Total elemental composition of soils in Sub-Saharan Africa and relationship with soil forming factors

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ABSTRACT

A thorough understanding of the variation in total soil element concentrations is important especially in the Sub-Saharan Africa (SSA) soil contexts for agricultural and environmental management at large scale. Fingerprinting of soil elemental composition may form a useful basis for evaluating soils in a way that relates to soil-forming factors and inherent soil functional properties. The objectives of this paper are to quantify the proportion of variability in total elemental composition by total X-ray fluorescence (TXRF) method of 1074 soil samples from the Africa Soil Information Service (AfSIS) Project baseline and to determine the relationships with soil forming factors. The samples were from 34 sentinel sites measuring 10×10 km, randomized within major climate zones in SSA. Within each sentinel site there were sixteen spatially stratified 1 km^2 clusters, within which there were ten 100 m^2 plots. The within and between site patterns of variation in total element composition of 17 elements; Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Sr, Y, Ta, and Pb, were explored. Total element concentration values were within the range reported globally for soil Cr, Mn, Zn, Ni, V, Sr, and Y and higher than reported range for Al, Cu, Ta, Pb, and Ga. There were significant variations ($P < 0.05$) in total element composition within and between the sites for all the elements analyzed with the greatest proportion of total variance and number of significant variance components occurring at the site (55–88%) followed by the cluster nested within site (10–40%) levels. The explorations of the relationships between element composition data and site factors using Random Forest regression demonstrated that soil-forming factors have important influence on total elemental composition in the soil. The fact that the soil-forming factors are related to the concentration of naturally occurring elements in the soil gives rise to the notion that they might be predicted from the soils' element composition. Results implied that >70% of variation in soil element composition patterns can be predicted using information in existing databases or readily observable features. Successful use of TXRF technique would open up possibilities for using total soil elemental composition fingerprints as a useful basis for characterizing soils in a way that relates to soil-forming factors and inherent soil functional properties.

1. Introduction

Knowledge of the distribution and baseline concentrations of major and trace elemental contents in soils will help to assess soil, land and environmental quality especially in developing countries in Sub-Saharan Africa (SSA). Fingerprinting of soil elemental composition may form a useful basis for classifying soils in a way that relates to soil-forming factors and inherent soil functional properties (Kabata-Pendias and Mukherjee, 2007; Rawlins et al., 2012). This is due to the fact that variations in the concentrations of soil chemical elements are derived from differences in the composition of the parent material and from fluxes of matter and energy into or from soils over time (Helmke, 2000; Rawlins et al., 2012). In addition, soil-forming factors (e.g., parent material, climate, topography, vegetation and time) are important drivers of total elemental concentrations in the soil (Jenny, 1941). The nature of the key variables explaining ecological diversity of soils can be related to the mineralogy of parent rock and although these relationships have been inferred, mineralogy of parent rock is a principal factor determining spatial patterns of land resources (Voortman, 2011). The mineralogy and elemental composition of soil are related to the nature

of the parent material and the degree to which this material has been weathered (Negrel et al., 2014).

Soil mineralogy is a key determinant of many soil functional properties, for example nutrient quantities and intensities, pH and buffering, anion and cation exchange capacity, aggregate stability, soil carbon protection, dispersion, and resistance to erosion. Primary associations of elements reflect mineralogy and some elements can thus be used as proxies for mineralogy including heavy minerals, carbonates and clays (Grunsky et al., 2009). While total elemental concentrations in soil reflect parent material concentrations are also impacted by weathering rates and over the longer term by land use and climate. Rawlins et al. (2009) demonstrated use of element composition for the prediction of particle size distribution and their errors.

There is potential for increasing the knowledge of the spatial extent of trace elements using recent advances in analytical chemistry and increasing applications. Total X-ray fluorescence spectroscopy (TXRF) is a relatively new technique that can provide for a rapid and simultaneous determination of the concentrations of many elements from Na to U in the periodic table with minimal sample preparation time and low matrix interferences (Stosnach, 2005; Towett et al., 2013). However, TXRF has not been widely used as an analytical technique for the total element composition of soils of SSA due to low number of well equipped soil labs. Towett et al. (2013) tested a method for the use of TXRF for direct quantification of total element concentrations in soils, demonstrating the potential utility of TXRF for rapid screening of total element concentrations in soils assuming sufficient calibration measures are followed. Successful use of the TXRF technique would open up the possibilities for using total element composition to improve global predictions of soil properties, such as cation exchange capacity and available nutrients, especially in Africa where variations in soil mineralogy and nutrient balance critically determine vegetation composition and agricultural potential (Voortman, 2011).

This paper uses data from several projects, including the first phase (2009–2012) of the Globally Integrated Africa Soil Information Service (AfSIS) project, which was a research-based project to develop a practical, timely, and cost-effective soil health surveillance service to map soil conditions, set a baseline for monitoring changes, develop global standards and methodologies, and provide options for improved soil and land management in Africa (Vågen et al., 2010). The AfSIS project area included about 17.5 million km² of continental Sub-Saharan Africa (SSA), excluding hot and cold deserts, encompassing more than 90% of Africa's human population living in 42 countries. All of the data used for this paper were taken from AfSIS sites surveyed using the Land Degradation Surveillance Framework (LDSF), (Vågen et al., 2010, 2015; Vågen and Walsh, 2012) in the period from January 2010 to March 2012. The LDSF utilizes novel data collection methodologies that are efficient, cost-effective, and vastly improve the analytical precision of the landscape level estimates by producing a suite of soil and vegetation indicators that are spatially specific and continuous across the surveyed landscape (Shepherd et al., 2015; Vågen and Walsh, 2012; Vågen and Winowiecki, 2013; Vågen et al., 2010, 2013; Winowiecki et al., 2015). These include new direct soil spectral methods using only light (visible, infrared and X-ray) that hold promise for providing rapid, low cost and reproducible soil characterization (Shepherd, 2010). The hierarchical, systematic and random sampling approach reduces sampling effort and cost. The LDSF is intended to provide a whole landscape (systems) perspective to land use planning and decision making to enable countries to both increase agricultural productivity and maintain ecosystem services (Winowiecki et al., 2015; Shepherd et al., 2015). The potential for spectroscopy as a key component of soil health surveillance systems has already been articulated (Shepherd and Walsh, 2007; Shepherd et al., 2015). This work thus set out to determine the usefulness of TXRF as an analytical technique for the total element composition of soils from 34 LDSF sentinel sites. Specific objectives of this paper were to evaluate the relationship between TXRF total element concentrations in soils and to test how well element composition is predicted by soil

forming factors as such relationships could then be used as proxies to infer soil functional properties.

2. Materials and methods

2.1. Study area and sampling

The current study was based on georeferenced samples associated with the AfSIS project taken from a set of thirty four 100-km² LDSF sentinel sites: Ghana (3 sites), Tanzania (8 sites), Ethiopia (4 sites), Mali (3 sites), Burkina Faso (1 site), Mozambique (4 sites), Nigeria (3 sites), Zambia (1 site), Kenya (3 sites), Guinea (2 sites), and Malawi (2 sites) (Fig. 1). Field sampling was conducted based on the field methods collectively referred to as LDSF protocol (Vågen et al., 2010), also described in Vågen et al., 2012, 2015, and Winowiecki et al., 2015. Within each sentinel site there were ten 1000 m² plots randomized within sixteen spatially stratified 1 km² clusters. Topsoil (0–20 cm) and subsoil (20–50 cm) samples were collected from Plot 1 from each cluster giving a total of 1074 samples (16 plots per site × 2 soil depths × 34 sentinel sites). A summarized description of the 34 sentinel sites from which the soil samples used for this study were collected, including the location, average elevation, annual total precipitation, temperature ranges, major soil classes (based on the IUSS Working Group WRB (2014) and the FAO/EC/ISRIC (2003) world soil resources map (scale 1:30,000,000 approx)), major landforms, topography, percentage of cultivated area and vegetation structure is given in Table 1.

2.2. Sample preparation and analyses

Samples were analyzed at the World Agroforestry Centre's Spectral Diagnostics Laboratory in Nairobi, Kenya using TXRF and X-ray diffraction spectroscopy (XRD) spectral methods on all samples collected. Soil samples were first air-dried and passed through a 2-mm sieve before sub sampling to 10 g using coning and quartering technique to ensure homogeneity of the sample. The 10 g subsamples were oven-dried at 40 °C and then 5 g were ground to a fine powder (<200 μm) using a Retsch RM 200 mill (Retsch, Düsseldorf, Germany). Approximately 3 g of each soil sample was then further ground to <50 μm using a McCrone micronising mill (McCrone, Westmont, U.S.A.). The TXRF methodology was used to analyze total elemental concentrations in each soil sample using a S2 PICOFOX™ TXRF spectrometer (Bruker AXS Microanalysis GmbH, Germany). Based on a recently developed and tested method (Towett et al., 2013), 50 mg of the finely ground (20–50 μm) sample was mixed with 2.5 ml of Triton X100 (Fischer Scientific, UK) solution (0.1 vol.%) to form a soil suspension and spiked with 40 μl of 1000 mg l⁻¹ Selenium (Fluka Analytical, Germany) as the internal standard. The suspension was placed into an ultrasonic water bath at room temperature and sonicated in a continuous mode for 15 min, and then mixed well using a digital shaker. 10 μl of the turbid soil solution was immediately dispensed on to a clean siliconized quartz glass sample carrier and dried for 10–15 min at 52 °C on a hot plate (Staurt® SD300) in a clean laminar flow hood. Samples were analyzed in triplicate with data acquisition time of 1000 s per sample. The evaluation of spectra and element quantification were performed using the software program SPECTRA 6.3 (Bruker AXS GmbH, Germany). Mineral profiling was done using XRD spectroscopy where finely ground (<50 μm) samples were loaded into steel sample holders and analyzed using a Bruker D2 Phaser XRD spectrometer instrument that was equipped with a LYNXEYE compound silicon strip, 1-dimensional detector with Theta/Theta geometry. The instrument was integrated with the DIFFRACplus TOPAS graphics based, non-linear least squares profile analysis program. Identification of X-ray minerals was achieved by comparing the X-ray diffraction pattern (diffractogram) obtained from an unknown sample with an internationally recognized database (powder diffraction file, PDF) containing reference patterns with more than 70,000 phases. Quantitative phase analysis of crystalline powder samples was then