposition of different fractions of the organic matter (OM), and are classed into physical and chemical decomposers. Physical decomposers include earthworms, mites, centipedes, springtails, and beetles, while chemical decomposers are bacteria, protozoa, fungi, and actinomycetes (Martin and Gershuny 1992). The physical aspects of the original material that influence the decomposition process are particle size, temperature, and structure which directly influence aeration. The chemical aspects germane to decomposition include pH, moisture, and C:N ratio which impact biological organisms and the speed of decomposition (Rynk 1992). The resulting end product, humus, is comprised of stable organic compounds and serves as a reserve of nutrients for plants and soil organisms (Berg and McClaugherty 2008).

When the decomposition process is well regulated and inputs are carefully monitored, the resulting material is a safe and effective product that can be used to improve soil texture and structure, buffer soil pH, neutralize toxins, and add OM and plant essential elements to the soil (Martin and Gershuny 1992). The source materials used to construct compost are collectively known as feedstocks, and they influence the finished compost's elemental composition, pH, structure, and biological content. As such, the use of industrial or municipal sludges (biosolids) as feedstocks risks contributing heavy metals or biological pathogens to the end product (Rynk 1992). If these materials are not properly managed, there is the potential to spread contamination to agricultural fields or home gardens when the compost is applied. To mitigate this risk, national standards that limit contaminants and defined test methods used to evaluate the material have been established (Brinton 2000). These standards help to qualify composted products prior to sale, ensure the material's safety, and promote the marketability of the material by providing basic information about the attributes of the product (Weindorf *et al.* 2011a). This is important for consumers due to the large range of materials used in commercial composting operations and the intrinsic heterogeneity of the material (Brinton 2000).

Many countries, including the United States, have regulatory testing for basic parameters and possible contaminants in composted products before they can be sold (Brinton 2000). The current standards for compost analysis in the United States are outlined in *Test Methods for the Examination of Composting and Compost (TMECC)*, which was released in 2001 by the US Department of Agriculture (USDA) and the Composting Council Research and Education Foundation (CCREF) (USDA-USCC 2002). The document outlines the procedures to assess the chemical, physical, and biological properties of finished and in-process compost for the composting industry. It was shaped using the environmental protection agency's (EPA) *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* as a guide (USDA-USCC 2002). The EPA regulates compost application to land and its elemental contaminant limits under "Title 40: Protection of environment, Part 503.13, Standards for the use or disposal of sewage sludge,*"* (USEPA 2012). Some states have local regulations that are stricter than national standards, and may vary based on the feedstocks used and their pollutant concentrations (Rynk 1992).

The TMECC outlines methods and procedures for analyzing the physical, chemical, biological, organic, synthetic organic compounds, and pathogenic properties of compost. Some of the specific tests include screening for anthropogenic inerts, biological stability, OM content, pH, soluble salt content, water-holding capacity, bulk density, particle size, porosity, moisture content, and elemental concentration (including plant essential elements) (USDA-USCC 2002). The tests germane to this study are OM and elemental concentration. The test for OM is important as “test determinations will correspond to compost’s stability status and aid in defining the commercial value of compost relative to its organic matter content” (USDA-USCC 2002). Elemental determination of secondary and micro-nutrient content is important as “compost provides essential nutrients for plant growth,” and is vital to awareness of heavy metals concentrations which, “are potential environmental pollutants at certain concentrations and as such are of regulatory concern relative to compost feedstocks and finished compost uses” (USDA-USCC 2002).

1.1 Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

The current TMECC recommended method for determination of the elemental composition of composted products is with inductively coupled plasma atomic emission spectroscopy (ICP-AES) (USDA-USCC 2002). The basis of ICP-AES is the excitation of digested, liquefied samples at high temperatures and measurement of the resulting wavelengths of light which are characteristic of the elements present and their relative concentrations (Fassel and Kniseley 1974; Warra and Jimoh 2011). The basic science and processes of the ICP-AES is applicable to several of the instruments that follow. As such, a detailed description of the technique follows.

In order to prepare solid samples for analysis via ICP-AES digestions must be performed because solid samples can clog the nebulizer and liquid samples are thus required (Warra and

Jimoh 2011). Acid digestion is utilized to bring elements present in a sample into solution (USDA-USCC 2002). Open and closed vessel digestion methods provide different levels of detection. Open vessel techniques do not require sample milling and provide less precision, while closed vessel methods do require milling and offer better accuracy (USDA-USCC 2002). Digestion may be conducted via a variety of different reagents, usually strong acids, including H_2SO_4-HNO_3, HNO_3-$HClO_4$ or others depending on the material to be analyzed and the elements of interest (Westerman 1990; USDA-USCC 2002). Digestion with nitric acid adequately digests most samples, is commonly utilized for biosolids and composts, and it is approved for use in determining most metals regulated under USEPA CFR 40 (USDA-USCC 2002). Nitric acid digestion results in the loss of volatile elements and does not dissolve elements bound by silicate structure, and if a "total" digest is warranted hydrofluoric acid must be utilized (USEPA 1996).

Excitation of a sample is the result of its exposure to an energy source that causes the outer-shell electrons in the sample to shift to higher energy orbits around the nucleus (Westerman 1990). Once the energy source is removed, the valence electrons return to their ground state in a stepwise manner and emit wavelengths of light. Multiple wavelengths are emitted due to the incremental release of electromagnetic energy (Westerman 1990). The relationship between energy and wavelength is defined by equation 1.1:

$$E = hv = hc/\lambda \qquad \textbf{Equation 1.1}$$

Where E= energy, λ= wavelength, h= Planck's constant (6.626×10^{-34} J) v= frequency and c= velocity of the electromagnetic radiation (Sparks 1996).

The energy source for excitation in ICP-AES is plasma created by argon gas. Argon is used due to its low reactivity and low chance of creating chemical interferences during analysis (Westerman 1990). The ICP-AES instrument consists of two parts: the inductively coupled plasma torch where the sample is introduced and subjected to excitation and the atomic emission spectrometer where the wavelengths resulting from sample excitation are processed and recorded (Figure 1.1).

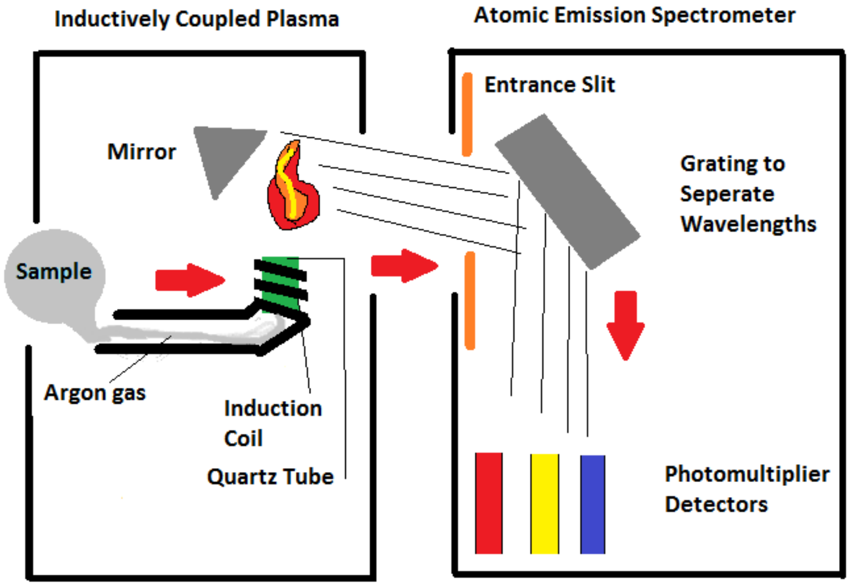

Figure 1.1 Diagram of inductively coupled plasma atomic emission spectroscopy

The plasma is generated by a quartz torch located inside of a copper coil which is connected to a radio frequency generator. The flow of electricity through the coil creates oscillating magnetic fields which vary in strength and direction over time and which create further electron and ion acceleration as they flow through the torch (Fassel and Kniseley 1974; Westerman 1990). Argon gas atoms collide with these electrons and ions, causing the gas to become ionized and form plasma. As the accelerated electrons and ions in the plasma collide they further ionize and cause ohmic heating at temperatures in the range of 6,000 to 10,000°K (Warra and Jimoh 2011). The sample is then introduced into the plasma via a stream of argon gas through a nebulizer which creates an aerosol or suspension of liquid particles in the gas (Westerman 1990; Warra and Jimoh 2011). Upon entrance into the hot plasma, thermal excitation of outer-shell electrons of the atoms occur, and upon returning to their ground states they emit photons of light at wavelengths characteristic of the elements present in the sample (Fassel and Kniseley, 1974; Westerman 1990; Warra and Jimoh 2011). A mirror in the ICP-AES reflects the resulting light through a slit in the spectrometer where the individual elemental wavelengths are separated onto detectors and are recorded along with their corresponding intensities by a computer system (Westerman 1990; Warra and Jimoh 2011). A spectrometer used for quantitative analysis functions based on the Beer- Lambert law. Changes in spectrometer response are related to changes in the concentration of the analyte material in the digested sample. Often the relationship is assumed to be linear, however this is not always the case (Workman and Springsteen 1998). The measured intensity of the energy at each wavelength is compared to a standard sample with known elemental concentrations. Each element has many characteristic lines (wavelengths) and expertise is required to select the best line for computations (Westerman 1990; Warra and Jimoh 2011).

Since the 1970's the use of ICP-AES has been wide-spread due to its capacity to analyze many elements at very low concentrations across many sample types, including saline and dilute acid samples (Westerman 1990; Warra and Jimoh 2011). There are several advantages to ICP-AES, including its ability to analyze all elements except for argon, its ability to detect trace levels of elements (1-100g/L), its low level of chemical interference, and its ability to detect many elements simultaneously (Westerman 1990). However, there are also several considerations, including the need for special facilities for handling radioactive fumes from the plasma when certain elements are determined, the lack of portability, a recurring expense for argon gas purchase, and necessity of experienced technician for interpretation of the wavelengths and for equipment maintenance (Westerman 1990; Warra and Jimoh 2011). Furthermore, the acid digest procedure is dangerous and requires the use of hydrofluoric and perchloric (HF + HClO4) or aqua-regia (HNO3 + HCl) acids which are extremely caustic (USDA-USCC 2002).

There is also the possibility of spectral interferences from a variety of sources. However, there are many techniques employed to address these challenges in modern instruments (Westerman 1990).

1.2 Loss on Ignition (LOI)

The method of OM determination outlined by the TMECC is the dry ashing procedure known as loss on ignition (LOI). The method uses a muffle furnace to induce high temperature oxidation of the OM in a sample of known weight. After ignition, a simple calculation of the remaining mineral fraction allows determination of the OM fraction which is assumed to be the material lost (Sparks 1996, Westerman 1990). The method determines only the quantity of OM present, and does not distinguish between plant and animal organic compounds from which OM is comprised (Sparks 1996). The method is used widely in soil and plant analysis, with the ignition temperature varying across discipline and application (Sparks 1996). LOI is subject to inaccuracies if the incorrect ignition temperature is used, if the temperature is too quickly increased and flaming of the material occurs, or incomplete oxidation occurs due to overloading of the furnace resulting in deficient O_2 presence for full oxidation (Westerman 1990).

1.3 Test Method Development

The standard method used for elemental determination of composts and soils has progressed from colorimetric procedures, to emission or adsorption spectroscopy and now to plasma spectroscopy which is capable of determining most elements in a sample in around 60 seconds (Westerman 1990). While this method is well established and reliable when conducted by an experienced technician, it is not portable and must be conducted in a laboratory due to the sample digestion and instrumentation required (Westerman 1990). While LOI testing requires a lesser amount of laboratory preparation, it similarly requires laboratory work as a muffle furnace for incineration of the material is required (USDA-USCC 2002). As field quantification of these properties would aid producers and testing laboratories, analytical methods that lend themselves to rapid *in situ* or field examination are sought. Field determinations of elemental concentrations of compost would most notably benefit producers who could then monitor incoming feedstocks and overall compost mixes for heavy metals and nutrient contents. Furthermore, OM content determined *in situ* would aid producers in monitoring the rate at which the material is decomposing and thereby the overall maturity of the product (Brinton 2010).

As *in situ* analysis of these qualities of compost would benefit producers or speed laboratory analysis, an investigation into the use of field-portable spectroscopy for rapid compost analysis is warranted. Portable spectroscopy is of interest due to its portability, speed, rapid replicate sampling, and capacity for non-destructive sampling (Potts and West 2008). As such the focus of this study involves the application of visible near-infrared diffuse reflectance spectroscopy (VisNIR DRS) and portable X-ray reflectance spectroscopy (PXRF) to compost for rapid, *in situ* analysis of OM and elemental composition, respectively.

1.4 Visible Near-infrared Diffuse Reflectance Spectroscopy (VisNIR DRS)

The basis of VisNIR DRS is the measurement of diffusely reflected spectra from the sample after it has been exposed to visible and near-infrared radiation (350-2500nm) (Sparks 1996; Workman and Springsteen 1998). The spectrometer is comprised of an energy source, a dispersive element, which enables the intensity at different wavelengths to be recorded and a detector (Workman and Springsteen 1998). With diffuse reflectance spectroscopy (DRS) the resulting spectrum does not produce a directly proportional relationship between wavelength intensity and analyte concentration. Corrections and statistical analysis therefore must be used to interpret the resulting data and will be discussed in a following section. The method of DRS however is ideal for application to samples of rough light-diffusing surfaces, like compost, and is not limited by optical effects occurring near to the sample surface as experienced with mid-infrared spectroscopy (Workman and Springsteen 1998). Of consideration to VisNIR DRS are the influences of sample moisture and particle size on spectral reflectance. Moisture content of samples is of particular interest as moisture interference in spectral readings has been noted in many studies (Morgan *et al*. 2009; Stevens *et al*. 2006; Van der Meer and De Jong 2000). However, it has also been shown that the influence of moisture on soil reflectance was stronger in the shortwave-infrared (SWIR) (1100–2500 nm) region than the VisNIR region (400–1100 nm) (Zhu *et al.* 2010). Other studies have indicated that air-drying of samples increases the accuracy of the prediction model as drying reduces the intensity of bands related to water signals and therefore does not mask other physicochemical properties (Waiser *et al.* 2007). The interaction between assessment of sample parameters and sample moisture in compost warrants further study. Particle size can influence VisNIR DRS's final spectra, and grinding of samples has been recommended (Workman and Springsteen 1998).

The identification of organic compounds and many signature band locations for compounds present in organic matter can be determined with VisNIR DRS (Workman and Springteen 1998). However to date, VisNIR DRS has not been widely applied to compost analysis. A few studies have shown its ability to assess microbial populations, nitrogen content, carbon content, pH, and compost salinity (Ben-Dor *et al*. 1997; Malley *et al.* 2005; Sharma *et al.* 2005). Promising results for correlation (r^2 values of 0.852) between predicted and measured values of percent ash were obtained by Sharma *et al.* and point to the promise of the technology for OM analysis. However a significant limitation of all of these studies has been the limited range of feedstocks tested, and in only investigating milled and dried samples (Ben-Dor *et al.* 1997; Malley *et al*. 2005; Sharma *et al.* 2005). All groups have indicated the need for studying a more diverse sample set. The use of VisNIR DRS has been more extensive in fields related to compost: agriculture and waste management. The technology has been shown in these fields to identify organic and inorganic soil carbon for soil characterization (Brown *et al*. 2006; Morgan *et al*. 2009), soil water (Zhu *et al.* 2010), clay mineralogy (Waiser *et al*. 2007), and to assess soil contaminants (Chakraborty *et al*. 2010; Chakraborty *et al.* 2012).

1.5 Portable X-ray Fluorescence Spectrometry (PXRF)

Portable X-ray fluorescence spectrometry (PXRF) is based on the measurement of fluorescence emitted from a sample after exposure to X-ray radiation. On the electromagnetic spectrum, X-rays are found between 0.01 to 10 nanometers (Sparks 1996). In the study, of PXRF an X-ray tube was used to generate X-rays which excite the target sample resulting in ejection of electrons from the K or L orbitals. The resulting instability forces electrons from outer orbitals, L or M, to fall down into the vacancies left in the inner K or L orbital. In doing so, secondary X-ray photons (fluorescence) are emitted and are characteristic of the atoms present in the sample (Figure 1.2) (Innov-X Systems 2010; Potts and West 2008; Westerman 1990).

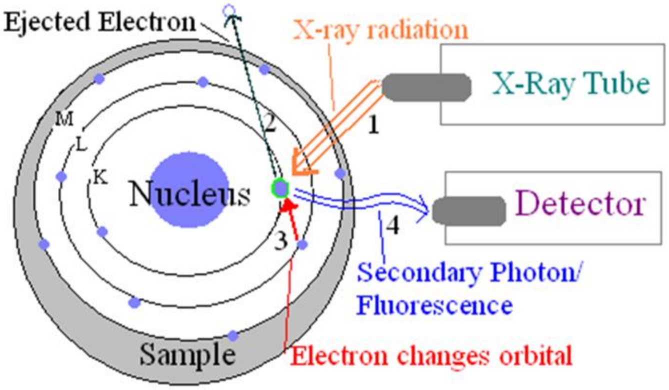

Figure 1.2 Diagram of the basis of portable X-ray fluorescence spectrometry (PXRF) with the sample's electron orbitals (K, L, M) and major processes outlined.

The element's presence is defined by its characteristic X-ray emission wavelength (λ) and the amount present is determined by measuring the intensity of the emission (Innov-X Systems 2010). Not all elements are detectable by PXRF under normal conditions as there is an attenuation, or gradual loss in intensity, of the low energy fluorescence X-rays as they pass through air. As a result, elements below Si (atomic number 14) cannot be adequately detected by PXRF (Potts and West 2008). Elements from the K-line series orbitals with adsorption edges just below the energy of the characteristic emission lines from the X-ray tube are best detected by PXRF, while elements larger than the given energy generally cannot be detected as they are not excited or detected to an adequate sensitivity (Potts and West 2008). Compton normalization calibration is often utilized to account for differences among samples matrices and the ensuing effects. The method is similar to the utilization of internal standards (Innov-X Systems 2010).

There are various factors that may influence PXRF results including particle size (related to heterogeneity of the matrix), the chemical matrix, and sample moisture (Potts and West 2008). Operational errors may result from inconsistent positioning of samples or poor instrument resolution; however these factors can be accounted for and controlled by the operator (Potts and West 2008). Sample moisture has been shown to create a dilution effect on PXRF (Argyraki *et al.* 1997). Moisture correction factors or sample drying have been implemented to account for such an influence (Innov-X Systems 2010; Weindorf *et al*. 2011b). In a previous study involving soil, particle size was not found to have a significant influence on PXRF analyzers, however this study was based on using sieved (<2 mm) samples (Kilbride *et al.* 2006). Additionally the influence of OM content on PXRF performance has been reported in soils and should be investigated considering the inherently higher OM concentrations of compost (Kilbride *et al.* 2006). The critical penetration depth of the X-ray photons is the depth below the surface beyond which 99% of the X-ray emission line of an element is absorbed and not available for detection (Potts and West 2008). Penetration depth varies for different elements; low atomic number elements have lower ranges (µm range) and higher elements have higher ranges (1-10mm) (Potts and West 2008). Absorption correction factors are available to correct for the discontinuities in the absorption properties for the analyzed materials in order to obtain an average for the scanned area (Innov-X Systems 2010; Potts and West 2008).

The use of PXRF has been applied to many materials for elemental characterization (Stallard *et al*. 1995; Lawryk *et al.* 2009; Palmer *et al*. 2009; Radu and Diamond 2009). Recent applications include identification of heavy metal concentrations in pollution monitoring for environmental assessment and soil and solid waste classification (Weindorf *et al.* 2011b; Zhu *et al.* 2011; Weindorf *et al*. 2012). The environmental protection agency (EPA) has certified a method for the use of PXRF in soil characterization as outlined in Method 6200: "Determination of Elemental Concentrations in Soil and Sediment" (USEPA 1998a). Current advances in PXRF technology have reduced the costs of the technology, improved correlations to laboratory based assessment and attained lower limits of detection (LOD) (Hettipathirana 2004; Potts and West 2008). For a given instrument, the LOD is defined as the smallest measurement that can be determined with reasonable certainty by the technique (IUPAC 1997). These improvements are due to the development of multiple beam instruments over single beam instruments and the advent of Si drift detectors that provide detection at much higher count rates, improving scanning speed and energy resolution (Innov-X Systems 2010; Potts and West 2008; Workman and Springsteen 1998).

Currently the use of PXRF in compost characterization has not been widely studied. The only investigation of note is Weindorf *et al*. (2008). The study investigated PXRF for elemental quantification in composted dairy manure using an alpha series PXRF (single X-ray beam instrument) (Innov-X Systems, Woburn, MA). An investigation of PXRF as applied to a wide range of feedstocks, the influence of moisture, particle size and OM on PXRF analysis and a consideration of advancements in the technology are detailed in chapter two of this document.

1.6 Statistical Analysis Techniques

While spectral reflectance can often be correlated linearly to elemental concentrations, in the case of VisNIR DRS there is a need for statistical analysis to interpret the resulting spectra and to build models. Multivariate regression techniques are often used for this application (Workman and Springsteen 1998). In Chapter 2, principle component regression (PCR) and partial least squares regression (PLS) are compared. The basis of PCR and PLS is not a direct regression of a single or selected group of wavelengths to known quantities of a given characteristic, but instead involves the creation of eigenvectors for regression model building. These new variables are formed via transformation of correlated response variables into a smaller group of uncorrelated response variables (Johnson 1998). The use of eigenvectors helps to account for variation between sample mixtures, inter-constituent interactions in the individual samples, instrument variation, and differences in sample variation by defining a finite number of interactions in the spectral data and by extracting underlying variables (Johnson 1998; Workman and Springsteen 1998). In theory these “variation spectra”, eigenvectors or principal components, represent all possible changes in spectra across every wavelength (Workman and Springsteen 1998). Additionally, these spectra are used with scaling constants, called scores, which help to account for different constituent concentrations of each component. The difference between PCR and PLS is in how the principal components are calculated (Workman and Springsteen 1998). The principal components are based on changes in the absorbance or reflectance data and not on the absolute value of the absorbance or reflectance. The PC’s are calculated using an algorithm that selects independent variation characteristics from each sample for removal with the motive of leaving only the changes in absorbance common to all. The components are calculated after being mean centered in order to remove changes in spectral data common to all the spectra (Workman and Springsteen 1998). Similarly PLS is calculated by decomposing the spectral matrix into PCs and then by regressing them against known concentration data to build the model, the difference being that the known concentrations of the variable of interest are taken into account when decomposing the spectra (Workman and Springsteen 1998). This allows constituents of higher concentration to be more influential than those of low concentration, when building the model. The result is two sets of vectors and two sets of scores. The benefit of combining regression and decomposition into one step is that the eigenvectors are directly related to the variable concentration. Cross-validation is necessary for model fitting for both techniques and involves using the training set data to imitate testing unknown data (Workman and Springsteen 1998). In general PLS has been shown to outperform PCR, however in certain instances PCR has been more accurate (Workman and Springsteen 1998). For this reason both PCR and PLS regression was utilized for VisNIR DRS analysis of OM in compost. The science and processes behind these calculations are briefly presented for consideration.

There are also many techniques applied to spectra prior to processing. Uniform light scatterings in reflectance measurements due to the surface of the material or the spectrometer result in a baseline shift, tilt, or curvature and have standard corrections (Workman and Springsteen 1998). Additionally, techniques like averaging replicate spectra, using a white reference Spectralon panel with 99% reflectance to compensate for drift in the spectrometer, and the application of spectral smoothing techniques for improved signal to noise ratios are often implemented prior to statistical processing (Workman and Springsteen 1998).

One technique commonly employed to handle baseline shifts is the use of derivative spectra; commonly 1st and 2nd derivatives are used (Workman and Springsteen 1998). First derivatives are simply a measure of the slope of the spectral curve at each point, and 2nd derivatives are a measure of the change in slope of the curve. These calculations are not influenced by baseline offsets or any linear tilt and thus effectively remove these influences from calculations where the derivatives are used. A significant disadvantage of using derivatives is that the resulting spectra may be difficult to interpret visually, and the identification of spectral impurities impossible (Workman and Springsteen 1998).

In the case of PXRF, spectral reflectance can be correlated linearly to elemental concentrations. For PXRF (Chapter 3), simple linear regression was used to relate PXRF determined elemental concentrations directly to ICP-AES determined elemental concentrations of compost using statistical analysis software (SAS) program (SAS Institute 2011). Simple linear regression was utilized in order to create predictor models, and to test the regression of PXRF to ICP-AES data. The program SAS includes many different procedures for data analysis with simple linear regression, including PROC REG and PROC UNIVARIATE. The basic procedure PROC REG is a general use procedure for regression, based on the method of least squares, that is capable of tests of linear hypothesis, producing collinearity diagnostics, residuals, and predicted values among other potential output statistics (Cody and Smith 2006; SAS Institute 2011). In order to obtain more descriptive statistics, PROC UNIVARIATE is used to compute the mean, standard deviation, variance, range and coefficients of variation in addition to many others (Cody and Smith 2006).

Ideally when using simple linear regression, the determined model equations will not differ significantly from values of 1.0 for slope and 0.0 for the y-intercept and if the equation varies greatly from these values it is indicative of a less accurate PXRF analyzer (USEPA 1998b). However there are also rules for model evaluation that analyze r^2 and relative standard deviation (RSD) in addition to the slope and intercept (USEPA 1998b). Other statistics can also be used to evaluate model or regression performance, including those provided by PROC UNIVARITATE (Cody and Smith 2006).

With the goal of investigating the use of portable spectrometers and their application to *in situ* conditions, two studies were conducted on a diverse range of collected compost samples. The objectives of the research were to evaluate the effectiveness of: 1) VisNIR DRS for quantifying OM in compost, and 2) PXRF for elemental quantification in compost. The following two chapters expand on methods employed, results obtained, and recommendations set forth.

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CHAPTER 2: VISIBLE NEAR-INFRARED DIFFUSE REFLECTANCE SPECTROSCOPY (VISNIR DRS) FOR RAPID MEASUREMENT OF ORGANIC MATTER IN COMPOST

2.1 Introduction

Visible near-infrared (VisNIR) diffuse reflectance (DRS) spectroscopy is a rapid, proximal sensing technology which has shown promise in a variety of agronomic and waste management applications, including quantification of multiple soil properties, waste products, and environmental hazards (Weindorf *et al.* 2011). The interests of this study lie in the technology's ability to assess the organic matter (OM) content of finished composted materials for quality control purposes. Compost is an inherently variable product hewn from a wide variety of organic source materials known as feedstocks, and world-wide serves as a means of recycling many types of organic wastes for use as soil-amendments and agricultural fertilizers. However, there are inherent risks of using certain types of waste products for feedstock material in compost production, and the potential for contamination of commercial compost is of concern (Tomati *et al.* 2002; Plaha *et al.* 2002). For this reason, in the United States and many countries across Europe, compost must be tested for basic parameters and possible contaminants before it can be sold (Brinton 2000). Standards and protocols vary across national borders, though most all have certifying agencies and requirements. The current United States standard is *Test Methods for the Examination of Composting and Compost* (TMECC) which provides the procedures and methods for compost analysis at certified labs as defined by the US Compostin[1]g Council (USDA-USCC 2002). In the United States, compost quality is regulated as a biosolid or fertilizer and regulations vary by state (Brinton 2000). These established testing methods often require extensive laboratory preparation and analysis, which can interrupt or delay the abilities of compost producers to manage their product. As such, a means to quickly test a basic and important parameter of compost, such as OM, with little or no laboratory preparation, or ideally *in situ* could enable compost producers to more efficiently measure this aspect of their product in order to ready it for sale.

The majority of current knowledge concerning spectroscopy for compost analysis has utilized near-infrared spectroscopy (NIRS), which focuses on a narrower range of the electromagnetic spectrum (800-2500 nm), than VisNIR DRS (350-2500 nm). However because the two technologies share a spectral range of interest, promising results involving NIRS are relevant to the use of VisNIR DRS for compost analysis. Near-infrared (NIR) spectroscopy has shown promising results in assessing organic matter, total organic carbon, nitrogen concentrations, physicochemical qualities (Vergnoux *et al*. 2009), nutrient metal content (Huang *et al*. 2008), and overall compost quality (Galvez-Sola *et al.* 2010). Sludges and compost-sludge mixtures have also been assessed with NIRS technology as to their carbon and nitrogen contents (Albrecht *et al*. 2008), heavy metal contents (Moral *et al.* 2007; Galvez-Sola *et al*. 2009), and humic acid contents (Polak *et al*. 2005).

Studies utilizing VisNIR DRS in the fields of agriculture or waste management have shown the technology's ability to identify organic and inorganic soil carbon for soil characterization (Brown *et al.* 2006; Morgan *et al*. 2009), clay mineralogical composition (Waiser *et al*. 2007), and in quantifying soil environmental contaminants such as hydrocarbon

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(Chakraborty *et al*. 2010). The history of the technology with compost analysis however is more limited, though studies have proven its applicability in assessing microbial population, nitrogen content, carbon content, pH, and compost salinity (Ben-Dor *et al*. 1997; Malley *et al*. 2005; Sharma *et al*. 2005). Sharma *et al*. (2005) obtained r^2 values of 0.852 for correlation between predicted and measured values for quantification of percent ash.

While these studies indicate the potential of the technology, they have been limited by various factors. Ben-Dor *et al*. (1997) focused on monitoring the material's composition and spectral changes throughout the composting process, instead of analyzing the material once it had reached a finished state. Malley *et al*. (2005) obtained useful calibration data for total C, organic C, total N, C:N, S, K, and pH and Sharma *et al*. (2005) for pH, salinity and ash percent. However, their studies were confined by studying only milled and dried samples from specific feedstocks and composting methods. Both groups noted the need for further study involving more varied sample sets and samples at variable moisture contents.

Moisture content of samples is of particular interest as moisture interference in spectral readings has been noted in many studies (Morgan *et al*. 2009; Stevens *et al*. 2006; Van der Meer and De Jong 2000). However, it has also been shown that the influence of moisture on soil reflectance was stronger in the shortwave-infrared (SWIR) (1100–2500 nm) region than the VisNIR region (400–1100 nm) (Zhu *et al*. 2010). Other studies (Waiser *et al*. 2007) have indicated that air-drying of samples increases the accuracy of the prediction model because air drying reduces the intensity of bands that are related to water so that signals associated with other physicochemical properties are not masked. The interaction between sample moisture and assessment of sample parameters in compost warrants further study.

In order to build on previous results that indicate a potential use of VisNIR DRS as a viable tool in the rapid assessment of OM in finished composted materials, the objectives of this study were to: 1) determine the capacity of VisNIR DRS to quickly and accurately quantify OM in finished composted products; 2) test un-ground samples at variable moisture contents to further assess the applicability of the technology for *in situ* analysis; and 3) to compare the accuracies of partial least squares (PLS) regression and principal component regression (PCR) in predicting OM in composts. If VisNIR DRS proves a reliable method for the quantification of OM in compost, it could replace more time consuming laboratory (loss on ignition) analysis and aid in compost product assessment.

2.2 Materials and Methods

2.2.1 Samples

Thirty six compost samples of diverse origin, feedstock, and composting method, were collected from across the United States in the spring of 2011 (Table 2.1), including one sample from Canada. Compost samples were tested according to standard TMECC (USDA-USCC 2002) laboratory procedures and later analyzed with VisNIR DRS. Diversity of sample type and composting method was ensured to test the applicability of the technology on a range of composted materials. Of the 36 samples, three were from a certified testing lab and were used to validate the accuracy of our laboratory results. Our results fell within the 95% confidence intervals set by the certified lab for most parameters. The 36 samples were divided into replicates and stored in plastic bags at 4°C upon receipt. Each replicate was tested independently and the resulting data were averaged to obtain a single data set for each parameter.

2.2.2 Standard Laboratory Testing

The TMECC standard method for loss-on-ignition (LOI) (Method 05.07-A) (USDA-USCC 2002) was used to analyze the 36 samples for organic matter percentage in a muffle furnace using a one gram sample (Fisher Scientific Isotemp Programmable Forced-Draft Muffle Furnace) (Thermo Scientific Barnstead, Dubuque IA). An Orion 2-Star pH meter (Thermo Scientific, Waltham, MA) was used to asses pH (Method 04.11-A 1:5 Slurry) (USDA-USCC

2002). Electrical conductivity (EC) was tested via the same method on a model 4063CC digital salinity bridge (Traceable Calibration Control Company, Friendswood, TX). Moisture percentage was assessed via Method 03.09-A (USDA-USCC 2002). Particle size divisions (Method 02.02-B) (USDA-USCC 2002) were determined using a sieve shaker with nested sieves (Model B Ro-Tap® Sieve Shaker) (W.S. Tyler, Pleasant Prairie, WI). Particle size, EC, pH, and moisture percentages were determined in order to evaluate the diversity of samples and thus to establish the applicability of the technology to all types of compost.

Table 2.1 Composting method, feedstock, origin, pH, OM, salinity, and moisture content data for 36 compost samples used in this study from various locations in the United States and Canada.

	Compost Method	Feedstock	Origin	pH	OM	EC	Moisture	Particle Size †
		-% (If number given)-			-%-	dS	-%-	-%-
1	Windrow	Grass, chicken litter, woodchip	LA	7.1	64.1	0.7	45.8	49.3
2	Windrow	Paper manufacturing sludge, pine sludge	LA	6.6	36.2	1.1	65.8	51.4
3	Windrow	40 paper sludge, bark woodchip	LA	7.7	30.8	0.8	48.9	68.5
4	Pile	Poultry litter	LA	8.6	71.2	21.9	29.1	65.6
5	Pile	Bagasse crop residue	LA	6.4	86.0	0.1	61.5	90.4
6	Pile	Woodchip, bark mix	LA	6.8	82.8	0.1	64.7	45.3
7	Windrow	Grass, chicken litter woodchip, cooking oil	LA	7.3	51.1	2.1	44.4	67.2
8	Windrow	Bark, stall sludge	LA	12.3	22.8	7.7	44.6	89.1
9	Windrow	Leaf, woodchip, glycerin, chicken litter,	LA	7.8	54.0	2.2	42.4	73.1
10	Unknown	Unknown	Pacific Northwest	6.7	81.7	1.9	75.7	51.8
11	Unknown	Unknown	VA	6.9	54.5	4.1	46.0	62.9
12	Unknown	95 Green waste, 4 bio solids, 1 wood	CA	7.8	45.2	3.0	40.11	85.1

13	Unknown	Unknown	CA	8.2	53.6	3.7	44.4	84.3
14	Unknown	Unknown	CA	8.0	51.3	2.2	49.8	79.9
15	Unknown	Grape pumice	CA	5.8	36.1	8.8	41.2	99.7
16	Unknown	Unknown	CA	7.0	27.7	5.7	24.5	87.5
17	Unknown	Spent mushroom compost	CA	8.1	55.1	8.9	59.0	57.8
18	Unknown	Unknown	CA	7.6	61.3	1.9	31.8	85.6
19	Aerated static pile	40 Biosolids, 60 Hulls	Southern USA	5.6	65.4	3.8	38.6	75.8
20	Windrow	Green Wastes / Food waste	CA	7.8	55.8	3.6	47.9	88.8
21	Windrow	100 Yard waste	Pacific Northwest	7.8	60.7	4.2	43.9	84.8

Table 2.1 continued

22	Unknown	Unknown	Pacific Northwest	7.4	58.6	2.2	55.0	59.5
23	Unknown	Unknown	Pacific Northwest	7.4	42.1	2.2	35.5	81.8
24	Unknown	Unknown	CA	8.4	32.0	5.1	19.9	88.7
25	None	Sawdust	LA	4.9	96.6	0.4	8.7	100.0
26	Unknown	Cow manure	FL	7.8	24.8	0.5	38.7	89.6
27	Unknown	Spent mushroom	FL	7.4	58.8	3.9	58.1	84.9
28	Unknown	Certified Compost	CO	9.0	22.3	5.1	29.3	87.3
29	Unknown	Certified Compost	Canada	7.8	35.2	0.2	54.1	23.3
30	Unknown	Certified Compost	CO	8.7	42.4	4.0	35.3	90.3
31	Pile	Dairy cow manure (grass fed)	TX	9.2	37.2	5.8	17.9	91.4
32	Pile	Turkey manure and bedding	TX	6.9	35.8	5.0	31.5	88.2
33	Pile	Mix:5 composts, granite, humate	TX	8.4	42.8	2.6	32.2	86.9
34	Unknown	Cattle manure, cotton burr	TX	8.4	57.6	6.4	59.5	63.8

† Percent passing <5mm sieve size

Compost OM was calculated using Equation 2.1:

$$OM = (OM = (1 - AshW \div dw) \times 100$$

Equation 2.1

Where, OM is LOI organic matter in percent, AshW is sample net weight (g) after ignition at 550°C, and dw is sample net weight (g) after drying according to Method 03.09-A before ignition (USDA-USCC 2002). The analysis was run twice to obtain an average for each sample.

2.2.3 VisNIR Scanning

In the laboratory, the 36 compost samples were scanned using a field portable AgriSpec VisNIR spectroradiometer (Analytical Spectral Devices (ASD), CO, USA) with a spectral range of 350 to 2500 nm (ultraviolet/VisNIR [350–965 nm], short-wave infrared 1 [966–1755 nm], and short-wave infrared 2 [1756–2500 nm]) as given by ASD. The spectroradiometer had a 2-nm sampling interval and a spectral resolution of 3- and 10-nm wavelengths from 350 to1000 nm and 1000 to 2500 nm, respectively. Before scanning, each sample was equally divided into two parts (weight basis). The first part was left intact to preserve the moist condition (as received) while the second part was oven dried at 70°C for 24 hours **(**Method 5.07-A) **(**USDA-USCC 2002)**.** Both moist and oven-dried samples were allowed to assume room temperature and then were scanned with a contact probe, having a 2-cm-diameter circular viewing area and built-in halogen light source (Analytical Spectral Devices, CO, USA). The contact probe was inserted into the plastic bag that held the sample and full contact with the sample was ensured to avoid outside interference. Each sample was scanned three times with a 90° rotation between successive scans to obtain an average spectral curve. A spectralon panel with 99% reflectance served as the standard white reference material, and was scanned every five samples to compensate for drift in spectrometer and source.

2.2.4 Pre-treatment of Spectral Data

For this study, derivative spectroscopy was used to preprocess compost spectra prior to analysis. Derivative spectra have the capability to improve the quantification accuracy by removing the baseline shift arising from detector inconsistencies, albedo, and sample handling

(Demetriades-Shah *et al*. 1990). Raw reflectance spectra were processed via a statistical analysis software package, R version 2.11.0 (R Development Core Team, 2008) using custom ‘R’ routines (Brown *et al*. 2006). These routines involved (i) a parabolic splice to correct for “gaps” between detectors, (ii) averaging replicate spectra, (iii) fitting a weighted (inverse measurement variance) smoothing spline to each spectra with direct extraction of smoothed reflectance, (iv) first derivatives at 10-nm intervals, and subsequently, (v) second derivatives at 10-nm intervals. The zero, first, and second order derivative spectra were calculated using spectra expressed as reflectance, R, as a function of wavelength, λ, using equations 2.2-2.4:

Zero order, $R=f(\lambda)$ **Equation 2.2**

First order, $dR/d\lambda= f'(\lambda)$ **Equation 2.3**

Second order, $d^2R/d\lambda^2=f''(\lambda)$ **Equation 2.4**

The resulting 10-nm average reflectance, first-derivative, and second-derivative spectra were extracted and individually combined with the laboratory measured OM. These processed data were used to build partial least squares (PLS) regression and principal component regression (PCR) prediction models. Reflectance data was chosen over absorbance spectra due to the advantages of the former for analyzing dark samples, and avoiding the over-expression of weak features.

2.2.5 Multivariate Modeling

Both PLS and PCR models were employed to help in predicting OM using the 10 nm average reflectance, first-derivative, and second-derivative spectra of the 36 samples. Quantitative PLS modeling is a powerful multivariate statistical tool that has been successfully applied to VisNIR data (Waiser *et al*. 2007; Morgan *et al.* 2009; Vasques *et al*. 2009; Chakraborty *et al*. 2010). The full spectrum multivariate tool PLS combines the signal averaging advantages of principal component analysis and classical least squares (Haaland and Thomas

1988). In the present study, to detect the effect of moisture on VisNIR DRS prediction of OM in compost, a total of 12 models (six models each for PLS and PCR) were made using Unscrambler 9.0 (CAMO Software, Woodbridge, NJ). The whole dataset (36 samples) was used for training with leave-one-out-cross-validation and in selecting PLS latent factors. Models with as many as nine factors were considered, and the optimal model was determined by selecting the number of latent factors with the first local minimum in root mean squared error of cross-validation (RMSEcv). The coefficient of determination (r^2), and ratio of standard deviation to root mean square error (RMSE) were used as measures in evaluating the quality of models in real-world situations. The significant wavelengths in the first-derivative PLS model for both moist and oven-dry pretreatments were plotted to identify what portions of the spectra were important for organic matter predictions. The significant wavelengths ($p<0.05$) were selected by 'R' based on Tukey's jackknife variance estimate.

Principal component regression provides a means of addressing ill-conditioned matrices. Instead of regressing with the reflectance, first-derivatives, and second-derivative on the response variable (OM) directly, the principal components (PCs) for each spectra of the whole dataset (36 samples) were used. Choosing the optimum number of PCs was based on leave-one-out-cross-validation. Since the principal scores for each spectra are orthogonal; the PCR is just a sum of univariate regressions and is used to address the problem of multicollinearity.

2.3. Results and Discussion

Thirty six compost samples were first analyzed and subsequently PLS and PCR prediction models were created. The OM contents were widely and normally (Shapiro-Wilk test statistic: 0.93 at $p=0.05$) distributed from 22.3 to 96.6% which reflect different feedstocks, composting methods, and origins. Among other measured properties, compost pH varied from 4.8 to 12.3 (Table 2.1). The highest salinity (21.9 dS m^{-1}) (sample 4) was identified in a sample where poultry litter was the main feedstock. Considerable variability was also observed for moisture content (8.7 to 75.7 %). Particle sizes also demonstrated considerable variability with percent of a sample that passed a 5mm sieve ranging from 45.3 to 100.0 (Table 2.1). While OM was better correlated to pH (correlation coefficient, ρ=0.48) than moisture % (ρ=0.21), no correlation was found between OM and EC (ρ=0.06). No correlation between particle size and scanning results was investigated as the study was focused on general applicability of the technology to a wide range of samples and not on a comparison of milled versus un-milled samples.

An average of the reflectance spectra, first-derivative, and second-derivative with respect to the reflectance for all pre-treatments is shown in Figure 2.1. Though fundamental vibration of organic molecules can be found in the mid-infrared region, their overtones and combination bands due to the stretching and bending of N-H, C-H, and C-O groups mostly occurred in the VisNIR region. In the reflectance, first-derivative, and second derivative plots the specific spectral signals for water (1400 and 1900 nm) were quite apparent. Any significant difference in overall reflectance (except 550-1050 nm and 1350-1550 nm) and first-derivative reflectance between moist and oven-dried compost could not be recognized. Perhaps the oven drying of compost samples was responsible for increasing the averaged reflectance at ~1400 nm which corresponds to water absorption.

Accuracy and stability of both PLS and PCR models were evaluated according to the RPD-based guidelines by Chang *et al*. (2001). For spectroscopic modeling, a satisfactory prediction model is characterized by a RPD of >2.0 with r^2 of ~0.80-1.00, fair models with potential for prediction improvement consist of RPD values from 1.4-2.0, while erratic models have RPD values of <1.40. It must be noted that for ideal application of these RPD values an independent validation is recommended. However, with leave-one-out cross validation these values are still suitable indicators for describing the potential of the technology, especially when considered with r^2 and additional error statistics like RMSEcv and bias (Table 2.2). For moist sample scans, the first-derivative PLS model performed slightly better (r^2=0.82) than reflectance (r^2=0.75) and second derivative (r^2=0.77) models (Table 2.2) (Figure 2.2). Despite continuous reduction of PLS latent factors (rotation of principal components for a different optimization criterion) between the reflectance, first-derivative and second-derivative based models (Table 2.2), RPD values were less than 1.40 for all three cases. Oven-dried model results were promising as the use of first-derivative reflectance spectra outperformed reflectance and the second-derivative based model in terms of r^2 (0.82), RMSE (10.1%), and RPD (1.72).

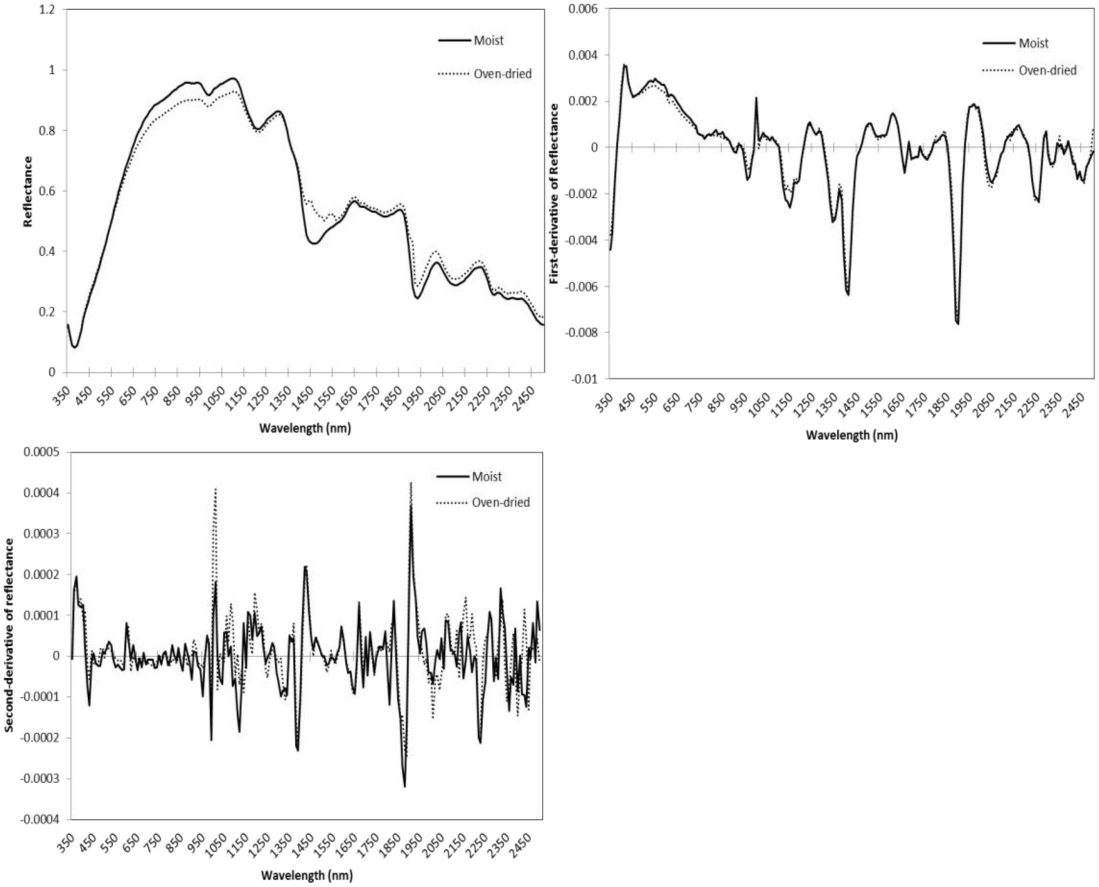


Figure 2.1 Averages of a) reflectance, b) first-derivative, and c) second-derivative with respect to reflectance for moist and oven-dried compost samples analyzed with VisNIR spectroscopy**.**

The trend of improvement of first-derivative models is consistent with other works using VisNIR, which also reported similar improvements (Reeves *et al*. 1999; Reeves and McCarty 2001; Brown *et al*. 2006; Chakraborty *et al*. 2010). Notably, in moist models a reduction of PLS latent factors was observed with increasing degree of higher derivative spectra as was apparent in oven-dried models. It is possible that the use of a higher degree of spectrally processed data helped to reduce the latent factors by removing viewing-geometry effects as reported by Demetriades-Shah *et al*. (1990). According to the law of parsimony, in chemometric analysis, it is logical to choose a simpler model (smaller latent factors) assuming no substantial decrease in predictive performance. Plots of actual versus PLS predicted OM and fitted regression coefficient curves on the spectrum are presented in Figure 2.2.

Table 2.2 Partial least squares and principal component regression results of 36 compost samples from across the USA evaluated for organic matter using visible near-infrared diffuse reflectance spectroscopy.

	Partial Least Squares Regression					Principal Component Regression				
	Latent factors	r^2	RMSEcv † (%)	RPD ‡	Bias (10^{-15}%)	Principal components	r^2	RMSEcv† (%)	RPD ‡	Bias (10^{-16}%)
			Moist					Moist		
Reflectance	7	0.75	14.1	1.29	1.9	8	0.74	25.5	0.71	2.2
1st-derivative	6	0.82	14.4	1.26	1.0	8	0.74	25.7	0.71	2.86
2nd-derivative	4	0.77	13.7	1.33	1.7	6	0.58	18.7	0.98	2.93
			Oven-dried					Oven-dried		
Reflectance	5	0.71	12.3	1.48	8.0	7	0.66	14.3	1.27	3.4
1st-derivative	4	0.82	10.1	1.72	-2.2	4	0.69	11.2	1.62	6.8
2nd-derivative	2	0.74	12.0	1.49	3.7	1	0.42	22.5	0.81	4.5

†RMSEcv: root mean square error of cross-validation

‡RPD: residual prediction deviation

In the oven-dried first-derivative model, predictions of OM more closely approximated the 1:1 line and had negligible bias (-2.2×10^{-15}%) (Table 2.2). The fair RPD (1.72) indicated that there is sufficient possibility for model enhancement. We believe that although the RPD was not as high as obtained for other constituents of soils (Malley 1998), the results are encouraging considering the complex and variable composition of compost.

For PCR, plots of actual versus predicted OM in compost samples and fitted regression coefficient curve on the spectrum are presented in Figure 2.3. Model statistics for the PCR models, summarized in Table 2.2, showed higher RMSEcv compared to PLS models. Moreover, in most cases PCR exhibited lower factors than PLS which were also reported by Yeniay and Goktas (2002). Ignoring the variability of OM content while calculating the PCs may have some effects on decreasing predictability of PCR as compared to PLS (Martens and Naes 1989). However, in terms of r^2 (0.69), RMSEcv (11.2%), and RPD (1.62) the first-derivative of the oven-dried model somewhat confirmed the PLS trend. Hence considering both PLS and PCR model statistics, the first-derivative oven-dried model seemed to perform most satisfactorily.

To investigate the rationale of the oven-dried first-derivative model's better performance over the moist first-derivative model, the significant regression coefficients (based on Tukey's jackknife variance estimate, $p < 0.05$) of the first derivative PLS model from each pretreatment were plotted in Figure 2.4. Markedly, both the number and intensity of significant wavelengths changed from moist to oven-dried models. We found more significant wavelengths for dried samples, which is the opposite of findings by Sakirkin *et al*. (2010, 2011) for manure. The change in numbers and intensities were apparent, specifically in the ~300-700, 1700, 1930, 2000-2100, 2200, and 2400 nm regions which could contain the spectral signatures of minerals (electronic transitions), alkyl asymmetric-symmetric doublets, carboxylic acids, amides, aliphatics, and carbohydrates; respectively as previously defined by Viscarra Rossel and Behrens

(2010). This masking effect from water was somewhat expected, and indeed has been well documented in soils. Stevens *et al*. (2006) noted an increase of 0.93 g organic C kg^{-1} of soil in the standard error of prediction between field moist and dry sample states when analyzing organic soil C. Van der Meer and De Jong (2000) recognized the problem of quantifying organic soil carbon with VisNIR due to the difficulty of isolating the reflectance of organic carbon from reflectance from water in a sample, as they share some significant wavelengths and due to their effect on reflectance.

Additionally, it has been observed that energy absorption by the water present in the sample can decrease the reflectance across the NIR range, and that at high moisture levels the position of maximum reflectance may shift to shorter wavelengths (Bishop *et al*. 1994). Harris (1996) noted that the polarity of the water molecule can affect the re-distribution of electrons during excitations, due to alterations in energy differences between the ground and excited states of the molecules which affects the wavelength of the sample’s absorbance or fluorescence. While a decrease in predictability in terms of RPD and RMSEcv was noted for the moist-first-derivative PLS model as compared to the oven-dried first-derivative PLS model, in terms of r^2 they did not perform significantly differently. Thus, while dry samples do permit a higher degree of accuracy, the convenience of using as received (moist) samples may, depending on the application, outweigh the slight loss in accuracy. Considering the heterogeneous nature and volatility of OM in composts combined with the difficulty of replicating a given calculation, most especially for OM, our results show promise for the use of VisNIR DRS for the quantification of OM in composts. While our results indicate drying of samples may still be required, the method of VisNIR DRS would still require less sample handling, and thus less chance of sample distortion than current standard methods like loss on ignition.

Fig 2.2 Predicted vs. measured organic matter (%). For a) moist reflectance, b) moist first-derivative, c) moist second-derivative, d) oven-dried reflectance, e) oven-dried first-derivative, and f) oven-dried second-derivative partial least squares regression models for 36 compost samples. The solid line is the regression line, and the dashed line is a 1:1 line.

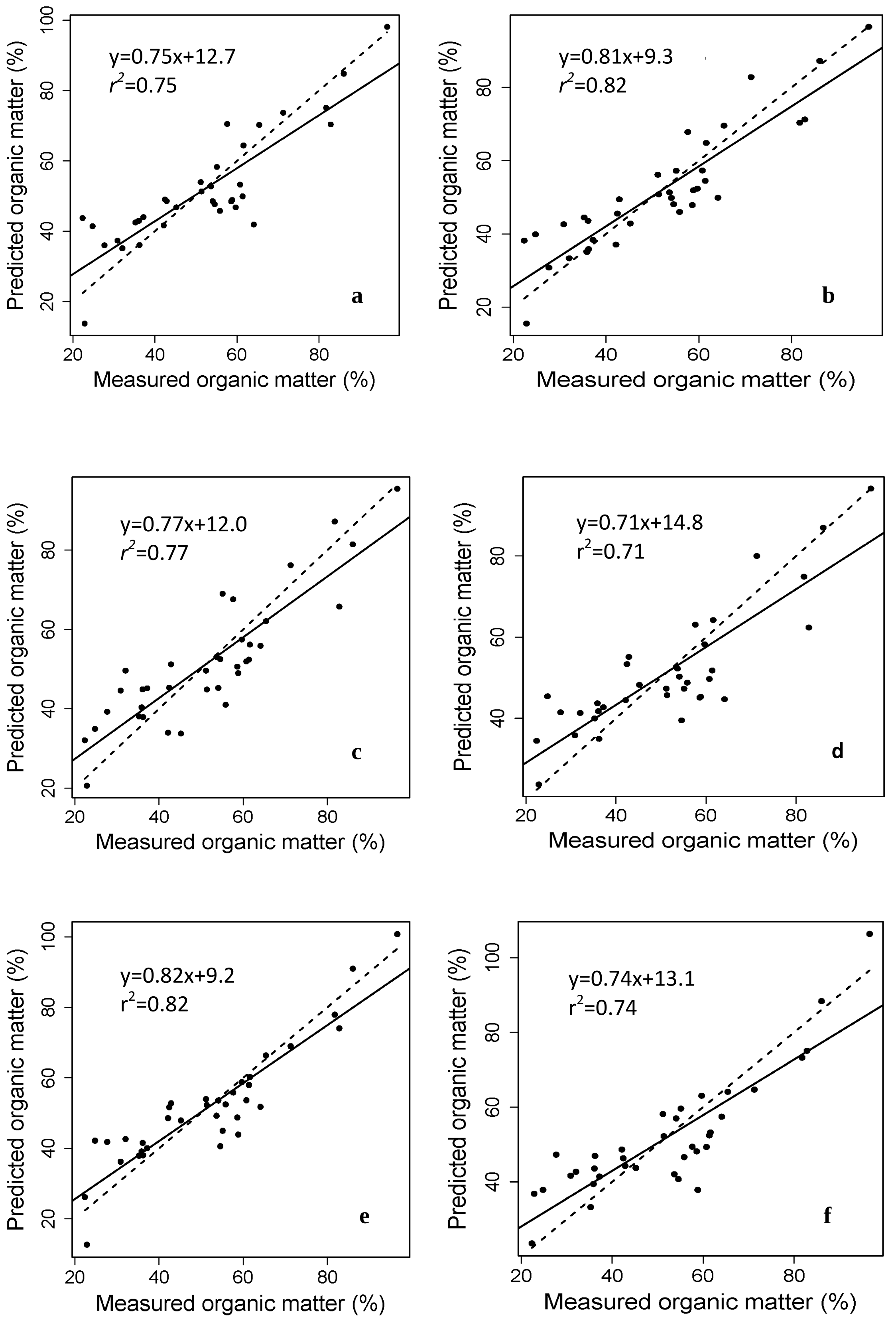
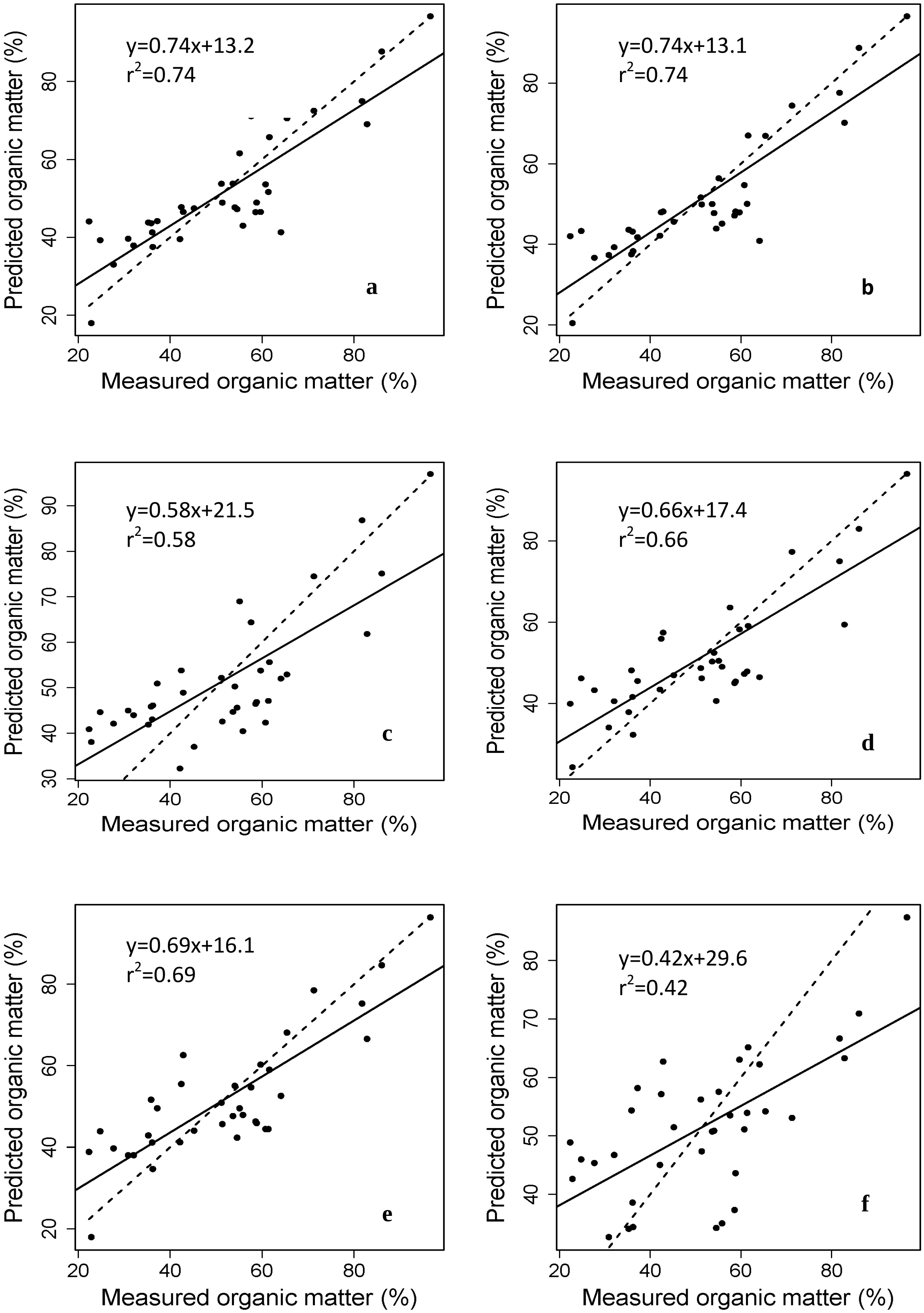

y=0.75x+12.7
r^2=0.75
a
y=0.81x+9.3
r^2=0.82
b
y=0.77x+12.0
r^2=0.77
c
y=0.71x+14.8
r^2=0.71
d
y=0.82x+9.2
r^2=0.82
e
y=0.74x+13.1
r^2=0.74
f
Predicted organic matter (%)
Measured organic matter (%)
20
40
60
80
100

Fig 2.3 Predicted vs. measured organic matter (%) for a) moist reflectance, b) moist first-derivative, c) moist second-derivative, d) oven-dried reflectance, e) oven-dried first-derivative, and f) oven-dried second-derivative principal component regression models for 36 compost samples. The solid line is the regression line, and the dashed line is a 1:1 line.


y=0.74x+13.2
r²=0.74
a
y=0.74x+13.1
r²=0.74
b
y=0.58x+21.5
r²=0.58
c
y=0.66x+17.4
r²=0.66
d
y=0.69x+16.1
r²=0.69
e
y=0.42x+29.6
r²=0.42
f
Predicted organic matter (%)
Measured organic matter (%)
20
40
60
80
30
50
70
90

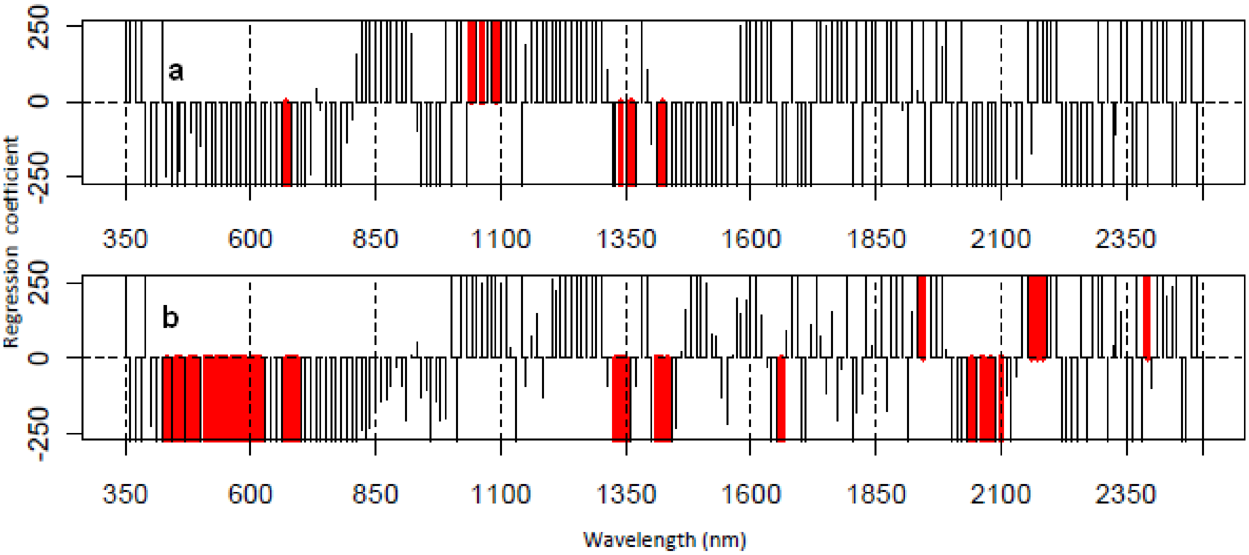


Figure 2.4 Regression coefficients (black) of the first-derivative partial least squares model of a) moist first-derivative and b) oven-dried first-derivative model of compost samples. The magnitude of the regression coefficient at each wavelength is proportional to the height of the bar. Significant wavebands ($p < 0.05$) as indicated by Tukey's jackknife variance estimate procedure are shown as thick, red bars. All plots are on the same x axis.

It has been noted that drying or other pre-treatments to samples to ready them for carbon analyses can result in "loss of volatile organic compounds or the decomposition and loss of other organic compounds present in the sample," (Schumacher 2002). Indeed, LOI while the least caustic method for organic carbon analysis, is also often considered the least accurate method of total organic carbon determination. In soils, studies done by the US Environmental Protection Agency (EPA) indicate the percent coefficient of variation for LOI among replicate samples ranged from 2.7% to 5.6% (Schumacher 2002). The borrowing of analytical methods from soils for analysis of compost and manures is common, and the same principles apply to either material (Karam 1993; Matthiessen 2005; Schumacher 2002). In our experiment, OM results from LOI fluctuated on average 8.1% among replicated samples. Thus, the advantages of VisNIR DRS for OM analysis are threefold; 1) speed of analysis and instantaneous obtainment of results, 2) less sample handling required as samples need not be weighed or further subjected to heat after initial drying, and 3) most importantly, the ability to take replicate scans and obtain an average for the sample. Thus VisNIR DRS shows promise as an addition to the TMECC certified methods for compost analysis.

The authors acknowledge that the limited number of samples (36) somewhat constrain the global applicability of the dataset. However, this pilot research was intended to investigate the viability of VisNIR DRS spectroscopy to quantify compost OM content under varying sample moisture states and to further ascertain which spectral processing and moisture contents show the most promise for future investigations. Testing the chemical heterogeneity of the compost was beyond the scope of this project and requires intensive studies before drawing stronger conclusions. More improvement could be achieved by increasing sample number and building a spectral library targeting an even wider range of compost samples. That notwithstanding, these results are especially encouraging given the wide and dynamic range of organic matter levels and other variables in the samples tested.

2.4 Conclusions

VisNIR DRS has shown the capacity to rapidly, reasonably and non-destructively quantify the OM of composted materials. Given the field portability of the VisNIR spectroradiometer, and our findings concerning the technology's accuracy with moist samples, further testing is warranted concerning the possibilities of its use *in situ*. When comparing PLS and PCR model statistics, first-derivative oven-dried models performed most satisfactorily for both model types, with PLS performing the best. Our results show promise for improving the speed of performing laboratory analysis and obtaining results almost instantly. We thus recommend the VisNIR DRS method, using dried samples, for further investigation concerning its possible inclusion among TMECC official testing methods and as a supplement to current time consuming laboratory methods. The goal for future research should be to develop a general model which can lead to reliable OM predictions under even more divergent compost matrix conditions.

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CHAPTER 3: RAPID ANALYSIS OF ELEMENTAL CONCENTRATIONS IN COMPOST VIA PORTABLE X-RAY FLUORESCENCE SPECTROMETRY

3.1 Introduction

Compost is a variable group of organic soil amendments used to enhance soil fertility. Effective sale and marketing of the material is dependent upon accurate characterization of the material's physicochemical properties (Weindorf *et al.* 2011a). To ensure that compost is safe for use, it must be tested for biological pathogens, heavy metals, salts, and other deleterious properties in order to certify the material for sale. One of the most time consuming analyses concerns elemental and heavy metal characterization via inductively coupled plasma atomic emission spectroscopy (ICP-AES). The analysis requires caustic acid digestion, expensive instrumentation, and an experienced technician. Even under optimal lab conditions, the acid digest procedure is dangerous and requires the use of hydrofluoric and perchloric ($HF + HClO_4$) or aqua-regia ($HNO_3 + HCl$) acids (USDA-USCC 2002). A method for rapid elemental analysis of composted products would speed laboratory analysis, remove the need for toxic and dangerous digests, and offer opportunities for *in situ* analysis.

Portable X-ray fluorescence spectrometry (PXRF) has a long history of use in characterizing the elemental composition of many types of materials (Stallard *et al.* 1995; Lawryk *et al.* 2009; Palmer *et al.* 2009; Radu and Diamond 2009). Current applications of the technique include environmental assessment and identification of heavy metal concentrations for pollution monitoring and characterization of soils or solid wastes (Weindorf *et al.* 2011b; Zhu *et al.* 2011; Weindorf *et al.* 2012). The US Environmental Protection Agency (EPA) has outlined the use of PXRF for soil characterization in Method 6200: "Determination of Elemental Concentrations in Soil and Sediment" (USEPA 1998a).

However, little research has been done using the technology to characterize compost. Weindorf *et al.* (2008) is the only investigation of note and focused on using PXRF for elemental identification of a single compost feedstock of composted dairy manure. The study compared elemental determination of compost via ICP-AES with that of PXRF. The correlation of elemental concentrations via the two methods produced noteworthy r^2 values for Cu (0.95), As (0.84), and Zn (0.81), and less substantial values for Mn (0.67), Fe (0.67), Ca (0.51) and poor values for K (0.14) using an Alpha Series (Innov-X, Woburn, Massachusetts) handheld XRF. Scanning took 5 minutes, and the study concluded that PXRF technology showed promise as an evaluation tool for Ni, Cu, Zn, Se, Mo, and Pb. However, the instrument used was not sensitive enough for evaluation of As and Cd due to inadequate limits of detection (LOD)(Weindorf *et al*. 2008). While this study is significant, recent advances in PXRF technology and further study with samples from a wide range of feedstocks warrant additional investigation.

The potential of PXRF to replace traditional laboratory analysis shows great promise given its speed, portability, cost, and requirements for little or no sample preparation. Recent technological advances have made PXRF less expensive, applicable for use *in situ*, and have greatly improved LOD (Hettipathirana 2004; Potts and West 2008). *In situ* analysis would benefit compost producers who import raw compost feedstock from municipal, industrial, or sludge materials where close monitoring is required to ensure compost is devoid of heavy metals in the finished product. In fact, the only obvious limitation of the technology is its uneven detection limits for certain elements (Kalnicky and Singhvi 2001; Migliori *et al*. 2011). Traditionally, PXRF has been shown to best identify elements of atomic weight greater than 19 (K), with lighter elements below atomic weight 14 (Si) being nearly non-detectable (Innov-X Systems 2010c; Miglirori *et al*. 2011). LODs also vary along similar trends; P, S, and Cl, have LODs in the 100's of mg km^{-1}, while K and Ca have LODs of ~20-40 mg km^{-1}, and heavier elements like Fe, Cu, and Zn have LODs as low as 3 mg km^{-1} (Innov-X Systems 2010b). Potential sources of error in using PXRF include heterogeneity in the sample matrix (influenced by particle size), moisture, inconsistent positioning of samples, instrument resolution, and chemical matrix effects (Potts and West 2008). However, many of these can be accounted for and controlled by the operator. Sample moisture has been shown to create a dilution effect on PXRF scans, yet this can often be offset with moisture correction coefficients, or has been described as a non-significant effect (Innov-X Systems 2010a; Weindorf *et al*. 2011b). Further investigation into the influence of moisture and particle size are warranted as they are physical properties that can be manipulated by the operator, and organic matter deserves further review as to its possible influence on PXRF analysis of compost (Argyraki *et al.* 1997).

With regard to compost, there are 14 elements commonly of interest that are quantified by both ICP-AES and PXRF. The elements As, Cd, Cu, Ni, Pb and Zn are of interest because of limits set for their concentrations by the EPA for sewage sludge (USEPA 2012). Information for Cr was also reported though it is no longer regulated by the EPA for sewage sludge (USEPA 2012).The remaining elements of interest in this study were P, Mn, K, Fe, and Ca; all of which are essential plant nutrients and influence crop production when compost is applied as a soil amendment. Additionally, Mo, Se, and Hg are of interest as they are regulated by the EPA however values were not determinable by ICP-AES in this study due to the reference solution used for ICP-AES standardization and potential interferences their inclusion in the standard may have caused.

Recent advances in PXRF technology include multiple beam devices which offer improvements over single beam machines, and Si drift detectors that provide increased sensitivity, speed and much improved LODs (Innov-X Systems. 2010a). As a result the objective of this study is to build upon previous research concerning PXRF and compost analysis as a potential alternative method of compost elemental analysis. Specifically the objectives of this study were to: 1) investigate the advancements in PXRF technology on elemental quantification sensitivity utilizing a wide range of compost types and feedstocks; 2) relate our findings to EPA mandated limits for regulated metals and quantify plant essential elements; and 3) investigate the influence of moisture, particle size and organic matter on relationships between PXRF and ICP-AES reported elemental concentrations. If PXRF proves a reliable method for the quantification of important elemental species in composted products, it could replace more time consuming and caustic laboratory analyses, thereby aiding producers by facilitating *in situ* compost characterization.

3.2 Materials and Methods

3.2.1 Sample Collection and Preparation

Thirty six compost samples were collected from various sources in order to represent a wide range of feedstocks, origins, and composting methods and thereby assess the applicability of PXRF under a range of circumstances. Feedstocks included manure, food and yard wastes, bio-solids, woodchips, industrial sludge, and spent mushroom compost, among others. Samples originated from 8 states across the United States of America and one source in Canada. Samples were left un-ground and were refrigerated upon receipt. A sub-sample from every sample was dried at 70° C for 24 hours to determine moisture percentage (Method 03.09-A)(USDA-USCC 2002). A replicate from each of the original 36 samples was made and moist and dried sub-units were separately analyzed for both the original and replicate.

3.2.2 PXRF Scanning

A Delta Premium DP-4000 (Olympus Innov-X, Woburn, MA, USA) PXRF was used for scanning. The instrument was operated in a proprietary three beam configuration known as 'soil mode'. The battery operated device is comprised of a Ta/Au X-ray tube, operated at ~15-40 KeV, and a silicon drift detector (<165 eV) for fluorescence quantification. Compton normalization was used to correct for surface irregularities and matrix effects (Innov-X Systems 2010a). Calibration checks were conducted by scanning a stainless steel '316' alloy clip after every 20 scans. A silica standard was also run, and corrections to the results were made accordingly. Dried and “as received” moist aliquots from each sample were scanned through a plastic bag containing each sample per Innov-X Systems (2010a). Samples were scanned three times for 90 seconds each and an average was determined. The instrument was repositioned between each consecutive scan in order to account for the material’s intrinsic heterogeneity as well as to replicate taking multiple scans from one compost pile *in situ*. Care was taken to insure that ≥2 cm of sample thickness was placed beneath the instrument aperture, as scanning rays may penetrate to a depth of 1−2 cm in a sample (Palmer *et al*. 2009). When calculating averages for PXRF data, any reported negative values were changed to 0, and then the average was obtained for use in regression.

3.2.3 ICP Digestion

Digestions were done in duplicate for each sample to obtain an average and were facilitated via nitric acid (Method 04.12-B) prior to quantification with ICP-AES (USDA-USCC 2002). A Ciros model ICP-AES (Spectro Analytical Instruments, Marlboro, MA, USA) was used to quantify elemental concentrations of the compost samples. To ensure data quality, 15% of samples were digested a second time to test replicability.

3.2.4 Statistical Analysis

For statistical analysis, SAS software (SAS Version 9.3) was used with PROC REG to run linear regression of PXRF results to predict ICP-AES lab determined results in order to obtain predictor models for both moist and dry sample sets (SAS Institute Inc. 2011). In addition to the formation of predictor models for the elements of interest, PROC REG and PROC UNIVARIATE were used to obtain model performance statistics. To further investigate the influence of moisture, particle size, and organic matter on PXRF analysis, samples were designated into distinct moisture, particle size, and organic matter classes for each property. The individual classes were regressed with ICP-AES results and class results were compared. Moisture classes consisted of 0-29.9%, 30-49.9% and 50-100% moisture. The lowest division was established based on previous recommendations that samples with >20% moisture should be dried prior to analysis (Kalnicky and Singhvi 2001; Potts and West 2008). However, samples with up to 29% were included in the "low moisture group" in order to enhance the size of the sample set. Two particle size classes were established as medium (50-89% of sample passes a 5mm sieve) and fine (90-100% of sample passes a 5mm sieve). These classes were established based on clear differences in our sample set that distinguished sample texture into these two categories. Two organic matter (OM) classes were established as low (0-49.9% OM), and high (50-100% OM).

3.3 Results and Discussion

3.3.1 Regression Models

Regression results between ICP-AES and PXRF for the 36 compost samples revealed dissimilar relationships for all elements. Model parameters (intercept and slope), coefficients of determination (r^2) and root mean square errors (RMSE) are presented in Table 3.1. Per EPA standards that provide criteria for characterizing data quality for PXRF, elements with an r^2 of 0.85 to1.00 and relative standard deviation (RSD) of ≤0.10 are definitive; r^2 of 0.70 to 0.84 and RSD <0.2 are qualitative; while r^2 <0.70 and RSD >0.2 are suitable for qualitative evaluation (USEPAa 1998). In terms of r^2 Zn, Cu, K, Ca, Mn, Fe, P, and Cr for dry sample scans were definitive according to these standards, Pb and Ni were qualitative, and As and Cd performed poorly for dry samples and could only be used for field evaluation (Table 3.1, Table 3.2). None of the samples met standards for RSD, and thus our model cannot fully explain the variation observed. For moist sample scans, Zn, Cu, Ca and K performed the best in terms of r^2 and fell in the definitive class for r^2. There were noticeable drops in r^2 for Cr, Fe, Mn, and Ni. The moist regression model for Cd was not significant, and results were not presented.

Table 3.1 Coefficients of determination (r^2), root mean square error (RMSE), intercept, and slope for dry and moist sample regressions of inductively coupled plasma atomic emission spectroscopy (ICP-AES) and portable X-ray fluorescence spectrometry (PXRF) determined elemental concentrations.

Moisture State	Element	r^2	RMSE	Intercept	Slope
Dry Samples	As	0.38	14.20	15.32	2.55
	Ca	0.88	16,178.00	8,864.77	0.74
	Cd	0.17	3.49	-0.79	0.28
	Cr	0.78	41.23	-6.73	1.62
	Cu	0.91	31.02	12.42	0.79
	Fe	0.81	4,900.28	1,894.44	1.14
	K	0.89	3,445.08	-1,372.30	0.78
	Mn	0.84	273.89	-195.28	1.54
	Ni	0.70	23.23	27.32	2.34
	P	0.78	3,181.61	4,008.18	4.13
	Pb	0.64	20.92	23.08	1.14
	Zn	0.92	58.26	6.49	0.88
Moist Samples	As	0.19	16.31	20.67	2.84
	Ca	0.71	25,388.00	5,828.31	1.61
	Cd	§	§	§	§
	Cr	0.56	57.81	-22.94	3.74
	Cu	0.86	39.11	41.76	1.21
	Fe	0.61	6,938.49	3,345.71	1.72
	K	0.71	5,530.17	2,441.14	1.01
	Mn	0.65	410.02	-165.69	2.47
	Ni	0.47	30.87	32.64	7.63
	P	0.61	4,172.90	4,687.75	8.98
	Pb	0.63	21.36	16.38	1.98
	Zn	0.89	70.93	49.04	1.23

§ Model not significant (<0.05), data not reported

Table 3.2 Comparison of ranges and distribution statistics of elemental concentrations (mg kg^{-1}) determined via inductively coupled plasma atomic emission spectroscopy (ICP-AES) and portable X-ray fluorescence spectrometry (PXRF) dry and moist scans for 36 compost samples from the USA and Canada. Means, minimums, maximums, standard deviations, and relative standard deviations (RSD) of the 36 sample populations were compared.

Method	Statistic	As	Ca	Cd	Cr	Cu	Fe	K	Mn	Ni	P	Pb	Zn
ICP-AES	Mean	25.19	44,070.00	1.08	51.05	105.22	14,765.00	12,131.00	583.05	42.43	5,928.00	50.75	227.36
	Minimum	0.00	668.27	0.00	0.00	7.15	18.45	115.41	70.59	0.11	31.65	0.00	15.20
	Maximum	74.39	183,536.00	17.94	359.91	542.36	48,261.00	39,420.00	3,713.00	217.94	29,967.00	152.45	1,116.00
	Standard Deviation	17.83	46,129.00	3.78	86.36	102.08	11,006.00	10,055.00	682.77	41.74	6,620.00	34.38	206.89
	RSD	0.70	1.03	3.46	1.56	1.67	0.74	0.82	1.15	0.97	1.10	0.67	0.90
PXRF (Dry)	Mean	3.86	47,516.00	6.60	35.56	117.81	11,259.00	17,319.00	506.61	6.45	465.20	24.38	250.63
	Minimum	0.00	456.00	0.00	2.05	17.67	34.83	293.33	86.17	0.00	0.00	3.77	17.32
	Maximum	17.12	290,340.00	22.83	269.30	580.17	42,913.00	45,934.00	2,111.00	72.83	6,634.00	120.03	1,160.00
	Standard Deviation	4.33	58,422.00	5.57	46.90	123.62	8,652.00	12,139.00	408.19	14.91	1,413.00	24.24	225.54
	RSD	1.10	1.21	0.83	0.75	1.30	0.76	0.69	0.79	2.28	2.99	0.98	0.89
PXRF (Moist)	Mean	1.59	23,690.00	3.03	19.78	52.60	6,626.00	9,619.00	303.63	1.28	138.15	17.39	145.50
	Minimum	0.00	408.50	0.00	0.00	0.00	0.00	271.50	40.07	0.00	0.00	4.43	5.47
	Maximum	10.58	106,386.00	10.33	94.90	377.83	23,385.00	32,792.00	921.17	17.50	2,544.00	78.65	807.57
	Standard Deviation	2.72	24,007.00	3.54	17.35	78.33	5,005.00	8,388.00	223.17	3.74	577.86	13.75	158.88
	RSD	1.68	1.00	1.15	0.79	0.86	0.74	0.86	0.72	2.88	4.12	0.78	1.08

Overall when comparing means, minimums, maximums, and standard deviations, PXRF moist scans produced overall lower means, except in the case of Cd, than both ICP-AES and PXRF dry data (Table 3.2). PXRF dry scans did not consistently predict lower or higher concentrations than ICP-AES, and instead varied between elements. Moist scan PXRF scans produced the lowest standard deviations of all three. For all three methods, Ca, Fe, and K, produced very large ranges and therefore larger standard deviations, while As, Cd, Ni, and Pb demonstrated relatively small ranges and standard deviations (Table 3.2). The wide range between minimums and maximums for all elements was a good representation of our diverse sample set, and certainly contributed to variation observed in the models and their respective RSDs.

3.3.2 Moisture Influence

To investigate the influence of sample moisture on PXRF, dry and moist scan results were regressed with ICP-AES determined elemental concentrations and then compared. Slight (<5%) to pronounced (>20%) decreases in r^2 were observed for all moist models when compared with the corresponding dry dataset (Table 3.1). Copper, Pb, and Zn showed slight to no change between moist and dry scans, while As, Ca, Fe, K, and P showed a moderate decrease in predictive ability between dry and moist scans, whereas Cr and Ni showed pronounced decreases in predictability. Cadmium's moist scans showed no significant relationship to ICP-AES data. A comparison of the coefficients of determination illustrates the superiority of dry PXRF scans overall (Figure 3.1, Table 3.1).

The influence of moisture was further investigated by separating the sample set into moisture classes based on moisture percentages of low (0-29%), medium (30-49%) and high (50-100%). Regressions of ICP-AES and PXRF moist scans when partitioned into separate moisture classes showed differences in r^2 between the groups. However, the same trends were found when

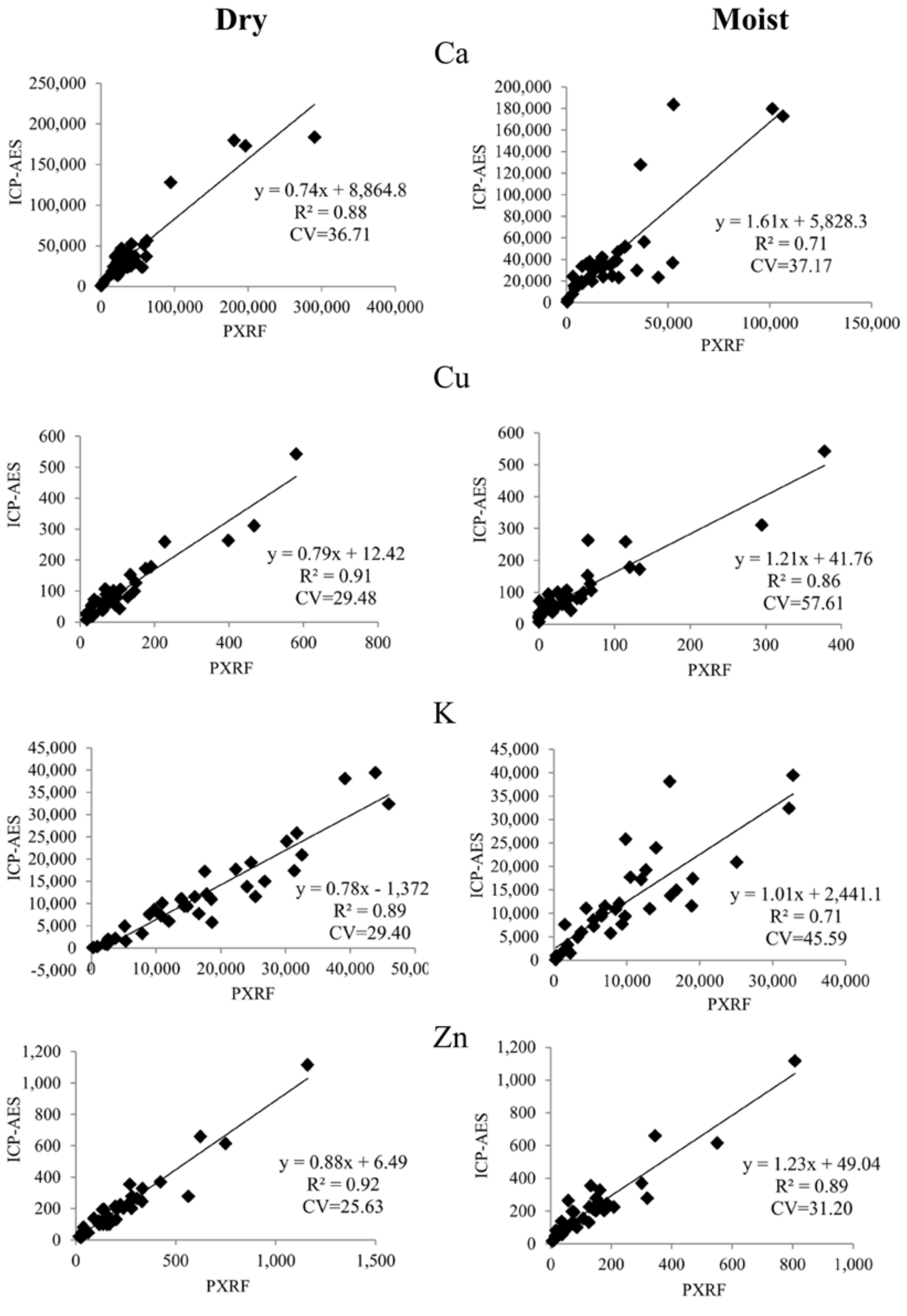

Figure 3.1 Regression plots of elemental concentration (mg kg^{-1}) via inductively coupled plasma atomic emission spectroscopy (ICP-AES) and portable X-ray fluorescence spectrometry (PXRF) for 36 dry and moist compost samples from the USA and Canada. The model, coefficients of determination (r^2), and coefficients of variation (CV) are reported.

the procedure was replicated using the same sample groups but for the PXRF dry data. Thus, there was an underlying difference among the groups that resulted in an improved r^2 that was not related to their moisture status. Increases in PXRF precision cannot be linearly correlated to decreases in sample moisture, and were thus not presented here.

Overall, PXRF would be most suitable for analyzing Cu, Pb, and Zn concentrations of compost samples *in situ* as sample moisture showed little influence on predictability. The need for more precise quantification of other elements may require drying of the sample prior to scanning or application of a correction factor to account for moisture's effect and the fact that elemental concentrations are reported on a dry weight basis (Innov-X Systems 2010a). While this would forego *in situ* application, it still offers considerable speed and sample preparation advantages over traditional ICP-AES digestion and quantification

3.3.3 Limits of Detection

When comparing the study done by Weindorf et al. (2008) and with our investigation, vast improvements in technology were clearly seen as demonstrated in Table 3.3. In our study, LOD improved for all elements concerned, most notably for Cd where the lowest limit of the LOD range dropped by a factor of 10 and now falls well below the EPA mandated limit. Improvements in predictability were also observed for nearly all elements. Notably for As we saw a decrease in predictability in comparison to the previous study. Possible factors will be discussed in the following section. The most notable improvements, increase in r^2 >0.20, were observed for Ca and K. The elements Cd, Cr, Ni, P and Pb cannot be compared to the previous study as no r^2 was reported by Weindorf *et al*. (2008). The previous study reported LOD's for Ni and Pb were sufficiently low in order to recommend the technology as a field evaluation tool for these elements. However, the LOD for Cd was not low enough to recommend the technology for use as an evaluation tool in Weindorf *et al*. (2008). Chromium and P were not considered in the previous study. In terms of percent recovery of determined concentrations of PXRF for ICP-AES, recovery rates varied widely across all elements. For dry scans, only 11% of As determined by ICP-AES was recovered by PXRF. More reasonable values were found for Cu, Fe, and Zn which had recoveries of 116, 88, and 112%, respectively.

Table 3.3 Comparison of coefficients of determination (r^2) for regressions of inductively coupled plasma atomic emission spectroscopy (ICP-AES) and portable X-ray fluorescence spectrometry (PXRF) and limits of detection (LOD) for the 36 compost samples from the present study and the 70 dried samples of Weindorf *et al*. (2008) utilizing PXRF for compost analysis. Environmental Protection Agency (EPA) mandated elemental limits are reported. Values for r^2 were not reported for several elements by Weindorf *et al*. (2008).

Element	r^2 Weindorf †	r^2 PXRF		EPA Limit‡	LOD	
		Dry	Moist		Weindorf †	PXRF
				mg kg $^{-1}$	mg kg $^{-1}$	mg kg $^{-1}$
As	0.84	0.38	0.19	< 41	4-19	1-3
Ca	0.51	0.88	0.71	–	–	20-30
Cd	–	0.17	§	< 39	64-95	6-8
Cr	–	0.78	0.56	–	–	5-10
Cu	0.95	0.91	0.86	< 1,500	13-52	5-7
Fe	0.67	0.81	0.61	–	–	5
K	0.14	0.89	0.71	–	–	30-50
Mn	0.67	0.84	0.65	–	–	3-5
Ni	–	0.70	0.47	< 420	29-96	10-20
P	–	0.78	0.61	–	–	500-700
Pb	–	0.64	0.63	< 300	5-18	2-4
Zn	0.81	0.92	0.89	< 2,800	6-30	3-5

† Weindorf et al. 2008

‡ USEPA. 2012

§ Not Significant

3.3.4 Inter-elemental Interactions

Elemental quantification via PXRF is known to be influenced by certain inter-elemental interactions. For example, high concentrations of Pb can influence the detection of low levels of As, and high Fe may inhibit detection of low levels of Cr (Hettipathirana 2004; Innov-X Systems 2003). The reason for the interference between As and Pb is their shared spectral peak, both at

10.5 keV (Innov-X Systems 2003). Such overlaps cannot be resolved, even by the best detector as they are inherent elemental properties associated with secondary fluorescent radiation. The Innov-X Delta PXRF automatically corrects the As data for the Pb interference and displays corrected results. However the interference is still present and detection levels and precisions are affected when Pb is present. The presence of Pb in a sample can produce elevated As detection levels, and decrease precision during the same testing time for a sample that contains no Pb (Innov-X Systems 2003). For example, in samples with <15 mg km^{-1} Pb the LOD for As is 7 mg km^{-1}, while for a sample of 100 mg km^{-1} Pb the LOD for As increases to 15mg km^{-1} and then further increases to a As LOD of 31 for a sample containing 1,000 mg km^{-1} Pb (Innov-X Systems 2003). In our sample set, there were several samples with concentrations >100 mg km^{-1} Pb and only three samples with concentrations of <15mg km^{-1} Pb (Figure 3.2). Per Innov-X Systems (2003), Equation 3.1 can be applied to determine the detection limit of As based on the concentration of Pb:

$$As_{Pb} = As_{No\ Pb} + b\,\sqrt{Pb} \qquad \textbf{Equation 3.1}$$

Where; As_{Pb} = Detection limit of As with Pb present in the sample, $As_{No\ Pb}$ = Detection limit of As without Pb present in the sample, b = 0.76 (fitting coefficient), Pb=Pb concentration in sample (mg km^{-1}).

For our sample set using Equation 3.1 and assuming 3 mg km^{-1} as the LOD for a sample without Pb present, the calculated As LOD's for our samples varied from 3 to 12.3 mg km^{-1} (Innov-X Systems 2010a). By contrast, ICP-AES generally has high µg kg^{-1} to low mg km^{-1} LOD (Palmer *et al*. 2009). This may have contributed to the weak relationship we found between ICP-AES and PXRF. Other studies have found much more robust r^2 values. For instance, Weindorf *et al*. (2008) obtained a value of 0.84 for As in regression of PXRF and ICP-AES. PXRF normally returns strong data (r^2 >0.90) for As in soil sampling (Kilbride *et al.* 2006;

USEPAb 1998). A major contributing factor in our study was that any negative values returned by PXRF were changed to zero for modeling purposes. Therefore, if samples with ICP-AES determined Pb:As ratios of >10 (there were four samples) were removed from the regression, the PXRF to ICP-AES r^2 improved to 0.48; a distinct improvement, yet still lower than previous studies.

3.3.5 Particle size Analysis

To study particle size's influence on PXRF, samples of different particle size grades were separated into two classes and individually regressed with ICP-AES. The results of this investigation demonstrated that the influence of particle size on detectability is different for each element (Table 3.4). In terms of r^2, Zn, K, Ca, and Cu showed little change between particle size classes.

However, As detection was clearly influenced by particle size. For As, the dry model was non-significant for the coarser particle size class but had an r^2 of 0.68 for the finer particle size class. Most notably, Ni dropped from an r^2 of 0.82 for the course textured samples to 0.31 for the finer dry samples. Changes in standard deviations and RMSEs followed similar trends as coefficients of determination between coarser and finer textures. Previous studies found that particle size of soils had no significant effect for As, Cu, Pb and Zn and had insufficient data for other elements (Kilbride *et al.* 2006). However their sample set was air-dried and consisted of <2mm soil fractions. Our study indicates that there are significant influences of particle size on elemental determinations in compost using PXRF. These changes are likely dually related to the inherent elemental differences of different particle size fractions, as finer fractions have been shown to accumulate heavy metals and to an interaction of PXRF with the sample matrices affects, namely particle size (Lopez *et al*. 2002; Potts and West 2008).

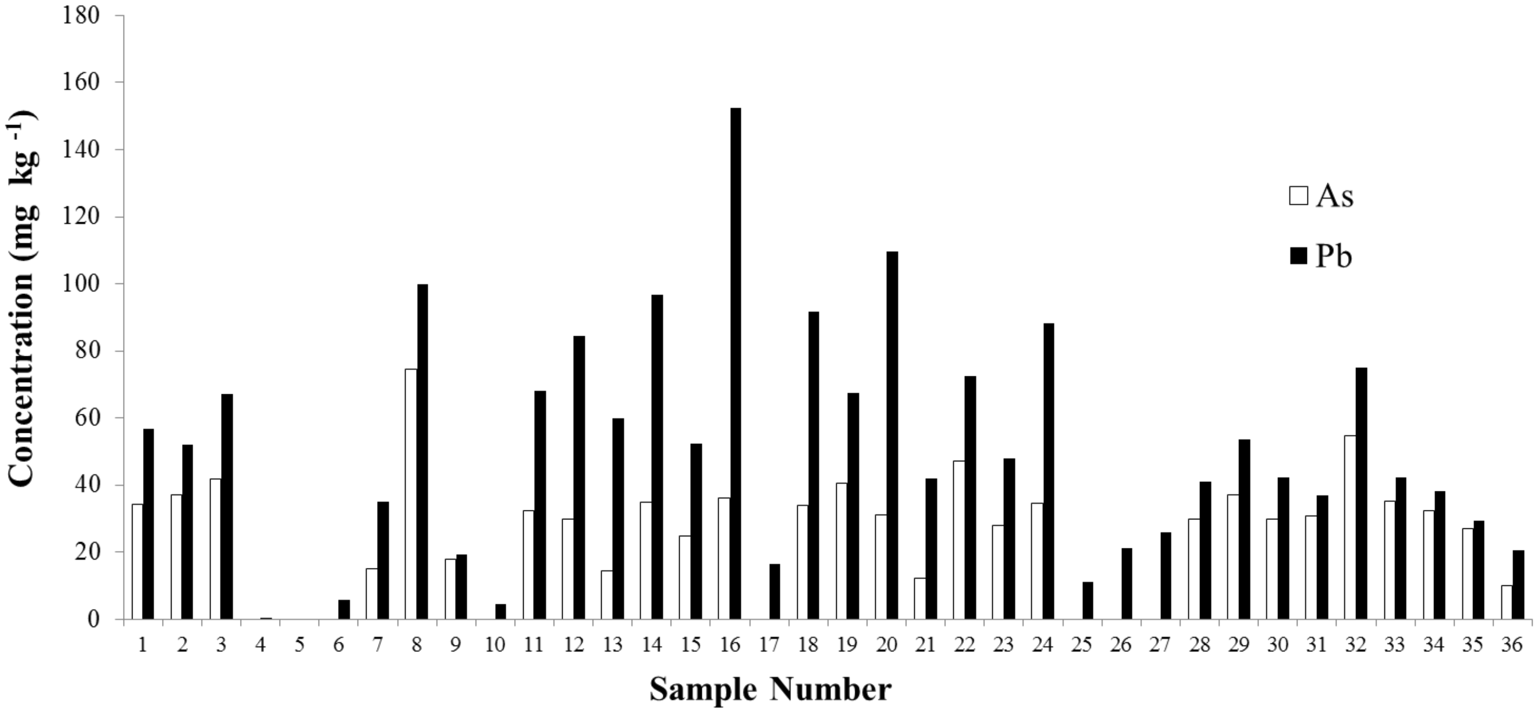

Figure 3.2 Arsenic and Pb concentrations of 36 compost samples from the USA and Canada as determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Table 3.4 Comparison of coefficients of determination (r^2), root mean square errors (RMSE), model equations and standard deviations for regressions of inductively coupled plasma atomic emission spectroscopy (ICP-AES) and portable X-ray fluorescence spectrometry (PXRF) of different particle size classes based on the percent of the sample that passes a 5mm sieve. Moist and dry populations are compared.

Sample (%) Passing 5mm Sieve

50-89%

	Dry					Moist				
	r^2	RMSE	Intercept	Slope	Std deviation	r^2	RMSE	Intercept	Slope	Std deviation
As	§					§				
Ca	0.90	18,067.00	14,497.00	0.68	17,493.12	0.75	27,980.00	11,569.00	1.82	27,091.46
Cd	0.26	4.73	-1.11	0.44	4.58	§				
Cr	0.77	57.61	9.96	1.56	55.78	0.64	72.29	-2.21	3.96	69.99
Cu	0.93	34.41	10.84	0.84	33.32	0.90	43.16	52.07	1.36	41.79
Fe	0.79	6,301.71	3,030.65	1.09	6,101.60	0.61	8,557.13	4,708.19	1.90	8,285.41
K	0.90	3,867.83	-2,319.55	0.87	3,745.01	0.73	6,295.47	2,107.03	1.23	6,095.56
Mn	0.81	399.19	-232.27	1.59	386.52	0.63	560.12	-116.19	2.64	542.34
Ni	0.82	24.85	29.96	2.70	24.06	0.56	38.39	37.50	9.28	37.18
P	0.90	3,867.83	-2,319.55	0.87	3,745.01	0.55	5,528.01	5,710.50	9.54	5,352.48
Pb	0.58	18.58	16.90	1.53	17.99	0.53	19.56	8.12	2.60	18.94
Zn	0.92	75.63	8.39	0.90	73.23	0.91	81.04	65.30	1.29	78.46

90-100%

	Dry					Moist				
	r^2	RMSE	Intercept	Slope	Std deviation	r^2	RMSE	Intercept	Slope	Std deviation
As	0.68	11.37	10.98	3.34	11.05	0.47	14.59	17.00	4.29	14.18
Ca	0.89	12,442.00	-185.98	0.93	12,091.33	0.77	18,448.00	1,398.05	1.41	17,928.41
Cd	§					§				
Cr	0.81	8.11	-8.37	1.18	7.88	0.39	14.49	-1.30	1.20	14.08
Cu	0.89	24.59	20.57	0.67	23.90	0.92	20.46	37.73	1.00	19.89
Fe	0.85	3,435.94	456.73	1.24	3,339.13	0.76	4,367.66	2,070.84	1.59	4,244.60
K	0.90	2,696.54	-201.34	0.69	2,620.56	0.76	4,236.78	2,596.25	0.88	4,117.41
Mn	0.94	62.24	-82.36	1.20	60.49	0.89	84.10	-27.69	1.47	81.73
Ni	0.31	14.37	27.32	0.92	13.96	0.23	15.12	28.82	2.81	14.69
P	0.81	2,297.60	3,785.02	5.35	2,232.87	0.81	2,297.60	3,785.02	8.30	2,232.87
Pb	0.66	23.20	24.63	1.07	22.54	0.66	23.44	18.65	1.86	22.78
Zn	0.93	39.55	13.06	0.83	38.44	0.88	50.88	47.50	1.08	49.45

§ model not significant ($p>0.05$)

3.3.6 Influence of Organic Matter

In order to briefly investigate organic matter's (OM) possible influence on PXRF, data from the dried samples was divided into two OM classes and regressed with ICP-AES. Overall there were differences in model predictability for dried samples between samples placed into low and high OM classes, these differences were most noticeable for Ca, Cr, Cu, Ni, P, Pb, and Zn (Table 3.5). Only Pb and Fe had better model results with samples in the high OM class, all other elements had improved r^2 with samples of lower OM. Generally RMSEs were steady between OM class and improved RMSE values generally followed improvements in r^2. The improvements in model fit point to an influence by organic matter on PXRF's predictability of certain elements. However, due to the complexities of the OM fraction in compost, and it's variability due to many other factors and properties, including particle size, a clear relationship between OM and PXRF determinations cannot be drawn (Lopez *et al*. 2002). However, considering the inherent high percentages of OM in compost, the influence and contributions in terms of bound metals and elements should be considered. Our observations of increased PXRF precision with samples of low OM may be related to increased OM mineralization (Lopez *et al*. 2002). However, as this trend was not observed with Pb or Fe, the relationship cannot be clearly defined and is thus presented here in brief.

3.3.7 Overall Comparison of PXRF and ICP-AES

In comparing ICP-AES and PXRF, the amount of the overall sample matrix that is analyzed by each technology must be considered. Most especially when considering that ICP-AES is able to analyze only a relatively small aliquot (around 1-2 grams) of the total sample, while PXRF produces X-ray excitation over 3 cm^2 and to a depth of 2.5 cm, which is equivalent to a sample volume of approximately 7.5 cm^3 (Innov-X Systems 2010a). Depending on sample density, PXRF has the capacity to analyze a greater portion of the sample, especially when combined with replicate scans, than ICP-AES. This may contribute to differences observed between ICP-AES and PXRF considering the extremely heterogeneous nature of compost, and potential errors that may be associated with analysis of small sample size.

Table 3.5 Influence of sample's organic matter content on regression of portable X-ray fluorescence spectrometry (PXRF) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) for prediction of elemental concentrations in dried compost samples. Coefficient of determinations (r^2) and root mean square errors are compared (RMSE).

	0-49% Organic Matter		50-100% Organic Matter	
	r^2	RMSE	r^2	RMSE
As	0.36	3.85	0.27	3.19
Ca	0.91	25,125.91	0.88	8,032.21
Cd	0.39	5.36	0.06	4.18
Cr	0.86	25.78	0.61	11.42
Cu	0.93	40.45	0.83	37.31
Fe	0.69	4,048.99	0.84	3,862.37
K	0.88	4,228.06	0.90	4,159.61
Mn	0.87	181.57	0.78	147.66
Ni	0.78	10.07	0.28	4.72
P	0.91	576.24	0.49	700.82
Pb	0.64	19.19	0.75	9.18
Zn	0.97	47.20	0.81	74.79

The absolute accuracy of ICP-AES must also be considered as it and the digestions necessary for sample preparations also have certain limitations. Nitric acid digestion has been indicated to give lower values than other digestion methods, however it is often used as it is less caustic (Baize 2000). However, the power of ICP-AES in terms of LOD, far out reaches PXRF, as the former is able to determine many elements to the µg kg^{-1} level (Palmer *et al.* 2009). In terms of applicability, such rigorous determinations are often un-necessary as the lowest limit for EPA mandated elemental concentration is 39 mg kg^{-1} for Cd. When considering the time consuming digestions, caustic chemicals, and expensive machinery required by ICP-AES, the portability, speed and lack of need for digestion are the obvious benefits of PXRF. Thus in scenarios where such precise determinations are un-warranted, PXRF may be able to replace ICP-AES for evaluation and monitoring of certain elements, especially for dried samples.

3.4 Conclusions

Analyzing compost for nutrient and heavy metal content is vital not only to the product's marketability, but also to its safe use by farmers, homeowners, and businesses. The limitations presented by current testing methods, namely lack of portability and slow processing times hinder producers and testing facilities abilities to monitor and quickly certify the material for sale. The dramatic improvements in PXRF's LOD between an older, single beam PXRF utilized by Weindorf *et al*. (2008) versus the newer, three beam PXRF utilized in the present study and our ability to demonstrate its applicability to a diverse range of compost feedstocks using un-ground samples displays the potential for its larger use for elemental determinations in compost. PXRF in this study was able to acceptably quantify the elements Ca, Cr, Cu, Fe, K, Mn, P, and Zn in dry samples and the elements Ca, Cu, K, and Zn in moist samples. The elements Ca, Cu, K and Zn showed widespread predictive stability across various tests of interference. However for other elements, most notably As, we were unable to clearly associate PXRF determinations to ICP-AES. Factors such a moisture, particle size, organic matter, and inter-elemental interferences were shown to influence the ability of PXRF to varying degrees. Moisture and particle size may be controlled by the operator, while the chemical matrix cannot. These limitations notwithstanding, this study has shown that PXRF can be useful for quantifying many elements, and its lower cost, speed, and portability may out-weigh slight losses in accuracy, especially where field evaluation of composted materials is a primary goal.

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CHAPTER 4: CONCLUSIONS

As a part of ongoing research and development, the TMECC has a goal of “removing antiquated methods,” and “soliciting for and adding missing test methods,” (USDA-USCC 2002). This research was conducted with the intent of investigating new methods for possible inclusion in the TMECC, with a focus on portable spectroscopic methods that can be applied *in situ*. The advantages of spectroscopy are the sample is not destroyed, analysis requires little to no sample preparation, and results are nearly instantaneous (Innov-X Systems 2010). For this reason, investigations into VisNIR DRS for OM determinations and PXRF for elemental quantification were carried out with un-milled and moist samples to reflect *in situ* conditions and as alternatives to current methods. Current lab methods consume the sample during analysis, require considerable sample preparation which slows sample processing, and are restricted to a laboratory setting. The technologies used in this investigation are distinguished by their portability (beyond that of a mobile laboratory), where they are operated from a backpack (VisNIR DRS) or are handheld (PXRF) (Westerman 1990, Potts and West, 2008).

The application of VisNIR DRS and PXRF to 36 compost samples, of diverse origin, feedstock and composting method was done to test the global applicability of these technologies to all compost types. While 36 samples cannot realistically fully represent the entire range of materials and methods used in composting globally, the sample set was extremely diverse and represented a wide range of OM, pH, salinity, moisture content, and particle size.

With regard to VisNIR DRS scanning for OM quantification, first-derivative PLS models built using dry sample spectra produced the best r^2 and best RPDs. However, given the relatively small sample set and inherent variability of organic compounds comprising compost, the models did not meet the criteria for definitive spectroscopic modeling as outlined by Chang *et al*. (2001). Additionally, the results do point to the potential of the technology for rapid, portable, and non-destructive compost analysis for a wide range of compost samples and provides direction for a larger study to follow up the results of this study.

The models produced by simple linear regression for PXRF vs. ICP-AES for compost elemental analysis gave definitive results for r^2 values of Zn, Cu, K, Ca, Mn, Fe, P, and Cr for dry sample scans and qualitative results for Pb and Ni. Models of As and Cd performed poorly overall. For all models, RSDs were not met, and thus the models do not fully explain the relationship between PXRF and ICP-AES determined elemental composition. For As and Cd, PXRF cannot be recommended as an alternative analytical tool. The influence of high Pb levels in some samples likely influenced the predictability of As by PXRF due to overlapping wavebands. Similar variation in predictability of elemental concentrations was noted between particle-size classes. For Zn, K, Ca, and Cu, little change was observed between particle size classes. However, marked changes were observed for As detection where the dry model was non-significant for the coarser particle size class but had an r^2 of 0.68 for the finer particle size class. The influence of OM on dry scan model performance was also noted for Ca, Cr, Cu, Ni, P, Pb, and Zn. All regressions were stronger in samples containing low OM, with the exception of Pb and Fe. Again, this relationship cannot be easily explained due to the complexity of OM and the interaction of other physical factors like particle size. If LODs in the $\mu g\ kg^{-1}$ range are desired, PXRF cannot be used and ICP-AES is required. However, in most instances such low LOD are not required and PXRF can sufficiently detect most elements regulated for compost.

One limitation to the application of spectroscopy to *in situ* analysis is the accuracy of these technologies with moist samples. A comparison of moist and dry samples generally showed the latter to be preferable. While no obvious differences in overall average spectral reflectance between moist and dry samples was observed for VisNIR DRS scans, there were observed differences between moist and dry prediction models. The dry models generally slightly outperformed moist models, perhaps due to the identification of a greater number of significant wavelengths in dry spectra. Additionally, the accuracy and stability of PLS and PCR models varied in their performance in relating VisNIR DRS determined OM to laboratory based LOI determined OM.

Differences between moist and dry model performance for PXRF were observed for Cr, Fe, Mn, and Ni, while smaller or no change was observed for Zn, Cu, Ca, and K. However, in general dry sample scan models out performed moist models. The reasons for these differences are not explained by a linear relationship of increasing moisture to a corresponding decrease in predictability.

Overall, both technologies had promising performance with dried samples. While using dried samples does exclude the use of these technologies for definitive *in situ* analysis, they still offer considerable speed and sample preparation advantages over traditional laboratory methods. As analytical methods progress and develop, technology that allows on site, instantaneous results are sought to replace existing testing labs, or at the very least, allow for field screening. This is especially important to the field of compost, where feedstocks have the potential to contain high concentrations of heavy and toxic metals, and the resulting material is often used in agricultural and residential settings where it comes in close contact to food and humans. While neither VisNIR-DRS nor PXRF can currently be recommended as a definitive replacement to current laboratory methods, their advantages of lower cost, speed, and portability may out-weigh slight losses in accuracy, especially where field evaluation of composted materials is the primary goal. Further investigation into improved prediction model development and their application to compost analysis is warranted and supported by the preliminary findings of these studies.

4.1 References

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APPENDIX A: BASIC COMPOST ANALYSIS RESULTS

Sample #	Rep	Moisture %	EC		pH	LOI %		Particle Size Fractions (% of each fraction)						
				unit		Rep 1	Rep 2	50mm	25mm	16mm	9.5mm	6.4mm	5mm	<5mm
1	A	43.04	716.00	u	7.01	67.80	64.10	0.00	0.00	1.82	13.45	17.34	12.22	55.27
	B	48.48	724.00	u	7.17	56.84	76.47	0.00	0.00	12.97	20.47	12.42	11.06	43.41
2	A	63.22	478.00	u	6.71	33.24	27.64	0.00	0.00	0.00	0.92	2.08	34.46	60.92
	B	68.28	1,726.00	u	6.45	38.52	51.05	0.00	0.00	0.00	0.00	31.42	25.82	41.95
3	A	48.68	850.00	u	7.65	25.89	41.02	0.00	0.00	3.29	10.24	6.97	10.54	69.39
	B	49.14	791.00	u	7.68	28.17	33.35	0.00	0.00	2.46	8.98	12.12	8.49	67.59
4	A	30.39	22.10	m	8.71	62.44	68.91	0.00	0.00	4.21	14.37	7.64	9.44	64.35
	B	27.80	21.60	m	8.51	63.84	99.52	0.00	0.00	8.53	9.39	6.82	8.50	66.75
5	A	59.50	90.50	u	6.38	86.07	92.46	0.00	0.00	0.00	0.66	1.80	6.52	91.08
	B	63.49	88.30	u	6.36	87.75	89.20	0.00	0.00	0.00	4.47	0.70	5.35	89.63
6	A	64.95	82.80	u	6.54	91.79	66.96	0.00	0.00	0.00	11.32	17.98	22.37	47.91
	B	64.53	71.60	u	6.96	91.67	91.90	0.00	0.00	16.58	11.78	11.32	17.48	42.63
7	A	46.07	2.08	m	7.33	46.99	55.47	0.00	0.00	0.00	12.46	13.81	14.41	59.10
	B	42.81	2.21	m	7.33	46.56	62.93	0.00	0.00	5.16	4.14	7.99	8.26	75.23
8	A	45.78	7.56	m	12.34	19.55	20.42	0.00	0.00	0.00	1.79	2.85	7.86	87.27
	B	43.38	7.77	m	12.25	18.59	36.84	0.00	0.00	0.00	0.00	0.97	7.68	90.85
9	A	42.28	1,936.00	u	7.75	53.40	64.65	0.00	0.00	5.84	3.97	14.27	10.05	66.28
	B	42.49	2.52	m	7.91	50.83	55.03	0.00	0.00	0.00	2.25	7.99	10.65	79.94
10	A	76.44	1,621.00	u	6.79	81.55	87.19	0.00	0.00	8.53	9.78	11.32	13.54	57.62
	B	74.87	2.23	m	6.70	80.87	88.26	0.00	0.00	11.24	16.09	16.20	11.46	45.95
11	A	47.18	4.62	m	7.02	54.16	61.34	0.00	0.00	0.00	5.07	11.29	13.97	69.49
	B	44.89	3.63	m	6.74	49.77	60.69	0.00	0.00	2.71	10.61	16.28	13.42	56.26
12	A	38.47	3.14	m	7.59	43.01	55.04	0.00	0.00	0.00	4.08	3.79	7.15	84.93
	B	41.76	2.89	m	8.01	40.80	48.57	0.00	0.00	0.00	1.82	4.01	8.55	85.28

Table Appendix A continued

13	A	40.95	4.06	m	7.68	43.76	53.23	0.00	0.00	0.00	0.79	5.76	8.62	84.91
	B	47.86	3.41	m	8.62	57.41	67.83	0.00	0.00	0.00	0.00	6.23	11.21	83.70
14	A	48.98	1,958.00	u	7.76	50.38	50.67	0.00	0.00	0.00	0.69	4.37	10.54	84.68
	B	50.69	2.40	m	7.82	52.74	58.96	0.00	0.00	0.00	4.25	8.12	12.23	75.14
15	A	41.29	8.96	m	5.90	39.06	40.72	0.00	0.00	0.00	0.00	0.00	0.00	99.93
	B	41.12	8.54	m	5.75	37.99	32.21	0.00	0.00	0.00	0.00	0.00	0.39	99.53
16	A	24.43	5.72	m	7.05	27.76	34.82	0.00	0.00	0.00	2.86	2.90	3.88	90.19
	B	24.57	5.63	m	6.88	26.07	26.67	0.00	0.00	11.56	0.00	0.45	3.16	84.84
17	A	64.06	10.32	m	8.10	55.23	55.80	0.00	0.00	3.00	14.32	6.06	16.34	60.52
	B	53.99	7.54	m	8.12	58.47	58.69	0.00	0.00	13.87	12.58	7.76	10.48	55.13
18	A	29.80	1,960.00	u	7.35	61.12	62.25	0.00	0.00	0.00	0.00	5.97	8.70	85.13
	B	33.78	1,878.00	u	7.79	63.48	67.12	0.00	0.00	0.00	0.83	2.59	10.63	86.00
19	A	37.26	3.70	m	5.82	65.75	66.09	0.00	0.00	0.00	0.32	8.14	13.84	77.43
	B	39.84	3.93	m	5.35	65.64	73.13	0.00	0.00	0.00	0.84	8.40	16.21	74.11
20	A	50.16	3.09	m	7.79	56.02	55.45	0.00	0.00	0.00	0.00	2.79	11.05	86.93
	B	45.57	4.09	m	7.89	49.21	70.48	0.00	0.00	0.00	0.00	0.00	9.06	90.71
21	A	43.51	3.99	m	8.06	61.04	74.43	0.00	0.00	0.00	1.69	6.51	4.63	87.31
	B	44.30	4.44	m	7.53	54.79	61.17	0.00	0.00	0.00	4.13	5.98	7.30	82.21
22	A	55.49	1,963.00	u	7.47	57.11	63.75	0.00	0.00	0.00	6.84	5.29	10.20	78.05
	B	54.45	2.35	m	7.27	55.88	65.81	0.00	0.00	6.90	17.13	14.68	19.73	40.99
23	A	35.36	2.32	m	7.44	40.01	46.67	0.00	0.00	0.00	0.00	7.94	13.26	78.97
	B	35.58	2.07	m	7.41	39.60	48.50	0.00	0.00	0.00	0.00	6.15	9.25	84.63
24	A	20.53	5.36	m	8.03	31.99	40.33	0.00	0.00	0.00	5.74	3.47	3.89	86.94
	B	19.30	4.77	m	8.69	29.31	31.65	0.00	0.00	0.00	2.21	2.81	4.48	90.52
30	A	8.93	701.10	u	4.38	99.70	99.73	0.00	0.00	0.00	0.00	0.00	0.15	100.45
	B	8.50	26.30	u	5.39	99.80	99.78	0.00	0.00	0.00	0.00	0.00	0.07	99.84
31	A	40.78	936.00	u	7.72	25.74	26.18	0.00	0.00	0.00	1.07	0.92	4.09	94.06
	B	36.62	2.32	u	7.85	24.44	27.00	0.00	0.00	0.00	3.00	4.85	7.06	85.19
32	A	58.34	3.33	m	7.40	57.76	62.44	0.00	0.00	0.00	1.50	5.39	8.91	84.53
	B	57.87	4.41	m	7.32	55.62	67.64	0.00	0.00	0.00	0.00	4.90	10.52	85.32

Table Appendix A continued

33	A	29.39	4.83	m	8.99	21.71	27.89	0.00	0.00	0.00	4.37	5.17	6.33	84.06
	B	29.11	5.36	m	9.04	20.97	22.81	0.00	0.00	0.00	1.18	1.39	6.69	90.55
34	A	52.84	170.40	u	8.15	37.55	40.81	0.00	0.00	5.91	32.02	23.64	14.39	23.52
	B	55.27	193.30	u	7.53	38.04	30.10	0.00	0.00	17.48	27.29	19.60	12.03	23.02
35	A	40.95	3.81	m	8.64	36.51	57.53	0.00	0.00	0.00	0.00	0.00	9.37	90.54
	B	29.64	4.22	m	8.83	35.83	46.14	0.00	0.00	0.00	0.00	2.46	7.55	90.06
37	A	17.70	5.91	m	9.21	32.68	47.97	0.00	0.00	0.00	0.00	1.55	6.36	92.05
	B	18.05	5.68	m	9.24	32.89	40.93	0.00	0.00	0.00	0.00	0.92	8.48	90.66
38	A	32.03	4.72	m	6.79	37.58	37.15	0.00	0.00	0.00	0.00	2.65	6.39	90.99
	B	30.95	5.28	m	7.01	37.95	36.32	0.00	0.00	0.00	3.57	4.59	6.43	85.39
39	A	30.49	2.53	m	8.36	42.81	56.48	0.00	0.00	0.00	1.96	5.68	8.45	84.05
	B	33.95	2.75	m	8.39	40.59	37.86	0.00	0.00	0.00	0.78	2.19	7.26	89.68
40	A	59.86	6.07	m	8.42	52.39	66.48	0.00	0.00	14.23	2.18	6.16	12.24	64.87
	B	59.19	6.74	m	8.32	53.15	66.46	0.00	0.00	0.00	11.36	13.92	11.86	62.78
41	A	28.58	7.60	u	8.31	51.86	71.06	0.00	0.00	0.00	2.36	9.85	12.93	74.54
	B	28.82	6.65	u	8.30	50.61	73.49	0.00	0.00	0.00	0.82	4.46	8.97	86.12
42	A	28.78	8.99	m	8.72	58.16	66.20	0.00	0.00	0.00	0.00	5.28	11.61	83.20
	B	29.52	9.96	m	8.69	62.43	68.10	0.00	0.00	0.00	0.26	3.24	8.91	87.54

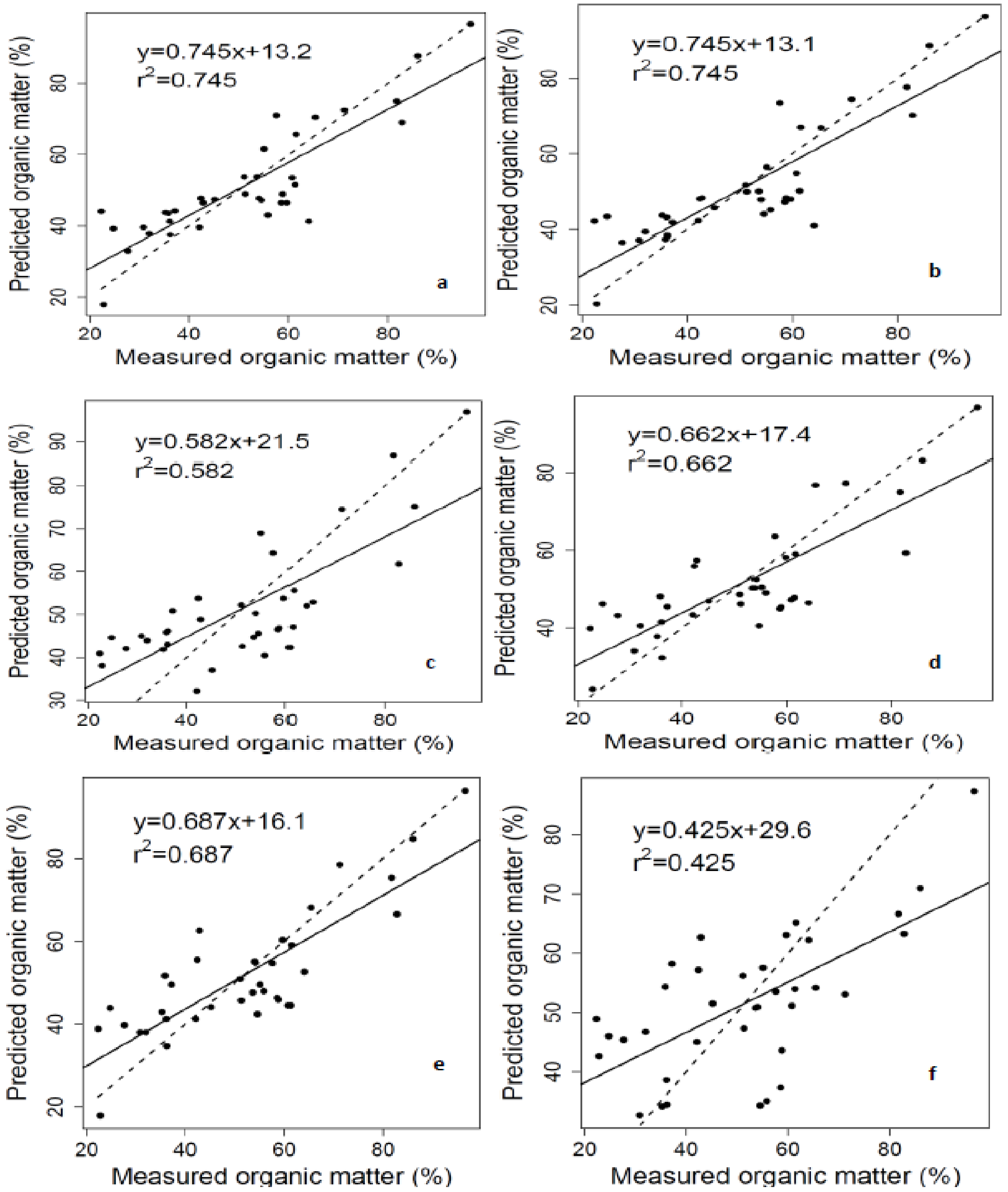
APPENDIX B: COMPARISION AND VALIDATION OF CERTIFIED TESTING LAB RESULTS

	McWhirt *et al*. 2012 Results						CAP Proficiency Results (Median and 95% CI given)		
Sample Number	**33**		**34**		**35**		**33**	**34**	**35**
Replicate	A	B	A	B	A	B			
Moisture %	29.39	29.11	52.84	55.27	40.95	29.64	29.5 ± 1.83	54.4 ± 2.50	40.4 ± 8.99
EC	4.83	5.36	170.40	193.30	3.81	4.22	5.9 ± 1.8	0.3 ± 0.11	4.3 ± 1.1
unit	dS/ m	dS/ m	dS/ u	dS/ u	dS/ m	dS/ m	dS/m	dS/m	dS/m
pH	8.99	9.04	8.15	7.53	8.64	8.83	8.80 ± 0.64	7.97 ± 0.67	8.68 ± 0.48
LOI%- 1	21.71	20.97	37.55	38.04	36.51	35.83	19.4 ± 4.3	35.4 ± 10.1	38.5 ± 4.9
LOI%- 2	27.89	22.81	40.81	30.10	57.53	46.14			
Particle Size									
% >50 mm	0.00	0.00	0.00	0.00	0.00	0.00			
% >25 mm	0.00	0.00	0.00	0.00	0.00	0.00			
% >16 mm	0.00	0.00	5.91	17.48	0.00	0.00			
% >9.5 mm	4.37	1.18	32.02	27.29	0.00	0.00	2.8 ± 4.4	25.1 ± 43.4	0.0 ± 7.11
% >6.4 mm	5.17	1.39	23.64	19.60	0.00	2.46		(Total % >9.5 mm)	

Table Appendix B continued

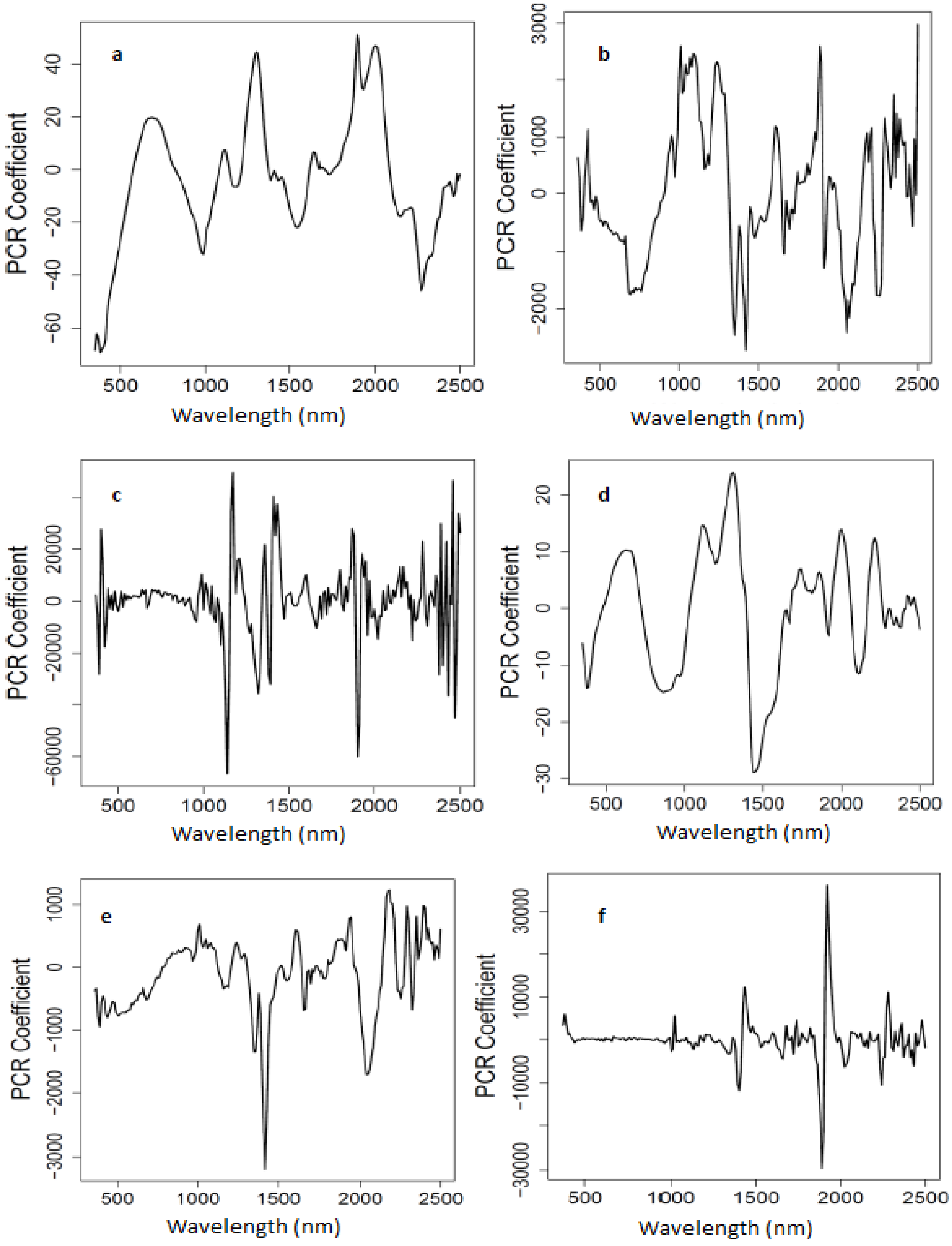
% >5 mm	6.33	6.69	14.39	12.03	9.37	7.55			
% < 5 mm	84.06	90.55	23.52	23.02	90.54	90.06			
Elemental	ppm						ppm		
As	25.93	33.51	39.71	34.41	31.65	27.72	2.62±0.42	2.80 ±0.45	2.89 ±0.48
Ba	99.59	112.64	222.04	208.03	133.85	126.43	74.0 ±21.9	182 ±35.0	93.5 ±23.2
Ca	29,858.75	38,796.86	13,807.81	12,150.03	37,596.57	40,053.31	2.78 ±0.54	1.28 ±0.35	3.43 ±0.63
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.41± 0.34	0.41 ±0.43	0.42 ±0.38
Cr	13.77	14.65	19.31	19.87	15.69	13.21	10.0± 12.7	15.0 ±13.0	10.9 ±9.6
Cu	155.91	200.70	45.52	99.63	103.70	94.00	131± 26	13.4 ±5.8	69.0 ±19.2
Fe	12,718.28	11,883.17	28,913.95	16,914.95	11,793.73	11,319.41	8,094± 2693	13,332 ±3062	7,512 ±2260
K	13,248.70	16,678.29	2,972.90	3,559.43	14,064.97	13,496.22	1.32 ±0.36	0.17 ±0.07	1.42 ±0.39
Mn	220.87	267.83	758.15	604.33	352.04	337.36	204 ±52	663 ±169	298 ±70
Ni	21.26	27.63	39.58	33.65	46.82	42.93	7.0 ±2.7	11.4 ±4.1	26.0 ±7.0
P	3,426.90	4,585.88	889.88	816.69	10,108.91	9,640.16	0.32 ±0.03	0.090 ±0.026	0.81 ±0.13
Pb	37.01	44.90	54.68	52.82	44.50	40.31	7.0 ±1.7	9.8 ±3.5	8.7 ±3.9
Zn	134.69	172.62	100.55	100.16	257.19	233.85	113 ±26	81 ±26	212 ±55

APPENDIX C: PREDICTED VS MEASURED ORGANIC MATTER PCR COMPARISION



Predicted vs. measured organic matter (%) for a) moist reflectance, b) moist first-derivative, c) moist second -derivative, d) oven-dried reflectance, e) oven-dried first-derivative, and f) oven-dried second-derivative principal component regression models for 36 compost samples. The solid line is the regression line, and the dashed line is a 1:1 line

APPENDIX D: PCR SPECTRAL COMPARISION



Fitted principal component regression coefficient curve on the spectrum for a) moist reflectance, b) moist first-derivative, c) moist second -derivative, d) oven-dried reflectance, e) oven-dried first-derivative, and f) oven-dried second-derivative partial least squares regression models for 36 compost samples.

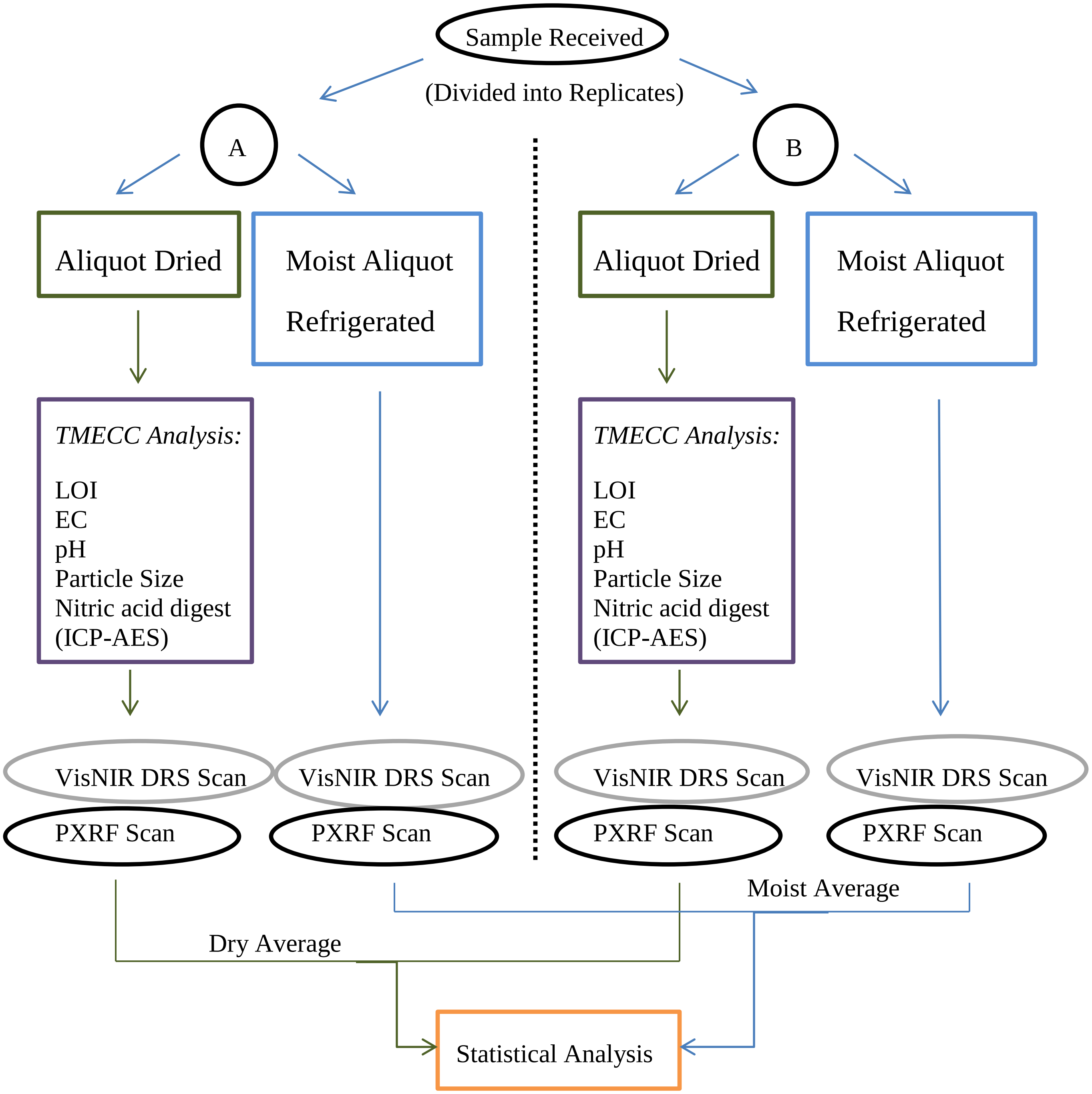
APPENDIX E: SAS CODE FOR PXRF AND ICP-AES REGRESSION

(Example given for comparison of Cu for PXRF dry scans)

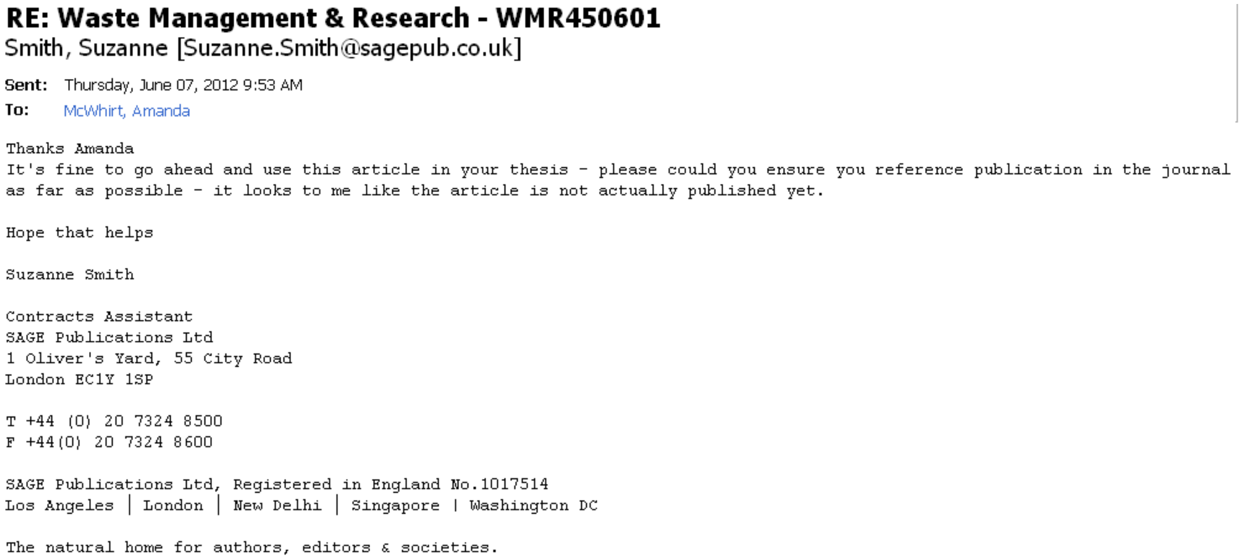
```
dm 'log; clear; output; clear';

options nodate nocenter pageno = 1 ls=78 ps=53;

title1 'XRF v ICP- Cu';

data elemental;

title 'Regression of XRF and ICP data for CU';

input Asnitric Banitric Canitric Cdnitric Conitric Crnitric Cunitric Fenitric Knitric Mnnitric
Ninitric Pnitric Pbnitric Znnitric Asxrfdry Baxrfdry Caxrfdry Cdxrfdry Coxrfdry Crxrfdry
Cuxrfdry Fexrfdry Kxrfdry Mnxrfdry Nixrfdry Pxrfdry Pbxrfdry Znxrfdry Asxrfwet Baxrfwet
Caxrfwet Cdxrfwet Coxrfwet Crxrfwet Cuxrfwet Fexrfwet Kxrfwet Mnxrfwet Nixrfwet Pxrfwet
Pbxrfwet Znxrfwet;

cards;

<INFILE READ HERE>

ODS RTF file= 'D on SPESS-S301-08:\Cu1.RTF';

run;

Proc Print data=elemental;

Run;

Proc plot data=elemental;

title2 'Scatter plot of Nitric versus XRF-Dry;

plot Cunitric*Cuxrfdry;

run;

Proc reg data=elemental;

title2 'Simple Linear Regression between xrfdry and ICP';

Model Cuxrfdry=Cunitric /p clb cli clm all influence collin partial;

OUTPUT out=outdata p=Predicted r=resid cookd=cooksd dffits=diffits H=hat

    STUDENT=student rstudent=rstudent lclm=lclm uclm=uclm lcl=ccl ucl=ucl;

run;
```

```
Proc print data=outdata;

title2 'Listing of Observation Diagnostics';

Var Cuxrfdry predicted resid student rstudent;

run;

Proc plot data=outdata;

Title3 ‘Residual plot’;

Plot Cunitric*Cuxrfdry;

Run;

Proc Univariate  data=outdata normal plot;

Title3 ‘Residual Analysis’;

Var Resid;

Run;

quit;
```

APPENDIX F: LABORATORY ANALYSIS SCHEME



APPENDIX G: PERMISSION TO REPRINT



RE: Waste Management & Research - WMR450601

Smith, Suzanne [Suzanne.Smith@sagepub.co.uk]

Sent: Thursday, June 07, 2012 9:53 AM
To: McWhirt, Amanda

Thanks Amanda
It's fine to go ahead and use this article in your thesis - please could you ensure you reference publication in the journal as far as possible - it looks to me like the article is not actually published yet.

Hope that helps

Suzanne Smith

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VITA

Amanda McWhirt was born in 1986 and grew up in Lee’s Summit, Missouri. She obtained a Bachelor of Science in Horticulture and graduated *summa cum laude* in 2007 from Tarleton State University in Stephenville, Texas. She then worked as a protected areas management advisor while serving as a Peace Corps volunteer in Honduras. She entered Louisiana State University in January 2011 to begin work on a Master of Science in Agronomy. The title of her thesis is, “Visible Near-infrared Diffuse Reflectance Spectroscopy and Portable X-ray Fluorescence Spectroscopy for Rapid Compost Analysis”.