Soil spectral diagnostics – infrared, x-ray and laser diffraction spectroscopy for rapid soil characterization in the Africa Soil Information Service

Keith D Shepherd[A]

[A]World Agroforestry Centre (ICRAF), PO Box 30677-00100, Nairobi, Kenya, Email k.shepherd@cgiar.org

Abstract

One of the key challenges in establishing the Africa Soil Information Service (AfSIS) is how to measure soil functional properties on tens of thousands of georeferenced soil samples in a consistent way. To solve this problem, AfSIS uses spectral diagnostics – low cost, high throughput analytical techniques based on reflectance of electromagnetic radiation. This paper describes use of infrared spectroscopy (IR), total x-ray fluorescence spectroscopy (TXRF), x-ray diffraction (XRD), and laser diffraction particle size analysis (LDPSA) techniques. The data generated by these high-throughput techniques can all be treated as spectra and used as input to pedotransfer functions for prediction of soil functional properties that are expensive or time-consuming to measure. In addition, comparative LDPSA data for different dispersion treatments can provide functional indicators of soil stability. Further research should establish the added value or redundancy in pedotransfer functions when IR is complemented with TXRF, XRD and LDPSA data.

Key Words

Spectral diagnostics, infrared spectroscopy, x-ray fluorescence, laser diffraction, Africa soils, pedotransfer functions

Introduction

The Africa Soil Information Service (www.africasoils.net) is being established to provide accurate, up-to-date and spatially referenced soil information to support agricultural development and scientific advancement in Africa. This need coincides with advances in technologies that allow for accurate collection and prediction of soil properties (Sanchez *et al.* 2009). The project will develop a practical, timely, cost-effective, soil health surveillance service to map soil conditions, set a baseline for monitoring changes and to provide options for improved soil management. Soil testing under AfSIS is designed to meet the diverse needs of different users: diagnosis of soil constraints for agriculture, monitoring of trends in soil health, land capability for agriculture, soil testing for engineering and stabilisation purposes, ecological and human health risk assessment; and prognostic testing to inform investment decisions (e.g. fertilizer rates, soil conditioners, soil drainage, soil conservation). Over the next four years the project will collect over 30,000 georeferenced soil samples from sub-Saharan Africa and characterize them. This paper describes how low cost high-throughput spectroscopy methods are being used both as a front line screening technique for development of pedo-transfer functions and for the direct development of indicators of soil functional properties.

Methods

Soil processing

All soil samples are initially air-dried and 2-mm sieved. A 20 g sub-sample of soil is obtained by coning and quartering and hand-ground using an agate pestle and mortar to pass a 75 µm sieve. These finely ground samples can be shipped at low cost and are adequate for analysis by mid-infrared diffuse reflectance spectroscopy (MIR), TXRF, XRD, LDPSA, and total CNS analysis by combustion.

Infrared spectroscopy

Diffuse reflectance infrared spectroscopy (IR) is an established technology for rapid, non-destructive characterization of the composition of materials based on the interaction of electromagnetic energy with matter. Both the visible near infrared (VNIR, 0.35-2.5 µm) and mid infrared (MIR, 2.5-25 µm) wavelength regions have been investigated for non-destructive analyses of soils and can potentially be usefully applied to predict a number of important soil properties. including: soil colour, mineral composition, organic matter and water content (hydration, hygroscopic, and free pore water), iron form and amount, carbonates, soluble salts, and aggregate and particle size distribution (Shepherd and Walsh, 2004; 2007). In AFSIS, IR is used as a frontline screening tool in regional laboratories using 2-mm sieved air-dried soil samples. The regional laboratories are equipped with fourier-transform NIR spectrometers with in-built gold reference and instrument validation routines to ensure reproducibility of results over time and among laboratories. All other measurements are centralized at the World Agroforestry Centre's Soil-Plant Spectral Diagnostics Laboratory, except for conventional extraction soil tests, which are done using ICP mass spectroscopy in an external certified laboratory. Fine ground samples are analysed with MIR using a robotic high-throughput system employing micro-titre plates (Shepherd and Walsh, 2007).

Total x-ray fluorescence spectroscopy
TXRF (KlocKenKämper 1997) provides for rapid simultaneous analysis of all elements from Na to U (except Mo) with minimal sample preparation time. The main principle of X-ray Fluorescence Spectroscopy is that atoms, when irradiated with X-rays, emit secondary X-rays – the fluorescence radiation. On this basis XRF analysis is possible because (i) the wavelength and energy of the fluorescence radiation is specific for each element, and (ii) the concentration of each element can be calculated using the intensity of the fluorescence radiation. Compared with conventional XRF, TXRF also has the advantages of greatly reduced background noise, and consequently much higher sensitivities, and a significant reduction of matrix effects. Standardisation is internal and only requires addition of an element that is not present in the sample for quantification purposes, and no external standardization is required in most cases. In AfSIS, TXRF is used to analyse total elements in soil (samples are suspended in detergent, pipetted onto carriers, and dried) and in soil water extracts after centrifuging the same sample. Lower detection limits are in the parts per million concentration range for suspended soil and parts per billion levels in soil water. The total element concentration profiles (essentially spectra) are used to fingerprint soils, to capture key mineralogical differences, and as an input to pedotransfer functions.

X-ray diffraction
Despite the critical importance of soil mineralogy in the determination of soil functional properties and as a soil forming factor, there has been relatively little work to move beyond largely descriptive studies (Dixon and Schulze, 2002) to the quantitative linking of soil function to soil mineralogy (Cornu *et al.* 2009). New instrumentation developments in benchtop high-throughput X-ray powder diffraction (XRD) and steady improvements in mineral identification databases and software have opened up new opportunities for quantitative determination of mineral phases on large sample numbers. AfSIS extends the infrared spectroscopy profiling approach (Shepherd and Walsh 2007) to include X-ray diffraction.

Finely ground (<50 µm) samples are loaded into sample holders and analysed using a X-ray diffractometer equipped with a compound silicon strip, 1-dimensional detector with Theta / Theta geometry. The angular range measured is 0 to 80° 2Theta with an accuracy of ± 0.02° throughout the measuring range. The raw XRD spectra (counts versus angle) can be used directly as input to pedotransfer functions, in the same way infrared spectra are used. Phase search, identification and semi-quantitative analysis are done using the International Centre for Diffraction libraries and fully quantitative phase analysis is proposed on subsets of samples using the Rietveld method. TXRF soil element information can also used to focus mineralogy searches.

Laser diffraction particle size analysis
Soil particle size distribution is a fundamental soil property that affects many soil functional properties, but its determination using conventional hydrometer or pipette methods suffers problems of poor repeatability and reproducibility and variable dispersion in many tropical soils, due to cementing actions of iron and aluminium hydroxides. There is uncertainty on what methods best reflect functional aspects of soil particle size distribution (e.g. dispersing aggregates using dispersion agents may not reflect functional effects in the field). In fact soil particle size is usually not interpreted directly to provide information on soil functions but is rather a covariate used in predicting or conditioning soil functional properties, such as nutrient retention, tillage properties, and hydraulic properties. Therefore emphasis should be on rapid and repeatable measures rather than accurate measures of particle size distribution.

Dry aggregate size distribution and dispersed and non-dispersed particle size distribution have been proposed as indicators of soil erodibility, even though erodibility may be affected by a number of variables. Various measures of dispersion have also been used to classify soil susceptibility to structural faults and piping in subsoil's (e.g. dam walls) and surface soil structural problems (e.g. hardsetting). Response of particle size distribution to different levels of ultrasonic energy can be used to derive an absolute measure of soil stability.

In AfSIS, laser diffraction particle size analysis is used to estimate particle size distribution and soil stability. The analysis can be done using small quantities of soil (<5 g). A representative cloud or 'ensemble' of particles passes through a broadened beam of laser light which scatters the incident light onto a Fourier lens. This lens focuses the scattered light onto a detector array and, using an inversion algorithm, a particle size distribution is inferred from the collected diffracted light data. Mie theory is used to provide a volume-based continuous distribution of particle sizes based on the correlation between the intensity and the angle of light scattered from particles.

AfSIS samples are analysed using a detectable size range of 0.01-3000 µm. The instrument allows continuous flow of a soil sample suspended in (i) a dry air stream or (ii) a water stream, to which different sonification cycles can be applied using an in-built ultrasonic probe. The protocol begins with measurement of particle size distribution of dry soil suspended in the air stream to provide a measure of micro-aggregation without wetting. Particle size distribution is then measured in water, followed by a second reading one minute later, and finally after full dispersion using Calgon and sonification. The shift in particle size distribution with these treatments is used to provide comparative indices of stability (Muggler *et al.* 1996). Destruction of organic matter and removal of soluble, salts, gypsum, carbonates, and iron and aluminium oxides is not done with this method, as comparisons of 'functional' particle size distribution are of primary interest, as opposed to accurate measurement of 'absolute' particle size distribution of primary particles. A subset of soils is also analysed using the conventional hydrometer method to provide correlations with the laser diffraction measurements.

Results

Total element concentration spectra for three contrasting soil types from Kenya are illustration in Figure 1. There is large variation in concentrations among soils in the range from element number 13 (Aluminium) to 40 (Zirconium), especially in levels of P, K, Ca, Mn, and Fe, indicating mineralogical differences. A key area of current research is how much redundancy there is in IR, TXRF, XRD and LDPSA data in prediction of functional properties such as soil water holding capacity and nutrient supply capacity.

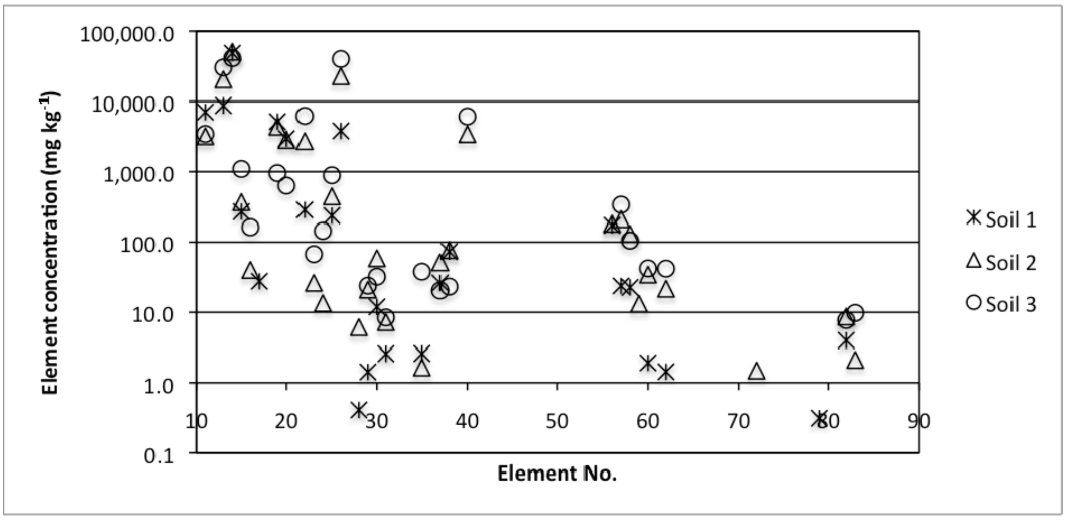

Figure 1. Total element concentration against element number for three soils from Kenya determined using total x-ray fluorescence spectroscopy. Missing data points indicate an element was not detectable in the sample.

The use of laser diffraction particle size analysis to assess soil stability on dispersion in water is illustrated in Figure 2. In the dry state, the unstable soil (a Fluvisol derived form lake sediments) actually had a higher proportion of aggregates >1 mm (51%) than the stable (Nitisol) soil (10%). On wetting, the stable soil showed little decrease in particle size distribution over the succession of wet treatments, whereas the unstable soil showed a successive decrease in particle sizes with the sequence of treatments. For the wet reading after one minute, the proportion of particles smaller than 10 µm was 56% in the unstable soil but only 14% in the stable soil. After the full dispersion treatment, the unstable soil had 83% of particles less than 10 µm, compared with 18% in the stable soil.

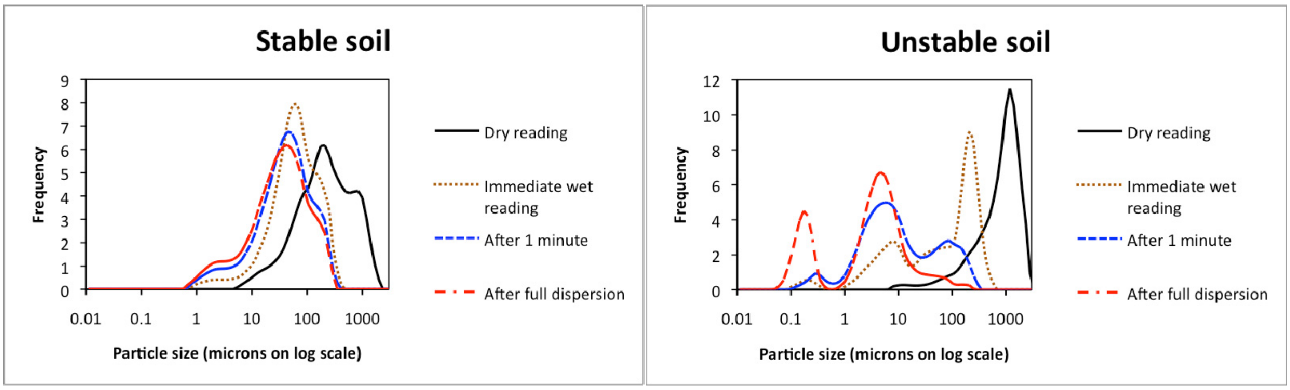

Figure 2. Frequency distribution of particle sizes in a stable soil (Nitisol) and unstable soil (Fluvisol) from Kenya measured in (i) a dry air stream, (ii) immediately on addition to water, (iii) one minute later, and (iv) after full dispersion with calgon and sonification.

Conclusion

Although infrared spectral measurements of soils can predict several soil properties (such as organic carbon, exchangeable calcium, pH, and total P) calibrations need to be adjusted for different soil types. High throughput TXRF, XRD and LDPSA measurements could supplement IR as an input to pedotransfer functions and help stabilize IR calibrations across soil types with widely different mineralogy. Further research should also test whether TXRF and XRD could be useful supplements to improve prediction of properties not predicted well from IR, such as soluble or extractable nutrients. Laser diffraction particle size analysis under different dispersion treatments can serve as a rapid, functional indicator of soil stability for environmental and engineering purposes.

References

Dixon JB, Schulze DG (2002) ‘Soil Mineralogy with Environmental Applications’. (Soil Science Society of America: Madison, WI).

Cornu S, Chevalier M, Hardy M, Bourenane H, Josiere O, Pernes M, Jolivet C, Boulonne L, Arouys D (2009) X-ray diffraction of minerals carrying trace elements in soil: application to the French soil quality monitoring network. *Comm. Soil Sci. Plant Anal*. **40**, 1138-1147.

KlocKenKämper R (1997) ‘Total-Reflection X-Ray Fluorescence Analysis’. (Wiley & Sons).

Muggler CC, Pape Th, Buurman P (1996) Laser grain-size determination in soil genetic studies. 2 Clay content, clay formation and aggregation in some Brazilian Oxisols. *Soil Sci*. **162**, 219-228.

Sanchez, PA (2009). Digital soil map of the world. *Science* **325**, 680-681.

Shepherd KD, Walsh MG (2004). Diffuse reflectance spectroscopy for rapid soil analysis. In ‘Encyclopedia of Soil Science’. (Ed R Lal) (Marcel Dekker Inc, New York. Online Published by Marcel Dekker: 04/26/200).

Shepherd KD, Walsh MG (2007) Infrared spectroscopy—enabling an evidence-based diagnostic surveillance approach to agricultural and environmental management in developing countries. *Journal of Near Infrared Spectroscopy* **15**, 1-19.