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COMPARATIVE STUDY OF THE MID-IR SPECTROSCOPY AND CHEMICAL METHOD FOR SOIL PHYSICAL AND CHEMICAL PROPERTIES

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ABSTRACT

Mid-IR spectroscopy is a fast soil analytical tool and can serve as alternative to the time consuming and hazardous chemical methods for the determination of soil physical and chemical analyses. To determine the degree of correlation between these two methods, 110 soil samples from the derived savanna region of Nigeria were analyzed using both chemical and spectroscopic methods. The MIR absorbance spectra were recorded in the range of 4000 to 400 cm-1 (2500-25000 nm) with 110 scans. Before the absorbance spectra were calibrated to predict soil properties, principal component analysis was conducted to detect sample outliers (6 out of 110 scans were identified as outliers) in the raw data set of the spectra and excluded. Satisfactory predictions (r2 = 0.65 - 0.75) were obtained for sand, silt and clay as regards the physical properties as well as total C, total N, P, Ca, Mg, K, Mn, Fe, Cu (all determined using mehlich-3 extractant) for soil chemical properties. However, poorer predictions (r2 = 0.61-0.64) were obtained for mehlich 3-Na and Zn only. With this high degree of prediction, it can be concluded that mid-IR spectroscopy has the potential to provide rapid and cost effective estimates of some soil physical and chemical properties.

Keywords: mid-IR spectroscopy, chemical methods, soil physical properties, soil chemical properties

INTRODUCTION

Information on soil chemical and physical properties is needed to give advice on land management. This is especially true in developing countries, where soil diagnostic surveillance systems have been proposed to overcome data shortages (Shepherd & Walsh, 2007). Conventional assessments (methods and measurements) of soil capacity to perform specific agricultural and environmental functions are time consuming and expensive. In addition, repeatability, reproducibility and accuracy of conventional soil analytical data are major challenges. Rapid methods as well as new to quantify soil properties are needed, especially in developing countries, where reliable data on soil properties is sparse, and to take advantage of new opportunities for digital soil mapping. Mid infrared diffuse reflectance spectroscopy (MIR) is gaining recognition globally as a rapid analytical tool (Reeves et al., 2006). IR is a proven technology for rapid, non-destructive characterization of the composition of materials based on the interaction of electromagnetic energy with matter. It is now routinely used for analyses of a wide range of materials in laboratory and process control applications in agriculture, food and feed technology, geology, biomedicine, and space exploration. It has also been a key technology in enabling the development of soil health surveillance systems by providing a rapid and reliable tool for soil health screening (Shepherd & Walsh, 2007).The infrared spectral measurements provide capability for rapid and low cost prediction of a suite of soil properties in one pass. On The African Soil Information Systems (AfSIS) had employed the system of analyzing 5% of the total soil samples using conventional laboratory measurements and the remaining 95% are predicted using the spectral method (Forkuor et al., 2017). Mid-infrared (MIR) diffuse reflectance spectroscopy has been discovered to be a reliable and fast soil analytical tool (Janik et al., 1998) that could form a basis for diagnostic surveillance systems. Soil properties are predicted either by direct absorption of the light associated with functional groups (properties such as organic C, total N, or clay composition; Van der Marel & Beutelspacher, (1976) or by correlation to such properties and the mineral composition of the soil (properties such as cation exchange capacity (CEC) and soil texture). New samples can be predicted only if they fall within the property range of the calibration set (Naess et al., 2002). In many situations, a rapid and approximate estimate of soil chemical and physical properties is adequate, and resources for an elaborate analysis may not be available (Vagen Tor-Gunnar et al., 2010). In a study at Sud-Kivu, Congo, Bashagaluke Janvier et al. (2013) reported the efficacy of MIR to predict pH, soil organic C, total N, Al, Ca, Mg K, CEC and soil texture for 536 composite soil samples taken from two locations at two depths (0-20 cm and 20-40 cm) using a spatially-stratified random sampling design within an area of 200 km2. Mid IR and near infrared spectroscopy (NIR) are being applied in soil analysis by other Australian research groups including the Department of Primary Industries in Western Australia and Queensland (Viscarra & Hicks, 2015). The CSIRO is concentrating their efforts on developing a national MIR/NIR database to focus on soil organic carbon analysis. Internationally there is considerable research effort being input into developing NIR and MIR calibrations for rapid estimation of soil parameters (Janik et al., 1998). However, in Nigeria, the use of mid-IR to determine soil properties is sparse or even not existing. Therefore, this study was set out to evaluate the ability of the mid-IR spectroscopy to predict some soil physical and chemical properties, and to correlate the results obtained with measured values through the wet chemistry

METHODOLOGY

Sample preparation

Each soil sample was air-dried by spreading the sample out as a thin layer on paper sheets. The drying was done, ensuring that no material from the whole sample was lost or discarded. Contamination from dust or other potential contaminants was avoided because of subsequent determination of trace elements.

Sieving and Sub-sampling

The whole dried soil sample was crushed using a wooden rolling pin, to pass through a 2 mm mesh size sieve while all plant materials were removed. The coning and quartering is a procedure whereby a quantity of soil sample was made into a cone shape and later flattened by means of a ruler this was done about three times before dividing it into four equal part, the alternate part were merged into one part and bulk for use while the other parts were stored away. The procedure was used to obtain a representative 20 g subsample of soil which was grinded with agate mortar and sieved using 0.2mm sieve to get a fine powder particle size for MIR spectral analysis. The sub-sampled soil was then placed in a zip-lock polyethene bag and labeled as “fines”.

Scanning

Infrared light energy was focused onto the surface of the air-dry soil sample in the cone. Some of this light is absorbed by the soil, but the rest is reflected back into the spectrophotometer, detected and analyzed. The spectral produced corresponds to the various properties of the soil scanned.

Chemical analysis by wet digestion

Particle size distribution was determined by the hydrometer method (Bouyoucos, 1962) using sodium hexameta-phosphate as the dispersing agent. Soil pH was determined in distilled water (1:1 soil water ratio) with a pH meter. Exchangeable cations (K, Na, Ca, and Mg) by extraction, with ammonium acetate (pH= 7). Available P was extracted with 0.03N NH4F in 0.025N HCl solution (Bray & Kurtz, 1945). The phosphorus in the extracts was determined by the methyl blue colour method of Murphy & Riley (1962). Soil organic C was determined by wet digestion with sulphuric acid (Walkey & Black, 1934).Total N was determined by the kjeldahl procedure of Bremner & Malvaney (1982). Micronutrients- Cu, Fe, Zn and Mn were extracted with 0.1N HCl as described by Osiname et al. (1973)

Statistical methods

All calculations and statistical analysis was done using R software (R development Core Team, 2008)

RESULTS

Physical and chemical properties of the soil by wet digestion

The sand fraction of the soil ranged between 326 and 775.2 g kg^{-1} while the silt fraction ranged between 74.6 and 600 g kg^{-1} and the clay fraction was between 54 and 799.4 g kg^{-1}. The results of the particle size distribution signifies that the soil was loamy sand in nature (Table 1).

The pH of the soil ranged between 4.88 and 7.58, signifying that the soil varied between strongly acidic and slightly alkaline. Total nitrogen (N) was very low with a range of 0.01 to 0.53 % while organic carbon (C) was either low or very high ranging from 0.13 to 5.28 %. As observed for organic C, available phosphorus was also either low or very high with a range between 0.06 and 36.98 mg kg^{-1}. Exchangeable potassium (K) and calcium (Ca) were very low in some of the areas whereas they were high some other areas with their values ranged from 0.16 to 1.39 and 0.14 to 3.15 cmol kg^{-1}, respectively.

Exchangeable magnesium (Mg) was low and ranged between 0.10 and 0.53 cmol kg^{-1}

while sodium in some areas was just adequate while other areas were above the preferred level of 1 cmol kg^{-1}. The micronutrients determined were all low. Available Fe ranged between 0.72 and 7.05 mg kg^{-1}, Mn between 0.52 and 20.23 mg kg^{-1}, Cu between 0.03 and 0.4 mg kg^{-1}, and Zn between 0.11 and 0.81 mg kg^{-1}.

Table 1: Physical and Chemical properties of the soil by wet digestion

	Range	Mean
pH	4.88-7.58	5.98
Sand (g kg^{-1})	326.00-775.20	591.60
Silt (g kg^{-1})	74.60-600.00	229.30
Clay (g kg^{-1})	54.00-799.40	189.40
Total N (g kg^{-1})	0.10-5.30	1.50
Organic C (g kg^{-1})	1.30-52.80	14.60
Exchang. bases(cmol kg^{-1})		
K	0.16-1.39	0.48
Na	0.60-1.15	1.09
Ca	0.14-3.15	0.73
Mg	0.10-0.53	0.30
Available P (mg kg^{-1})	0.06-36.98	6.43
Cu	0.03-0.40	0.16
Zn	0.11-0.81	0.37
Fe	0.72-7.05	2.96
Mn	0.52-20.23	5.80

Physical and chemical properties of the soil by dry analysis

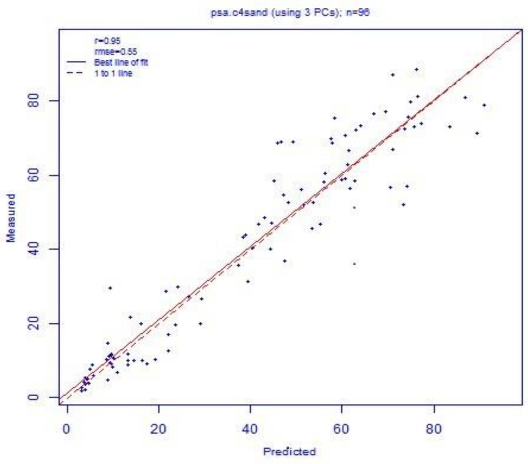
The results of the particle size distribution showed that most soil were either loamy sand or sandy clay in nature with the sand fraction ranging between 399.9 and 735.4 g kg^{-1}, clay fraction between 81 to 340.5 g kg^{-1} and the silt fraction were between 151.7 and 286.4 g kg^{-1} (Table 2). The soil pH varied from strongly acidic to neutral with a range between 5.52 and 6.82. Total N was very low and ranged between 0.02 and 0.40 % while available P was either low or moderately available with a range between 1.42 and 13.48 mg kg^{-1}. Exchangeable K was either low or slightly high with a range between 0.21 and 0.87 cmol kg^{-1}. Exchangeable Ca was either low or moderately available with a range between 0.50 and 2.06 cmol kg^{-1} while Mg was low with a range between 0.16 and 0.45 cmol kg^{-1}. Exchangeable K was either low or slightly high with a range between 0.21 and 0.87 cmol kg^{-1} while Na was either adequate or above the preferred level in some locations with a range between 0.81 and 1.44 cmol kg^{-1}. The available micronutrients were all low, Fe ranged between 2.02 and 3.74 mg kg^{-1}, Mn between 0.89 and 16.33 mg kg^{-1}, Cu between 0.08 and 0.24 mg kg^{-1} and Zn between 0.23 and 0.60 mg kg^{-1}.

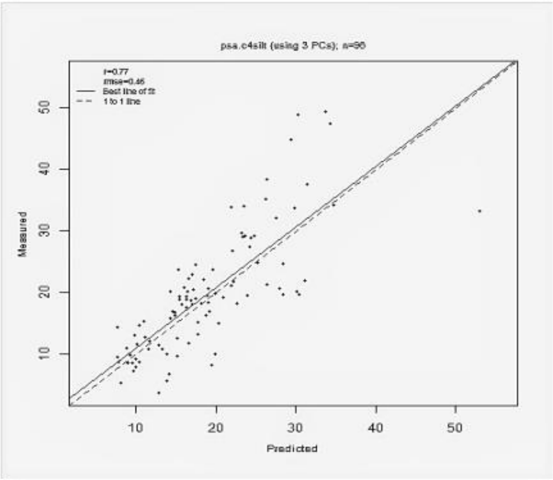
Table 2: Physical and Chemical properties of the soil by dry analysis

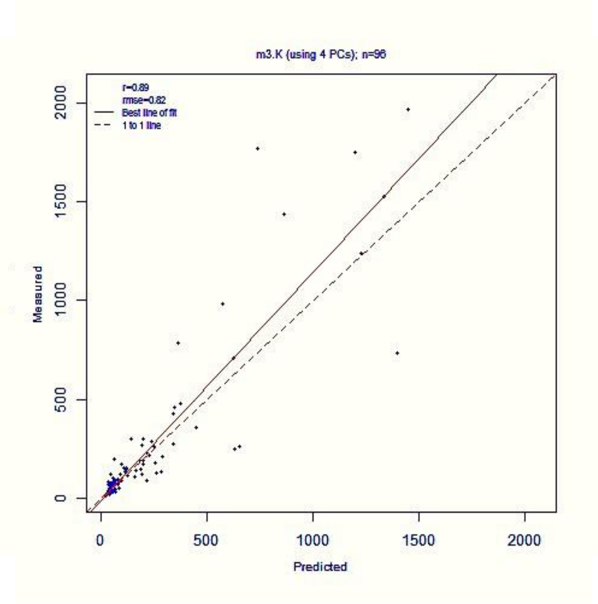
	Range	Mean
pH	4.88-7.58	5.98
Sand (g kg-1)	399.90-735.40	584.70
Silt (g kg-1)	151.70-286.40	214.80
Clay (g kg-1)	81.00-340.50	175.70
Total N (g kg- 1)	0.20-4.00	1.30
Organic C (g kg-1)	2.00-39.70	13.00
Exchangeable bases (cmol kg-1)		
K	0.21-0.87	0.44
Na	0.81-1.44	1.07
Ca	0.50-2.06	1.34
Mg	0.16-0.45	0.29
Available P (mg kg-1)	1.42-13.48	4.67
Cu	0.08-0.24	0.15
Zn	0.23-0.60	0.36
Fe	2.02-3.74	2.85
Mn	0.89-16.33	5.18

Relationship between the wet and dry analysis methods

The relationship between wet and dry analysis of silt fraction and available micronutrients such as Fe and Cu showed high correlations with coefficient of determination of 0.77, 0.70 and 0.79 respectively while other soil fractions had higher coefficient of determination of 0.95 for sand and clay (Fig 1). Coefficient of determination of exchangeable Ca was 0.89 while exchangeable Mg had its own coefficient of determination (r^2) to be 0.94. Exchangeable K was also better correlated with coefficient of determination of 0.89 while total N and organic C were best predicted with a coefficient of determination of 0.96 each. However, poorer predictions (at 5% probability) were observed for Zn (r^2 = 0.62), pH (r^2 = 0.65) and Na (r^2= 0.53)



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r=0.89
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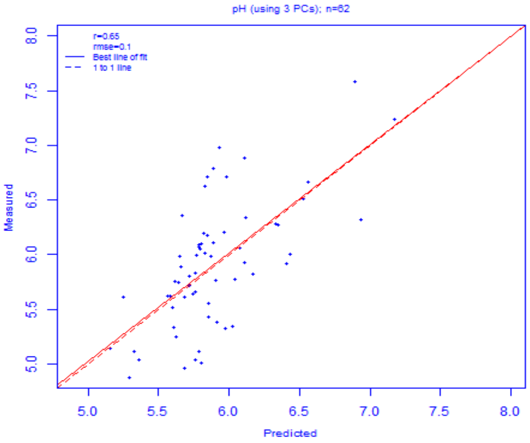
1 to 1 line
Measured
0
500
1000
1500
2000
Predicted
0
500
1000
1500
2000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rmse=0.1
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1 to 1 line
Measured
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5.5
6.0
6.5
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7.5
8.0
Predicted
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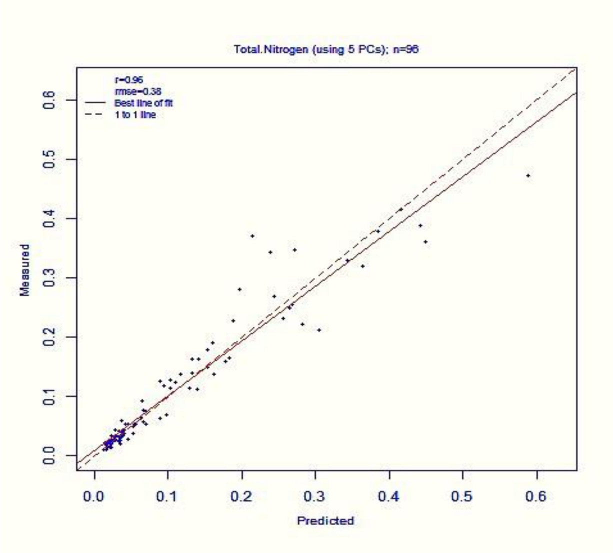
5.5
6.0
6.5
7.0
7.5
8.0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1 to 1 line
Measured
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0.1
0.2
0.3
0.4
0.5
0.6
Predicted
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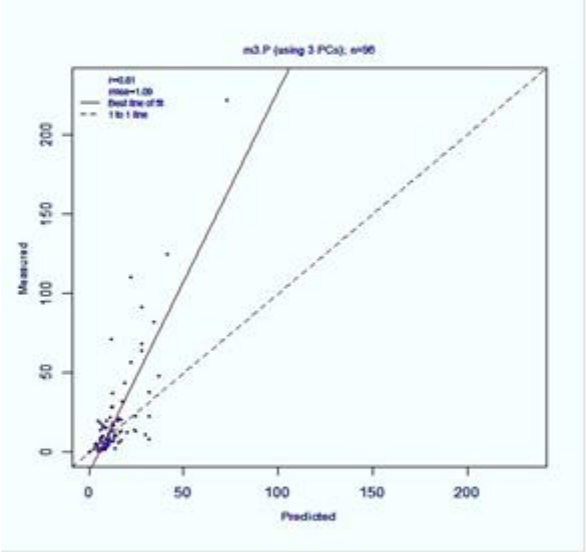
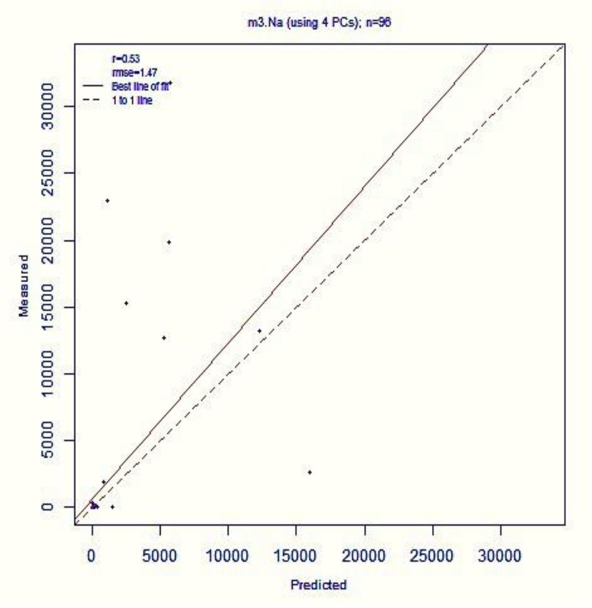
0.3
0.4
0.5
0.6


m3.P (using 3 PCs); n=96
r=0.81
rmse=1.09
Best line of fit
1 to 1 line
Measured
0
50
100
150
200
Predicted
0
50
100
150
200


m3.Na (using 4 PCs); n=96
r=0.53
rmse=1.47
Best line of fit
1 to 1 line
Measured
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10000
15000
20000
25000
30000
Predicted
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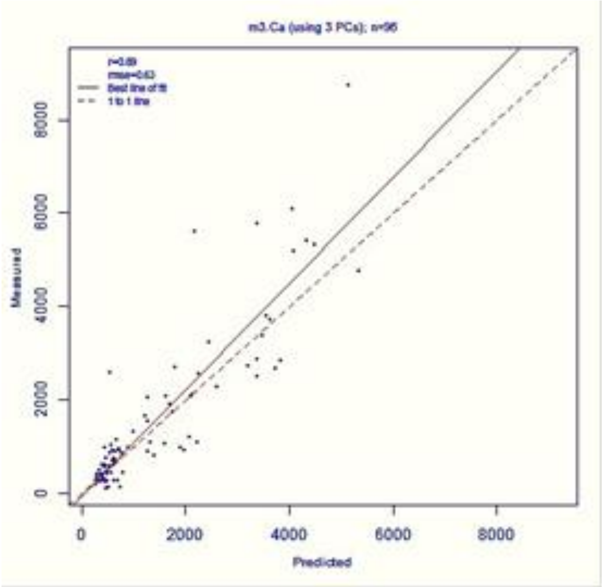
5000
10000
15000
20000
25000
30000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rmse=0.63
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4000
6000
8000
Predicted
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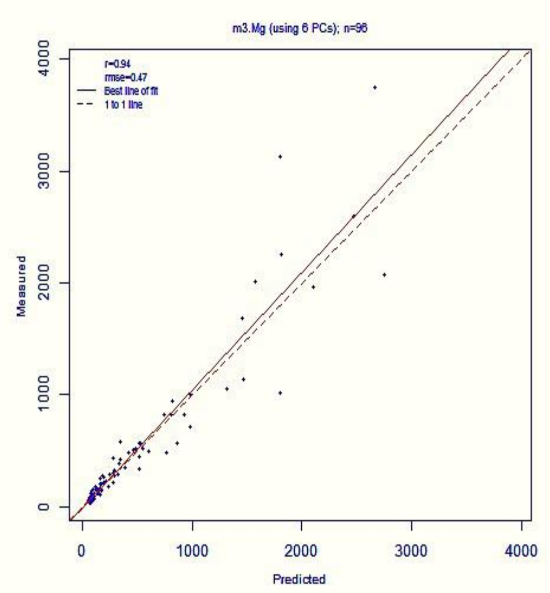
2000
4000
6000
8000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r=0.94
rmse=0.47
Best line of fit
1 to 1 line
Measured
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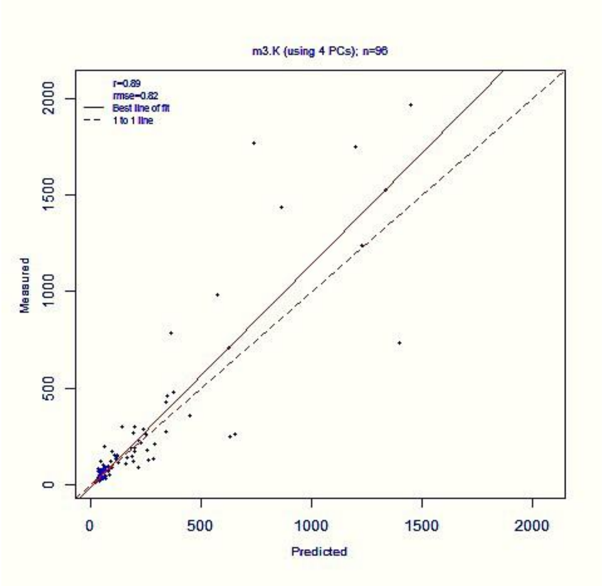
1000
2000
3000
4000
Predicted
0
1000
2000
3000
4000


m3.K (using 4 PCs); n=96
r=0.89
rmse=0.82
Best line of fit
1 to 1 line
Measured
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500
1000
1500
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Predicted
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500
1000
1500
2000

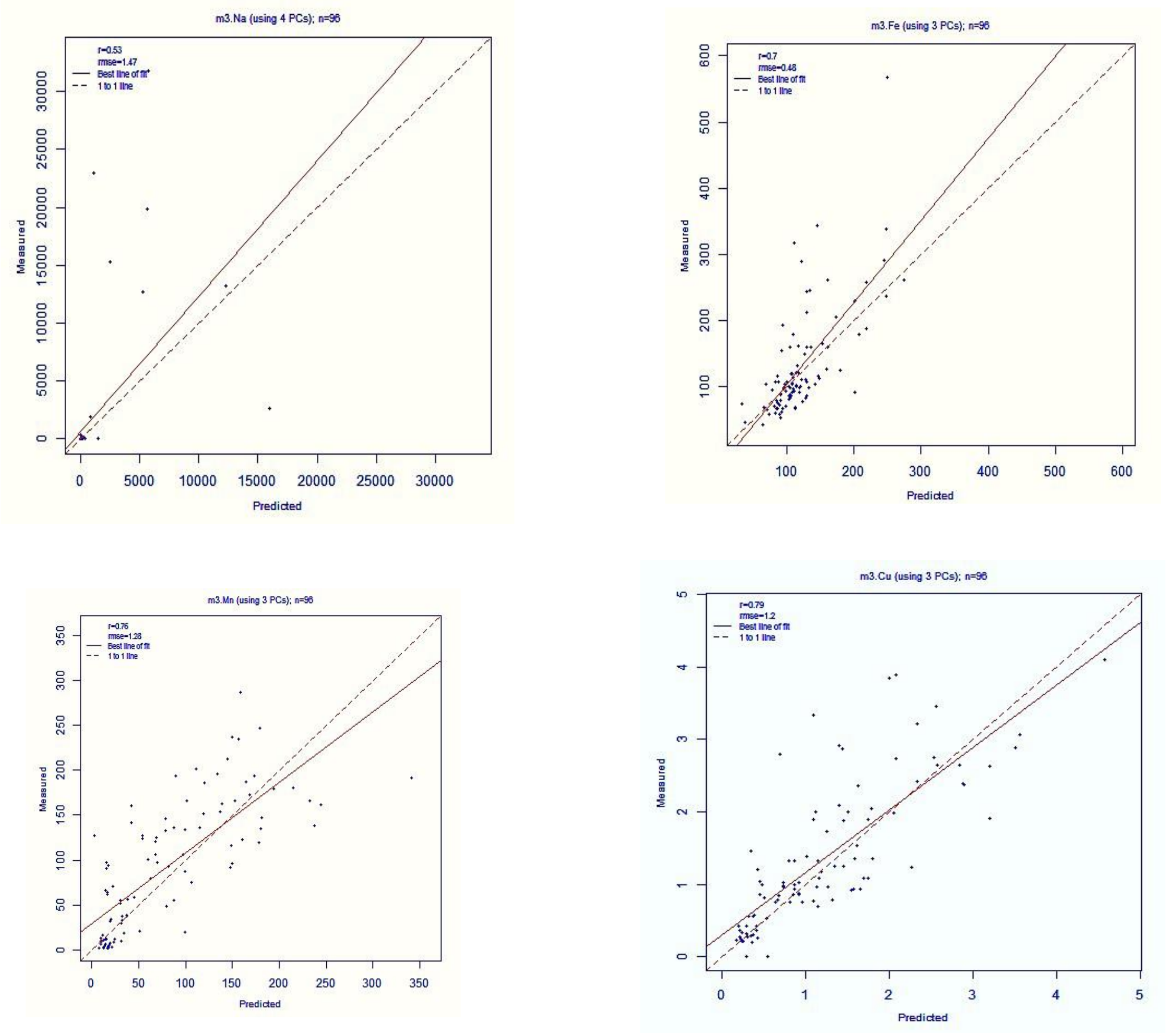

Fig 1: The relationship between values measured by wet digestion and predicted using the mid-IR Spectroscopy

Discussion

Comparison of wet and dry analysis for soil chemical properties determination

Recent studies have shown the possibility of using infrared reflectance spectroscopy and in order to obtain qualitative and quantitative assessment of some chemical and physical parameters of the soil rapidly and at low cost (Shepherd & Walsh, 2002, Terhoeven et al, 2010). This was further confirmed in the similarities obtained between the results by wet digestion and through the use of mid-IR. Similar results were obtained for most of the parameters especially pH, total N, organic C, available P, K, Na, Ca and Mg. These results brings an assurance that the recommendation of AFSIS can be relied on and which says a random subset of samples(10%) should be analyzed using standard wet chemistry methods while the remaining 95 % by scanning using the mid-IR (Bashagaluke et al., 2015). Numerous studies have also demonstrated the effectiveness of MIR in performing quantitative analysis of soils (Reeves et al., 1999; Shepherd & Walsh, 2002; Christy, 2009).

Correlation between the wet and dry analysis methods

Soil spectroscopy in the MIR region with a partial least squares regression (PLS) model in this study has shown to be a promising method for the determination of soil chemical properties in this study and was demonstrated using partial least squares regression (PLS) to compare the two methods. Earlier studies (Brown et al., 2006; Bashagaluke et al., 2013; Madari et al., 2005) showed that MIR gave good predictions for organic C and total N. For instance, Brown et al. (2006), using a sample set of 416 samples. obtained correlation coefficient (r2) of 0.83 – 0.91 for organic C while in another study, Bashagaluke et al., (2013) recorded coefficients of determination of between 0.71 and 0.93 for soil organic C, total N, Ca and Mg. These results were similar to the coefficients of determination obtained in our study. Also, Madari et al (2005), using 1135 soil samples from Brazilian National soil collection, obtained good predictions (r2= 0.95) for total C using MIR spectra while Misun (2002) obtained coefficient of determination of 0.96 for soils from the flood plains in the US.

Conclusion

Analysis of soil properties have been carried for years using the wet digestion method. However, the mid-IR (MIR) spectrophotometry method provides a rapid, non-destructive, cheap measurements of both physical and chemical parameters. The results obtained showed great similarities between the results obtained through wet digestion and the use of MIR. This was further confirmed through correlation between the measured and predicted values. Most of the soil properties were well predicted and satisfactory and therefore the use of MIR for determination of soil properties can be depended upon.

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