Soil Spectroscopy: An Alternative to Wet Chemistry for Soil Monitoring

M. Nocita[*, §, 1]**, A. Stevens**[§]**, B. van Wesemael**[§]**, M. Aitkenhead**[¶]**,
M. Bachmann**[∥]**, B. Barthès**[#]**, E. Ben Dor**[**]**, D.J. Brown**[§§]**, M. Clairotte**[#]**,
A. Csorba**[¶¶]**, P. Dardenne**[∥∥∥]**, J.A.M. Demattê**[##]**, V. Genot**[†]**,
C. Guerrero**[***]**, M. Knadel**[§§§]**, L. Montanarella**[*]**, C. Noon**[§]**,
L. Ramirez-Lopez**[¶¶¶]**, J. Robertson**[¶]**, H. Sakai**[∥∥∥∥∥]**,
J.M. Soriano-Disla**[###]**, K.D. Shepherd**[****]**, B. Stenberg**[§§§§]**,
E.K. Towett**[****]**, R. Vargas**[¶¶¶¶]** and J. Wetterlind**[§§§§]

*European Commission, Joint Research Centre, Institute for Environment and Sustainability, Ispra, Varese, Italy
†Université de Liège — Ulg, Gembloux Agro–Bio Tech, Gembloux, Belgium
§Georges Lemaître Centre for Earth and Climate Research, Earth and Life Institute, Université Catholique de Louvain, Belgium
¶The James Hutton Institute, Aberdeen, United Kingdom
∥German Aerospace Agency (DLR), Weßling, Bavaria, Germany
#Institut de Recherche et de Developpement, IRD, UMR Eco&Sols, INRA-IRD, Montpellier, France
**Tel Aviv University (TAU), Tel Aviv, Israel
§§Washington State University (WSU), Pullman, WA, USA
¶¶Szent István University, Gödöllő, Hungary
∥∥∥Wallon Agricultural Research Centre (CRA-W), Gembloux, Belgium
##University of Sao Paulo, Sao Paulo, Brazil
***Department of Agrochemistry and Environment, University Miguel Hernández, Valencia, Spain
§§§Aarhus University, Aarhus, Denmark
¶¶¶Swiss Federal Research Institute (WSL), Birmensdorf, Switzerland
∥∥∥∥∥ISO/TC 190/SC 3/WG 10/Railway Technical Research Institute, Japan Railways, Tokyo, Japan
###CSIRO Land and Water, Adelaide, Australia
****World Agroforestry Centre (ICRAF), Nairobi, Kenya
§§§§Swedish University of Agricultural Sciences (SLU), Skara, Sweden
¶¶¶¶Food and Agriculture Organization (FAO), Rome, Italy
[1]Corresponding author: E-mail: marco.nocita@gmail.com

Contents

1

Abstract

The soil science community is facing a growing demand of regional, continental, and worldwide databases in order to monitor the status of the soil. However, the availability of such data is very scarce. Cost-effective tools to measure soil properties for large areas (e.g., Europe) are required. Soil spectroscopy has shown to be a fast, cost-effective, environmental-friendly, nondestructive, reproducible, and repeatable analytical technique. The main aim of this paper is to describe the *state of the art* of soil spectroscopy as well as its potential to facilitating soil monitoring. The factors constraining the application of soil spectroscopy as an alternative to traditional laboratory analyses, together with the limits of the technique, are addressed. The paper also highlights that the widespread use of spectroscopy to monitor the status of the soil should be encouraged by (1) the creation of a standard for the collection of laboratory soil spectra, to promote the sharing of spectral libraries, and (2) the scanning of existing soil archives, reducing the need for costly sampling campaigns. Finally, routine soil analysis using soil spectroscopy would be beneficial for the end users by a reduction in analytical costs, and an increased comparability of results between laboratories. This ambitious project will materialize only through (1) the establishment of local and regional partnerships among existent institutions able to generate the necessary technical competence, and (2) the support of international organizations. The Food and Agriculture Organization (FAO) of United Nations and the Joint Research Centre of the European Commission are well placed to promote the use of laboratory and field spectrometers for monitoring the state of soils.

1. INTRODUCTION

The Millennium Ecosystem Assessment (2005) stated that soil provides a multitude of land–based ecosystems goods and services supporting and regulating life on the planet. Thus the preservation and sustainable

management of soils is crucial to tackle the main challenges humanity is facing such as food security, climate change, environmental degradation, water scarcity, and biodiversity (Sanchez et al., 2009). Assessing the state of the soil requires complex analytical approaches with high number of parameters at a large number of sites. Unfortunately, consistency of the approaches and the analytical methods among soil surveyors is often lacking (Sanchez et al., 2009; Louis et al., 2014), hindering the exchange of quantitative data with other disciplines, and the implementation of policies for mitigating the main soil threats (e.g., European Commission, 2006). Hence, the growing demand for high-resolution soil data to cover large areas is difficult to be met, due to the lack of such data (Grunwald et al., 2011; Ben-Dor and Banin, 1995). The consistent monitoring of soil health at continental scale depends on the development and implementation of in situ, low-cost, and fast analytical methods, provided that the results obtained by different operators are comparable and that they can be stored in accessible databases, including the standards and raw data for eventual reinterpretation. Over the past 30 years, soil visible, near-, and mid-infrared (Vis–NIR–MIR) reflectance spectroscopy has proved to be a fast, cost-effective, environmental-friendly, nondestructive, reproducible, and repeatable analytical technique (Viscarra Rossel et al., 2006; Soriano-Disla et al., 2014). The technique is mainly used in the laboratory, but its application in situ (Viscarra Rossel et al., 2009), as well as from air- and space-borne sensors, is growing (Ben Dor et al., 2009). As there is large body of evidence showing that spectroscopy can be used to estimate important soil properties, it is time to ask whether this technique is mature enough for routine soil analysis.

- Can the errors associated with spectroscopic predictions be reduced by joining spectral databases, increasing calibration diversity and density, developing focused calibrations for each type of soil or region, or using local samples to augment calibrations for individual fields?
- Are the larger errors associated with soil spectroscopy mitigated by the larger number of samples possible to analyze with this technique?
- What is required to turn soil spectroscopy into an operational technique for soil assessment at field, country, and continental scales?

The main aims of this paper are to (1) describe the actual status of soil spectroscopy, and (2) propose actions to encourage the application of this technique as an alternative to traditional laboratory analyses.

2. VISIBLE AND INFRARED SPECTROSCOPY

2.1 The Visible

Visible (Vis) light covers only a small portion of the electromagnetic radiation in the wavelength range between 0.4 and 0.78 μm. Interaction of visible radiation with soil produces energy transition in atoms, mainly due to processes known as crystal field effect and charge transfer. Generally, electronic transitions yield broad absorption bands that control the soil color that is captured by the human eye. Although the spectral response in the Vis region is weak, it is possible to derive quantitative information from the spectra (Viscarra Rossel et al., 2006). Owen (2000) wrote an extended review about origin, principle, and applications of UV−Vis spectroscopy.

2.2 The Infrared

Infrared (IR) radiation covers the range of the electromagnetic spectrum between 0.78 μm and 1 mm. Vibrational energy transitions in molecules typically require energy of a frequency that corresponds to the IR region of the electromagnetic spectrum. Hence IR radiation will activate molecular interatomic vibrations, and this provides the basis of the IR spectroscopy technique. An IR spectrum essentially gives a chemical profile of the sample. Electromagnetic radiation consists of electric and magnetic components, but it is the electric vector of IR radiation that interacts with the molecular interatomic bonds to activate different vibrations, resulting in absorption of the IR radiation. There are many types of molecular vibrations that occur on absorption of IR radiation including stretching, bending, and wagging of the constituent atoms in the molecule. For a compound to be IR active, it is required to have covalent bonding. In addition, there must be an oscillating electric field produced during the chemical bond vibrations of the atoms in the molecule (net change in dipole moment). Absorptions of IR radiations are due to vibrations of molecular bonds such as O−H, C−H, N−H, C=O, C−N, N−O, or C=C. Stretching of some symmetric bonds in which the electrons are equally shared will not give rise to IR-active vibrations, e.g., stretching in N_2 molecules (no net change in dipole moment during its chemical bond vibrations).

There are numerous textbooks on the principles and interpretation of IR spectroscopy, including those by Herzberg (1945) and Alpert et al. (1970). IR radiation is divided in three main regions: the near-infrared (NIR: 0.78−2.5 μm), mid-infrared (MIR: 2.5−25 μm) and the far-infrared

(FIR: 25—1000 (m[1]). The NIR region shows overtones and combination modes of the fundamental atoms vibrations in molecules that are active in the MIR and FIR regions. The full description of basics, history, and functions of IR spectroscopy can be found in Stuart (2004) and Aenugu et al. (2011). NIR spectroscopy finds applications in several fields such as food science, semiconductor electronics, pharmaceutics, substances identification, and analysis of soil properties (Davis, 1998). Absorptions in MIR spectra can be interpreted in terms of the fundamental vibrations of functional groups present in a sample as the MIR is dominated by fundamental atoms vibrations mostly in bending, stretching, and rotation vibrational modes. It should be noted that the term FTIR (Fourier transform infrared) spectroscopy is often used to describe IR spectroscopy in the MIR range, and the name derives from the way in which modern instrumentation works.

3. SOIL VIS AND IR SPECTROSCOPY

3.1 Background

Soil spectroscopy is about the identification and analysis of the interaction of Vis-IR wavelengths with soil properties. The main chemical components in soils that interact with electromagnetic radiation across the Vis-NIR, termed also "chromophores," are OH in free water and clay mineral lattice, organic matter, and nonclay minerals, such as iron oxides, carbonates, and salts (Ben Dor et al., 1999). In the MIR, more information on soils is available, such as Si-bearing minerals (mainly quartz) and other fundamental vibrations groups without overtones in the NIR (Janik and Skjemstad, 1995). In general, the MIR region provides better resolved and more intense peaks than the NIR because fundamental vibrations are taking place in this region (Soriano-Disla et al., 2014).

Soil reflectance across the NIR is characterized by well-defined absorption features associated to overtones of O—H and H—O—H stretch vibrations of free water (1.455 and 1.915 μm) and overtones and combinations of O—H stretch and metal-OH bends in the clay lattice (1.415 and 2.207 μm). A large absorption centered on 0.665 μm can be attributed to organic matter (Ben Dor et al., 1997). Generally speaking, soil reflectance

---

[1] In the remote sensing community, the shorter infrared wavelengths (0.78—1 μm) are termed near-infrared, while the portion of the electromagnetic spectrum between 1 and 2.5 μm is named shortwave infrared. At lower frequencies, the spectrum is divided into mid-wave infrared (3—5 μm), low-wave infrared (8—14 μm), and far-wave infrared (14—1000 μm).

decreases with organic matter (Ben Dor et al., 1997) and water content (Whiting et al., 2004). Absorptions around 0.4, 0.45, 0.51, 0.55, 0.7, 0.87, and 1 μm are characteristics of the presence of ferrous and ferric iron oxides, and are due to the electronic transitions of the iron cations (Ben Dor et al., 1999). Tables of absorption positions and their related soil components are published in Ben Dor et al. (2002), Viscarra Rossel and Behrens (2010), and Soriano-Disla et al. (2014). In addition to chemical soil components, physical soil properties, such as particle size distribution and aggregate size and density, may lead to changes in baseline height, and absorption intensities of the spectral curves through the phenomenon of light scattering or reflection. Ben Dor et al. (1999) extensively reviewed the fundamentals of soil spectroscopy in the Vis-NIR.

In the MIR, due to strong vibration fundamentals, soil spectra are characterized by clearly identifiable peaks linked to organic or mineral compounds. The first two peaks around ($3800-3600$ cm^{-1}) are associated to O$-$H stretching in clay minerals (Calderon et al., 2011). They are followed by two less pronounced peaks ($3000-2800$ cm^{-1}) linked to the aliphatic C$-$H stretching (Zimmermann et al., 2007). Between 2000 and 1790 cm^{-1}, three successive peaks indicate the presence of quartz (Calderon et al., 2011). The peaks around $1600-1500$ cm^{-1} and $1450-1400$ cm^{-1} are mainly associated to aromatic and aliphatic compounds, respectively (Bornemann et al., 2010; Demyan et al., 2012; Tivet et al., 2013). Below 1000 cm^{-1}, the interpretation of the different peaks is more difficult because the spectrum results from a mixture of minerals and organic compounds (Calderon et al., 2011; McCarty et al., 2002).

3.2 Spectroscopy for Soil Property Prediction

The use of spectroscopy for soil analyses is fast, cost-efficient, and nondestructive. Furthermore, there is no need for chemical reagents, and it requires minimal sample preparation (Malley et al., 2004; Viscarra Rossel et al., 2006). A single spectrum may contain comprehensive information on various soil components, and can be used to predict these simultaneously (Islam et al., 2003). The rapid development of portable and handheld spectrometers allows using the technique on-site. Bowers and Hanks (1965) were among the first to investigate the spectral characteristics of soil samples by showing correlation between soil spectra and soil moisture. Later, Stoner and Baumgardner (1981) collected a spectral library containing representative soil samples of the United States, and identified five typical spectral curves corresponding to five soil classes. Early studies, such as those of Dalal

and Henry (1986) and Ben Dor and Banin (1995), started to produce soil property predictions based on spectral data and multivariate statistics. Since then, most of the studies adopted the same quantitative approach and spectroscopy has been exploited to predict soil properties such as organic carbon (Gobrecht et al., 2014), texture (Sørensen and Dalsgaard, 2005), cationic exchange capacity (CEC) (Cañasveras Sánchez et al., 2012), total phosphorus (P) (Abdi et al., 2012), exchangeable potassium (K) (He et al., 2005), and electrical conductivity (Ben Dor et al., 2002; Viscarra Rossel et al., 2006; Todorova et al., 2011). Soriano-Disla et al. (2014) extensively reviewed soil spectroscopic models published in the literature, and listed soil properties that could be determined by means of diffuse reflectance spectroscopy: soil water content, clay, sand, soil organic carbon (SOC), CEC, exchangeable Ca and Mg, total N, pH, and total concentration of potential pollutant metals/metalloids (As, Cd, Hg, and Pb). Moreover, the indirect interaction between the chromophores and other soil properties can provide additional quantitative information about some soil properties with no active chromophores (Ben Dor et al., 1999). Obviously, soil properties that are directly related to the chromophores (organic carbon, carbonates, etc.) are generally better predicted than the other properties for which the prediction mechanism relies on their correlation with the chromophores within a given spectral library (Reeves et al., 2006). The prediction of soil properties based on spectroscopy registered a tremendous increase in the last decades (Bellon-Maurel and McBratney, 2011). Due to the minor sample preparation, and more applicability under field condition, Vis–NIR instruments are more widespread than MIR, although the latter, being less affected by water content, particle size, and light penetration than the former, generates more accurate predictions and measurement reproducibility (Reeves et al., 2010).

Building upon the approaches successfully developed for field and laboratory spectroscopy in the reflective (Vis–NIR) and thermal (MIR–TIR) domain, imaging spectroscopy using airborne sensors has shown the potential to map and to quantify topsoil properties (e.g., Stevens et al., 2010; Eisele et al., 2012; Gerighausen et al., 2012). Upcoming spaceborne sensors will cover not only the Vis–NIR region (EnMAP from Germany, HSUI from Japan, PRISMA from Italy, and SHALOM from Italy and Israel) but also the thermal infrared (TIR) region (HyspIRI). These instruments, contributing to, e.g., the COPERNICUS/GMES programme, could therefore provide global spectroscopic data for mapping soil properties at low costs.

3.3 Cost/Benefit Analysis of Soil Spectroscopy

Besides the previously mentioned advantages, soil spectroscopy is also characterized by the fast delivery of results, and the need for only basic analytical infrastructure. For many soil assessment and monitoring applications, overall accuracy might be improved by obtaining soil data in more locations, depths, and times despite reduced accuracy for each measurement. O'Rourke and Holden (2011) calculated the costs per sample, analytical accuracy, and time involved in SOC analysis, in order to identify the best method among Walkley-Black, total organic C (TOC) analyzer, Vis-NIR diffuse reflectance spectroscopy, and laboratory hyperspectral imaging. They found that Vis-NIR spectroscopy and laboratory hyperspectral imaging (800—1720 nm), although less accurate than TOC analyzer, outperformed the latter, mainly as a result of the lower price (10 times cheaper). Schwartz et al. (2012) showed that the use of spectral analysis to monitor petroleum contamination in soils provided much better results at lower cost compared to certified laboratories using traditional analytical chemistry methods. This difference of cost is even more important for large-scale soil assessment, where the number of measurements is very high. The World Agroforestry Centre (ICRAF) reports that the price of SOC analysis by spectroscopy for the African soil information system (AfSIS) project, is one-third of that by a C/N analyzer. The Joint Research Centre of European Commission contracted a laboratory to analyze about 20,000 samples for the land use/cover area frame survey (LUCAS) soil monitoring network (Tóth et al., 2013). For SOC analyses, the cost per sample using spectroscopy was less than one-third compared to reference analyses (Soil Service of Belgium, pers. Comm.).

3.4 Spectral Libraries: State of the Art and Potential Use

Predictions are obtained by calibrating spectral data against reference soil analytical data. Spectroscopic calibrations are empirical and hence cannot produce accurate predictions for samples not represented in the spectral libraries. The usefulness of spectral libraries covering and producing prediction models for small areas has already been proven, and is not discussed in this paper. Hence, we focus on large spectral libraries, which are needed to provide general and robust models over large areas that are characterized by a large soil diversity. Below, we describe the characteristics of existing spectral libraries covering large areas.

The ICRAF-ISRIC world soil spectral library is composed of 4438 samples from 785 soil profiles distributed in 58 countries from Africa,

Asia, Europe, North America, and South America selected from the Soil Information System (ISIS) of the International Soil Reference and Information Centre (ISRIC) archives. Samples were scanned in the Vis–NIR spectral range (350–2500 nm), with a FieldSpec FR spectroradiometer (Analytical Spectral Devices, Boulder, CO). The soil reference measurements were acquired by ISRIC in different laboratories according to ISRIC Procedures for soil analysis (Van Reeuwjik, 2002).

Viscarra Rossel and Webster (2012) described a large library of 21,500 Vis–NIR spectra from around 4000 soil profiles covering the Australian continent. The soil samples were scanned using an ASD LabSpec Pro spectrometer with a spectral range of 350–2500 nm and spectral resolution of 3 nm at 700 nm and 10 nm at 1400 and 2100 nm. The collection of soil spectra was realized with a high-intensity contact probe with halogen bulb illumination. The samples were collected from different soil surveys conducted at different scales (continental, regional, and farm). The soil analyses were realized in multiple laboratories, following different analysis protocols.

A spectral library covering the United States has been collected under the Rapid Carbon Assessment project (USDA, 2013). The library is composed of 144,833 Vis–NIR spectral scans, derived from samples collected from the upper 1 m of 32,084 soil profiles at 6017 randomly selected locations. The instrument used to scan the samples was an ASD LabSpec Pro spectroradiometer with a spectral range of 350–2500 nm, 2 nm sampling resolution and spectral resolution of 3 nm at 700 nm and 10 nm at 1400 and 2100 nm. Soil spectra were acquired using a high-intensity contact probe. SOC was determined by combustion method.

The European spectral library LUCAS consists of about 20,000 topsoil (0–20 cm) samples, collected from all over Europe, measured for 13 soil properties in a single laboratory (Stevens et al., 2013). The Vis–NIR soil spectra were measured with a FOSS XDS Rapid Content Analyzer (FOSS NIRSystems Inc., Denmark), operating in the 400–2500 nm wavelength range, with 2 nm spectral resolution and 0.5 nm spectral data interval.

In addition to continental-scale libraries, a number of national and regional soil spectral libraries have been constructed, such as the ones for France (Gogé et al., 2012 for NIR and Grinand et al., 2012 for MIR), Czech Republic (Brodsky et al., 2011), Denmark (Knadel et al., 2012), Florida (Vasques et al., 2010), and Brazil (Bellinaso et al., 2010).

Soil spectral libraries might be a strong base for the forthcoming hyperspectral remote sensing of soils from space. The laboratory soil spectra may enable appropriate validation of the reflectance information extracted from

radiance data acquired from remote platforms. Moreover soil spectral libraries can play a major role in tracking temporal spectral changes over the sampling locations (Deng et al., 2013).

3.5 Soil Spectroscopy for Large-Scale Soil Property Prediction

Predicting soil properties for large and diverse areas is especially challenging, and results in higher prediction error than for local scale spectroscopic models (Stevens et al., 2013). For instance, Brown et al. (2006) obtained a root mean square error (RMSE) of 7.9–9.9 g C kg^{-1} for an SOC content calibration model obtained from samples distributed all over the world. In Europe, spectral models of SOC content achieved an RMSE of 3.6–8.9 g C kg^{-1} for mineral soils and 50.6 g C kg^{-1} for organic soils (Nocita et al., 2014; Stevens et al., 2013). Vasques et al. (2010) developed spectroscopic models of SOC in Florida achieving an RMSE of 6.5–7 g C kg^{-1}. These prediction errors are large compared to the standard error of laboratory (SEL) of established methods of soil carbon analysis, such as dry combustion (SEL = 1–2 g C kg^{-1}; Gerighausen et al., 2012). Large-scale libraries tend to span over a wider range and a higher variability of the soil property under study, which actually appear to be the dominating factor influencing prediction errors (Stenberg et al., 2010). The lack of accuracy shown by spectroscopic models built with large-scale spectral libraries is also due to the complexity of the relationship between soil properties and spectra for heterogeneous soil samples. It has been long recognized that the spectral signature of soils in the Vis–NIR region is not unique (Price, 1994). Many absorption features overlap so that absorptions related to one soil component can be masked, distorted, or shifted where other soil components vary. For instance, spectral variations related to changes in iron oxide content may cancel variations in absorptions due to organic matter (Adar et al., 2014). Not only chemical chromophores interact with each other. For instance, for the same amount of SOC content, an increase in sand content induces an increase in SOC absorption depths, which can be easily confounded with an increase in SOC (Stenberg, 2010; Stevens et al., 2013). To overcome this, it has been proposed to include additional variables such as particle size distribution in the modeling of soil spectra (Brown et al., 2005; Nocita et al., 2014).

The use of large spectral libraries has been proposed also for field and farm scale soil mapping. In order to overcome the large biases often experienced when using them at the local scale, the spiking technique, consisting

in the combination of large-scale libraries with local calibrations, was developed (Guerrero et al., 2010). Basically only a handful of local samples are included in a large-scale library to shift its weight towards the target site. In this approach, a few representative samples from the target site (spiking subset) are added to recalibrate the model, ensuring that the models contain samples similar to those to predict. This approach implies some analytical efforts, since the spiking subset must be analyzed with the reference method. Consequently, this subset should be as small as possible, in order to maintain most of the advantages of spectroscopy.

The poor calibration results at large scales are not only due to the geographical extent and the resulting complexity as such, but also to the sampling density of the current spectral libraries. Based on the LUCAS spectral library ($\sim$20,000 points across Europe), Nocita et al. (2014) showed, for instance, that, using a local regression approach (i.e., for each spectrum to predict, a calibration equation is developed based on the samples with the most similar spectra or the closest samples in the geographical space), soils with high SOC content (80 g C kg^{-1}) were poorly predicted because of the lack of suitable nearest neighbors (i.e., samples with similar soil and spectral properties to the ones to predict). Generally, the analyses of such large databases need dedicated chemometrics tools, such as local regressions that are able, to some extent, to handle their complexity (Ramirez-Lopez et al., 2013). Development costs of large databases are high, so that such spectral libraries are often developed from archived soil samples and legacy soil databases with analytical measures (Viscarra Rossel and Webster, 2012). Although these libraries contain an enormous wealth of information on soils, they cannot be easily merged into a uniform database because they have been collected with different protocols, instruments, and analytical methods which can severely affect the prediction performance of spectroscopic models (Soriano-Disla et al., 2014). For instance, Brown et al. (2005) computed an RMSE of 6 g C kg^{-1} for 1175 samples analyzed for SOC both by dry combustion and the Walkley-Black method. Such error would be included in the total error budget of SOC spectroscopic models based on samples analyzed with the two different methods. Obviously this represents a waste of resources since most spectral libraries cannot be exploited together to create robust models over large areas and with diverse soil types.

3.6 Parameters Causing Spectral Variation in the Laboratory

Not only the soil components but also the laboratory protocols have an influence on the spectra. Depending on the instruments, samples are prepared

following a procedure specific to each laboratory, which may result in difference in spectral shapes for the same sample between different laboratories. Often, soil samples are dried, sieved, and grinded. Differences in water content of air-dried samples, due to fluctuations in relative humidity of the ambient air in the laboratory, affect the spectral shape and peaks, especially around 1.415 and 1.915 μm (Whiting et al., 2004; Nocita et al., 2012). Spectral reflectance is also affected by the grinding of soil. This can generate important differences of accuracy in the prediction models due to the variation of particle sizes (Soriano–Disla et al., 2014). Unfortunately, there is no protocol specifying at which caliber samples should be grinded. The same is true for sieving. This makes the construction of comparable spectral libraries difficult, and precludes the sharing of spectra among laboratories with different measurement conditions and protocols. Pimstein et al. (2011) showed that the use of a common protocol and an internal standard reduced significantly the differences between spectral measurements of the same samples by different operators in three laboratories.

The comparison of analytical results among laboratories is traditionally addressed by performing ring tests with a standard sample being sent and analyzed by all participating laboratories. For spectral analysis, it is recommended to send both a reference material, such as bleached inert sand, and a standard soil sample to the laboratories. The spectra of these materials can then be used to determine transfer function for the spectra determined in one laboratory to be used in a spectral library of another laboratory.

3.7 Metadata and Soil Spectroscopy

Metadata are structured information that make an information resource easier to access, use, and understand. Just as for any other kind of information derived in the field or the laboratory, the utility of soil spectroscopy data is only as good as how well it can be explained and understood. Capturing the metadata at the observation stage is a lot more cost-effective than trying to work out all of the necessary information later on, and can aid in the integration of the data within global frameworks, and its later extraction and use.

Many different definitions and frameworks for metadata have been developed, reflecting the wide variety of data and information types that can be generated. Existing examples of metadata standards of relevance to soil spectroscopy include ISO 19115 (ISO, 2003), the Dublin Core Metadata Initiative (DMCI, 2013), and the Directory Interchange Format (NASA, 2013).

The seven questions that the notion of metadata addresses are all relevant to soil spectroscopy, and are listed below:

- *What* was measured? This can include the spectroscopic information, additional environmental parameters, and soil analysis results obtained later in the lab.
- *Who* carried out the measurements? Some field observations and laboratory analyses are operator-dependent, and it can be useful to know who carried out the work in order to calibrate for this (and also to be able to ask them questions about the data if the need arises).
- *Where* were the measurements made? Geographical location of field observations can allow later site characterization information to be derived.
- *When* were the measurements made? This information is particularly important when long-term monitoring or changes over time are of interest.
- *How* were the measurements made? Type of equipment, field sampling protocols any other seemingly innocuous information about how the data were derived can be useful later.
- *Why* was the work carried out? Was it in relation to some other project, and were the observations intended to satisfy some specific requirement?
- *Whose* is the data? Intellectual property is a topic that tends to be ignored until it becomes an unavoidable issue—having information about ownership, rights of use, and referencing of the material available to the user early on can facilitate license negotiations and prevent problems occurring once work has been carried out.

Suggestions for implementation of metadata standards within soil spectroscopy are likely to cover a wide range of topics, from the adoption of preferred standards to the inclusion of specific types of information (and the formatting of the metadata framework). There is a great deal of flexibility available in how such a system could be adopted, and we are not attempting here to prescribe how this should be achieved. However, any successful metadata framework should aim at the very least to be compliant with the INSPIRE directive (http://inspire.ec.europa.eu/), and it is proposed that the information and guidance available in relation to this directive would be a suitable starting point for discussions.

4. THE WAY FORWARD

The growing demand for high-resolution soil data to cover large areas on the one hand, and the lack of availability of such data on the other hand,

is one of the biggest challenges in contemporary soil science (Grunwald et al., 2011), encouraging thereby the development of cost–effective methods of soil analysis, such as Vis-IR spectroscopy. While research on soil spectroscopy has rapidly grown and showed a great potential (Guerrero et al., 2010), it is now time for soil spectroscopy to enter an operational phase where, just as for other established soil analytical techniques, measurements are standardized, soil analyses are reliable across diverse environments and data are delivered in an automated mechanism. To achieve this goal, one prerequisite is the development of databases that can provide robust spectral models over large geographical extents. It is unlikely that the high sampling density, required to appropriately describe soil variation at these scales, could be reached by a single research group. However, the combination of existent and future local, regional, and continental spectral libraries is an achievable target, provided that they are built using a common protocol for the collection of laboratory soil spectra, or that they contain spectral reference measurements so that spectral transfer functions could be calculated. Similarly to spectral measurements, the use of reference analytical methods that spectroscopic predictions rely on should be standardized. Obviously, a joint effort of the soil spectroscopy community is required to allow better interoperability between soil spectral libraries and facilitate data exchange. Such initiative is not only a way to unlock current limitations of soil spectroscopy, but also a lever that would directly promote the use of spectroscopy in academic and commercial soil laboratories, favoring the development of monitoring networks able to assess quickly and efficiently the state of the soil resources at minimal costs. In the next sections, we present some ideas that, once implemented, could contribute to the expansion of soil spectroscopy as an established soil analytical method.

4.1 Establishment of a Common Protocol for Laboratory Spectroscopy

Since calibration and management represent a large part of costs and efforts in the use of IR techniques, standardization and centralization of reference methods are strongly needed. This represents the first step for the sharing of small- and large-scale spectral libraries, which could help in achieving calibration models that are valid for larger areas. So far, all the national and continental spectral libraries have been built using slightly different protocols for each library including sampling technique, sample preparation, instrument specifications, and spectral acquisition, which hinder interoperability of spectral libraries. The use of different reference methods and the problems

related with quality control of reference measurements within and across laboratories provide major challenges for the development of reliable calibrations. Iterative development of centralized spectral libraries is efficiently achieved by screening spectral libraries and then conducting reference measurements on outlying samples. An international standard for the collection of laboratory spectra and the inclusion of spectra of reference materials will dramatically drop the costs linked with the collection of new samples. Moreover, the development of a common standard, together with a common network for scientists and technicians from all over the world, will give rise to new applications, such as the transfer of calibration models from laboratory to spectra of the soil surface collected by remote sensing.

4.2 Scanning of Existent Soil Archives

Sampling campaigns are costly, and soil archives stored by universities, research centers, agriculture associations, and government agencies could provide an opportunity to enlarge spectral libraries. Even if many samples were acquired decades ago, they still contain spectral information that could be used to improve the representativity of spectroscopic calibration models. These samples could be scanned to a cost basically corresponding to the working hours of a technician. In many cases, however, considerations on the property of reference data and on the confidentiality of some metadata (especially location) have to be addressed. A common framework could be proposed for negotiating with data owners (e.g., access to spectra, and imprecise geographical coordinates). The impact of this mobilization, realized following a common protocol, might be part of the answer to the demand for robust calibration model across regions and soil types. Since 2006, ISO/TC 190 (soil quality)/SC 3/WG 10 (screening methods) has been developing standards to screen soil for chemical compounds including heavy metals, petroleum, the total carbon, and nitrogen as well as harmful anions such as chromium (VI) and cyanides, under the guidance established in 2011 as ISO 12404 on screening methods to be applied to soil monitoring.

4.3 Storing Spectra and Associated Soil Archives

The spectrum of a soil sample contains abundant information. Once scanned, a spectrum can be stored easily. It is probable that, in the future, soil scientists might be measuring some properties which at the present time are not measured, because neither the knowledge nor appropriate analytical techniques are available. The characteristics of the soils stored as spectra will remain unaltered, while soil properties will change after a long

storage. This is why soil spectral libraries should be accompanied with soil banks that conserve the soil samples to be scanned or analyzed in the future.

4.4 Spectroscopy to Acquire Standardized Soil Information and Enhance Monitoring

The implementation of soil spectroscopy could find valuable application in the soil information system and would represent a great progress in the field of soil analysis. For instance, soil classification can be realized by several methods (Soil Survey Staff, 1999; IUSS Working Group WRB, 2006), but the high costs for its implementation has hindered the collection of this information. Soil spectroscopy can be applied for the classification of soil types (Viscarra Rossel and Webster, 2012). Demattê and Terra (2014) demonstrated the potential of spectroscopy for the evaluation of the changes in soil type along topo–sequences, as a basic tool for soil mapping. Moreover, Demattê et al. (2004) showed that soil spectroscopy can be used to map soil types, as the basis for land–use planning.

At the same time, soil spectroscopy could be integrated and thus regulate the use of fertilizers based on routine soil testing. For example, one of the main problems of a reliable fertility status is the lack of knowledge of the CEC and clay content of our soils. Indeed, those properties are the key to compare samples to the regional reference system and deliver an appropriate agronomic diagnosis. The determination of CEC and clay content using standard procedures is not feasible for each soil sample as it is too costly and time-consuming. An alternative is to predict them with Vis–NIR spectroscopy which represents thereby a real opportunity to improve the fertility advice (Genot et al., 2011). In Wallonia, these analyses are routinely carried out since 2008 in the laboratories of the http://www.requasud.be/. Another example of soil spectroscopy application for routine analysis is the AfSIS. They have adopted Vis–IR spectroscopy as its main screening tool in characterizing 20,000 soil samples taken from a stratified random sampling frame across Sub-Saharan Africa. There is a growing network of Vis–IR laboratories in Africa, with more than 10 laboratories established, including two private sector soil testing companies.

Recently soil spectroscopy was reported as an accurate method to monitor temporal changes in SOC of Danish soils (Deng et al., 2013). Basically, this study used topsoil (0–25 cm) samples from 1986 to 2009. Spectra collected from both time series revealed that Vis–NIR spectroscopy could soundly detect the SOC temporal decrease observed with wet chemistry, but at much lower cost.

In conclusion, given the adherence to a common protocol, spectroscopic analyses could both increase the reliability and the comparability of the results and, at the same time, contribute to the construction of the spectral libraries. The latter requires quality assessment/quality control steps to be built in the database for the input of new spectra. Diffusing the use of Vis–NIR and MIR spectrometers at all levels, especially farmers' consortia and agriculture organizations, responsible for the soil analyses of thousands of samples collected over large areas, could bring important advantages. The long-term cost cuts from which these associations would benefit will no doubt justify the investment in instruments. Many regional laboratories already operate Vis–NIR spectrometers to infer soil properties. This implies that the establishment of local and regional partnerships among existent institutions will already generate enough competence for the soil monitoring based on soil spectra. The development of this kind of project requires the support of international organizations, such as the Food and Agriculture Organization (FAO) of United Nations and the European Commission's JRC, and their acknowledgment of soil spectroscopy as a valuable tool to integrate the established techniques of soil chemical analyses for the control of the state of soils (Clark and Roush, 1984).

REFERENCES

Abdi, D., Tremblay, G.F., Ziadi, N., Bélanger, G., Parent, L.-É., 2012. Predicting soil phosphorus–related properties using near-infrared reflectance spectroscopy. Soil Sci. Soc. Am. J. 76, 2318−2326.

Adar, S.Y., Shkolnisky, Y., Ben Dor, E., 2014. Change detection of soils under small-scale laboratory conditions using imaging spectroscopy sensors. Geoderma 216, 19−29.

Aenugu, H.P.R., Sathis Kumar, D., Srisudharson, P.N., Ghosh, S.S., Banji, D., 2011. Near infrared spectroscopy- an overview. Int. J. ChemTech Res. 3, 825−836.

Alpert, N.L., Keiser, W.E., Szymanski, H.A., 1970. Theory and Practice of Infrared Spectroscopy. Plenum Press, New York.

Bellinaso, H., Dematte, J.A.M., Araujo, S.R., 2010. Spectral library and its use in soil classification. Braz. J. Soil Sci. 34, 861−870.

Bellon-Maurel, V., McBratney, A., 2011. Near-infrared (NIR) and mid-infrared (MIR) spectroscopic techniques for assessing the amount of carbon stock in soils − critical review and research perspectives. Soil Biol. Biochem. 43, 1398−1410.

Ben-Dor, E., Banin, A., 1995. Near-infrared analysis as a rapid method to simultaneously evaluate several soil properties. Soil Sci. Soc. Am. J. 59, 364−372.

Ben Dor, E., Inbar, Y., Chen, Y., 1997. The reflectance spectra of organic matter in the visible near-infrared and short wave infrared region (400−2500 nm) during a controlled decomposition process. Remote Sens. Environ. 61, 1−15.

Ben Dor, E., Irons, J.R., Epema, J.F., 1999. Soil reflectance. In: Manual of Remote Sensing: Remote Sensing for the Earth Sciences, vol. 3. John Wiley & Sons, New York, pp. 111−188.

Ben Dor, E., Patkin, K., Banin, A., Karnieli, A., 2002. Mapping of several soil properties using DAIS-7915 hyperspectral scanner data. A case study over clayey soils in Israel. Int. J. Remote Sens. 23, 1043—1062.

Ben Dor, E., Chabrillat, S., Dematte, J.A.M., Taylor, G.R., Hill, J., 2009. Using imaging spectroscopy to study soil properties. Remote Sens. Environ. 113, 38—55.

Bornemann, L., Welp, G., Amelung, W., 2010. Particulate organic matter at field scale: rapid acquisition using mid—infrared spectroscopy. Soil Sci. Soc. Am. J. 74, 1147—1156.

Bowers, S., Hanks, R.J., 1965. Reflectance of radiant energy from soils. Soil Sci. 100, 130—138.

Brodsky, L., Klement, A., Penizek, V., Kodesova, R., Boruvka, L., 2011. Building soil spectral library of the Czech soils for quantitative digital soil mapping. Soil Water Res. 6, 165—172.

Brown, D.J., Bricklemyer, R.S., Miller, P.R., 2005. Validation requirements for diffuse reflectance soil characterization models with a case study of VNIR soil C prediction in Montana. Geoderma 129, 251—267.

Brown, D.J., Shepherd, K.D., Walsh, M.G., Dewayne Mays, M., Reinsch, T.G., 2006. Global soil characterization with VNIR diffuse reflectance spectroscopy. Geoderma 132, 273—290.

Calderon, F.J., Reeves III, J.B., Collins, H.P., Eldor, P.A., 2011. Chemical differences in soil organic matter fractions determined by diffuse-reflectance mid-infrared spectroscopy. Soil Sci. Soc. Am. J. 75, 568—579.

Cañasveras Sánchez, J., Barrón, V., Del Campillo, M., Viscarra Rossel, R.A., 2012. Reflectance spectroscopy: a tool for predicting soil properties related to the incidence of Fe chlorosis. Span. J. Agric. Res. 10, 1133—1142.

Clark, R.N., Roush, T.L., 1984. Reflectance spectroscopy: Quantitative analysis techniques for remote sensing applications. J. Geophys. Res. 89, 6329—6340.

Dalal, R.C., Henry, R.J., 1986. Simultaneous determination of moisture, organic carbon, and total nitrogen by near infrared reflectance spectrophotometry. Soil Sci. Soc. Am. J. 50, 120—123.

Davis, T., 1998. The history of near infrared spectroscopic analysis: past, present and future - from sleeping technique to the morning star of spectroscopy. Anal. Mag. 26, 17—19.

Demattê, J.A.M., Campos, R.C., Alves, M.C., Fiorio, P.R., Nanni, M.R., 2004. Visible-NIR reflectance: a new approach on soil evaluation. Geoderma 121, 95—112.

Demattê, J.A.M., Terra, F., 2014. Spectral pedology: a new perspective on evaluation of soils along pedogenetic alterations. Geoderma 217—218, 190—200.

Demyan, M.S., Rasche, F., Schulz, E., Breulmann, M., Muller, T., Cadisch, G., 2012. Use of specific peaks obtained by diffuse reflectance Fourier transform mid-infrared spectroscopy to study the composition of organic matter in a Haplic Chernozem. Eur. J. Soil Sci. 63, 189—199.

Deng, F., Minasny, B., Knadel, M., McBratney, A., Heckrath, G., Greve, M.H., 2013. Using vis-NIR spectroscopy for monitoring temporal changes in soil organic carbon. Soil Sci. 178, 389—399.

Dublin Core Metadata Initiative, 2013. http://dublincore.org/.

Eisele, A., Lau, I., Hewson, R., Carter, D., Wheaton, B., Ong, C., Cudahy, T.J., Chabrillat, S., Kaufmann, H., 2012. Applicability of the thermal infrared spectral region for the prediction of soil properties across semi-arid agricultural landscapes. Remote Sens. 4, 3265—3286.

Genot, V., Colinet, G., Bock, L., Vanvyve, D., Reusen, Y., Dardenne, P., 2011. Near-infrared reflectance spectroscopy for estimating soil characteristics valuable in the diagnosis of soil fertility. J. Near Infrared Spectrosc. 19, 117—138.

Gerighausen, H., Menz, G., Kaufmann, H., 2012. Spatially explicit estimation of clay and organic carbon content in agricultural soils using multi-annual imaging spectroscopy data. Appl. Environ. Soil Sci. 23.

Gobrecht, A., Roger, J.M., Bellon-Maurel, V., 2014. Major issues of diffuse reflectance NIR spectroscopy in the specific context of soil carbon content estimation: a review. Adv. Agron. 123, 145−175.

Gogé, F., Joffre, R., Jolivet, C., Ross, I., Ranjard, L., 2012. Optimization criteria in sample selection step of local regression for quantitative analysis of large soil NIRS database. Chemom. Intell. Lab. 110, 168−176.

Grinand, C., Barthès, B.G., Brunet, D., Kouakoua, E., Arrouays, D., Jolivet, C., Caria, G., Bernoux, M., 2012. Prediction of soil organic and inorganic carbon contents at a national scale (France) using mid-infrared reflectance spectroscopy (MIRS). Eur. J. Soil Sci. 63, 141−151.

Grunwald, S., Thompson, J.A., Boettinger, J.L., 2011. Digital soil mapping and modeling at continental scales − finding solutions for global issues. Soil Sci. Soc. Am. J. 75, 1201−1213.

Guerrero, C., Zornoza, R., Gomez, I., Mataix-Beneyto, J., 2010. Spiking of NIR regional models using samples from target sites: effect of model size on prediction accuracy. Geoderma 158, 66−77.

He, J., Song, H., García Pereira, A., Hernández Gómez, A., 2005. A new approach to predict N, P, K and OM content in a loamy mixed soil by using near infrared reflectance spectroscopy. Adv. Intell. Comput. 3644, 859−867.

Herzberg, G., 1945. Molecular Spectra and Molecular Structure: Infrared and Raman Spectra of Polyatomic Molecules. D Van Nostrand, New York.

International Organization for Standardisation (ISO), 2003. ISO 19115. http://www.iso.org/iso/catalogue_detail?csnumber=26020.

Islam, K., Singh, B., McBratney, A., 2003. Simultaneous estimation of several soil properties by ultra-violet, visible, and near-infrared reflectance spectroscopy. Soil Res. 41, 1101−1114.

IUSS Working Group WRB, 2006. World Reference Base for Soil Resources, second ed. FAO, Rome. World Soil Resources Reports No. 103.

Janik, L.J., Skjemstad, J.O., 1995. Characterization and analysis of soils using mid-infrared partial least-squares. II. Correlations with some laboratory data. Austr. J. Soil Res. 33, 637−650.

Knadel, M., Deng, F., Thomsen, A., Greve, H.M., 2012. Development of a Danish National Vis-NIR Soil Spectral Library for Soil Organic Carbon Determination. Digital Soil Assessments and beyond. CRC Press, Boca Raton, FL, pp. 403−408.

Louis, B.P., Saby, N.P.A., Orton, T.G., Lacarce, E., Boulonne, L., Jolivet, C., Ratié, C., Arrouays, D., 2014. Statistical sampling design impact on predictive quality of harmonization functions between soil monitoring networks. Geoderma 213, 133−143.

Malley, D.F., Martin, P.D., Ben-Dor, E., 2004. Application in analysis of soils. In: Roberts, C.A., Workman Jr., J., Reeves III, J.B. (Eds.), Near-Infrared Spectroscopy in Agriculture. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, pp. 729−784.

McCarty, G.W., Reeves III, J.B., Reeves, V.B., Follett, R.F., Kimble, J.M., 2002. Mid-Infrared and near-infrared diffuse reflectance spectroscopy for soil carbon measurement. Soil Sci. Soc. Am. J. 66, 640−646.

NASA, 2013. Directory Interchange Format Writer's Guide. http://gcmd.gsfc.nasa.gov/add/difguide/index.html.

Nocita, M., Stevens, A., Noon, C., Van Wesemael, B., 2012. Prediction of soil organic carbon for different levels of soil moisture using Vis−NIR spectroscopy. Geoderma 199, 37−42.

Nocita, M., Stevens, A., Toth, G., Panagos, P., van Wesemael, B., Montanarella, L., 2014. Prediction of soil organic carbon content by diffuse reflectance spectroscopy using a local partial least square regression approach. Soil Biol. Biochem. 68, 337−347.

O'Rourke, S.M., Holden, N.M., 2011. Optical sensing and chemometric analysis of soil organic carbon − a cost effective alternative to conventional laboratory methods? Soil Use Manage. 27, 143−155.

Owen, A., 2000. Fundamentals of Modern UV-visible Spectroscopy. Agilent Technologies.

Pimstein, A., Notesco, G., Ben Dor, E., 2011. Performance of three identical spectrometers in retrieving soil reflectance under laboratory conditions. Soil Sci. Soc. Am. J. 75, 746−759.

Price, J.C., 1994. How unique are spectral signatures? Remote Sens. Environ. 49, 181−186.

Ramirez-Lopez, L., Behrens, T., Schmidt, K., Stevens, A., Demattê, J.A.M., Scholten, T., 2013. The spectrum-based learner: a new local approach for modeling soil vis- NIR spectra of complex datasets. Geoderma 195−196, 268−279.

Reeves III, J.B., Follett, R.F., McCarty, G.W., Kimble, J.M., 2006. Can near or mid-infrared diffuse reflectance spectroscopy be used to determine soil carbon pools? Commun. Soil Sci. Plant Anal. 37, 2307−2325.

Reeves III, J.B., 2010. Near-versus mid-infrared diffusive reflectance spectroscopy for soil analysis emphasizing carbon and laboratory versus on-site analysis: where are we and what needs to be done? Geoderma 158, 3−14.

Sanchez, P.A., Ahamed, S., Carre, F., Hartemink, A.E., Hempel, J., Huising, J., Lagacherie, P., McBratney, A.B., McKenzie, N.J., Mendoca-Santos, M.L., Minasny, B., Montanarella, L., Okoth, P., Palm, C.A., Sachs, J.D., Sheperd, K.S., Vagen, T.G., Vanlauwe, B., Walsh, M.G., Winowiecki, L.A., Zhang, G.L., 2009. Digital soil map of the world. Science 325, 680−681.

Soil Survey Staff, 1999. Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys In: Natural Resources Conservation Service. U.S. Department of Agriculture Handbook, second ed., vol. 436.

Sørensen, L.K., Dalsgaard, S., 2005. Determination of clay and other soil properties by near infrared spectroscopy. Soil Sci. Soc. Am. J. 69, 159−167.

Soriano-Disla, J.M., Janik, L.J., Viscarra Rossel, R.A., MacDonald, L.M., McLaughlin, M.J., 2014. The performance of visible, near-, and mid-infrared reflectance spectroscopy for prediction of soil physical, chemical, and biological properties. Appl. Spectrosc. Rev. 49, 139−186.

Stenberg, B., Viscarra Rossel, R.A., Mouazen, A.M., Wetterlind, J., 2010. Visible and near infrared spectroscopy in soil science. Adv. Agron. 107, 163−215.

Stenberg, B., 2010. Effects of soil sample pretreatments and standardised rewetting as interacted with sand classes on Vis-NIR predictions of clay and soil organic carbon. Geoderma 158, 15−22.

Stevens, A., Udelhoven, T., Denis, A., Tychon, B., Lioy, R., Hoffman, L., Van Wesemael, B., 2010. Measuring soil organic carbon in croplands at regional scales using imaging spectroscopy. Geoderma 158, 32−45.

Stevens, A., Nocita, M., Tóth, G., Montanarella, L., van Wesemael, B., 2013. Prediction of soil organic carbon at the European scale by visible and near infrared reflectance spectroscopy. PLoS One 8 (6), e66409.

Stoner, E.R., Baumgardner, M.F., 1981. Characteristic variations in reflectance of surface soils. Soil Sci. Soc. Am. J. 45, 1161−1165.

Stuart, B., 2004. Infrared Spectroscopy: Fundamentals and Applications. John Wiley & Sons, New York.

Schwartz, G., Ben-Dor, E., Eshel, G., 2012. Quantitative analysis of total petroleum hydrocarbons in soils: comparison between reflectance spectroscopy and solvent extraction by 3 certified laboratories. Appl. Environ. Soil Sci. 11.

Tivet, F., de Moraes Sa, J.C., Lal, R., Milori, D., Briedis, C., Letourmy, P., Pinheiro, L., Borszowskei, P.R., Hatman, D., 2013. Assessing humification and organic C compounds by laser-induced fluorescence and FTIR spectroscopies under conventional and no-till management in Brazilian Oxisols. Geoderma 207−208, 71−81.

Todorova, M., Atanassova, S., Lange, H., Pavlov, D., 2011. Estimation of total N, total P, pH and electrical conductivity in soil by near-infrared reflectance spectroscopy. Agr. Sci. Tech. 3, 50−54.

Tóth, G., Jones, A., Montanarella, L., 2013. The LUCAS topsoil database and derived information on the regional variability of cropland topsoil properties in the European Union. Environ. Monit. Assess. 185, 7409−7425.

USDA – United States Department of Agriculture, 2013. Rapid Carbon Assessment (RaCA) Methodology. Available at: http://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs142p2_052841.pdf.

Van Reeuwjik, L.P., 2002. Procedure for Soil Analysis, sixth ed. ISRIC.

Vasques, G.M., Grunwald, S., Harris, W.G., 2010. Spectroscopic models of soil organic carbon in Florida, USA. J. Environ. Qual. 39, 923−934.

Viscarra Rossel, R.A., Walvoort, D.J.J., McBratney, A.B., Janik, L.J., Skjemstad, J.O., 2006. Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. Geoderma 131, 59−75.

Viscarra Rossel, R.A., Cattle, S.R., Ortega, A., Fouad, Y., 2009. In situ measurements of soil colour, mineral composition and clay content by vis−NIR spectroscopy. Geoderma 150, 253−266.

Viscarra Rossel, R.A., Behrens, T., 2010. Using data mining to model and interpret soil diffuse reflectance spectra. Geoderma 158, 46−54.

Viscarra Rossel, R.A., Webster, R., 2012. Predicting soil properties from the Australian soil visible near infrared spectroscopic database. Eur. J. Soil Sci. 63, 848−860.

Whiting, M.L., Li, L., Ustin, S.L., 2004. Predicting water content using Gaussian model on soil spectra. Remote Sens. Environ. 89, 535−552.

Zimmermann, M., Leifeld, J., Fuhrer, J., 2007. Quantifying soil organic carbon fractions by infrared-spectroscopy. Soil Biol. Biochem. 39, 224−231.