Geoderma 158 (2010) 15–22

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Effects of soil sample pretreatments and standardised rewetting as interacted with sand classes on Vis-NIR predictions of clay and soil organic carbon

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ARTICLE INFO

Article history:
Received 9 February 2009
Received in revised form 5 January 2010
Accepted 12 April 2010
Available online 13 May 2010

Keywords:
Clay content
Near infrared spectroscopy
Partial least squares regression
Soil organic carbon
Spectral features
Water effect

ABSTRACT

Numerous studies have examined the soil analytical potential of diffuse reflectance spectroscopy in the near infrared range, alone or combined with the visible range (Vis-NIR). Soil organic matter (SOM), soil organic carbon (SOC) and clay content are the most commonly and successfully predicted parameters, but predictions are quite variable due e.g. to the range of soil types covered by the calibrations. Especially organic matter predictions are also suggested to be influenced by for example soil moisture content and inclusion of the visible range in the calibration. Excess quartz sand is also suggested to have a negative influence. This study was undertaken to examine the effect of a selection of standardised sample pretreatment procedures, including rewetting, on predictions of clay and SOC content. A subset of 400 samples was selected from a dataset of 3000 Swedish agricultural soils to cover clay and organic matter contents without co-variation. The selected samples were analysed by NIR and Vis-NIR on air dry samples, either carefully mixed to avoid stratification of particle size classes or shaken to promote separation, resulting in predominantly larger particles being analysed. Unshaken samples were also analysed immediately after standardised additional drying at 35 °C for 12 h and stepwise volumetric rewetting up to 30%. Shaking and additional drying had small negative effects on clay predictions, while drying only had small positive effects on SOC predictions. Volumetric rewetting to 20 or 30% before scanning reduced clay prediction errors by up to 15%, RMSEP reduced from 5.4% clay to 4.5% clay, and SOC prediction errors by up to 30%, from 0.9% SOC to 0.6% SOC, indicating that standardised rewetting should be considered. The mechanisms concerned could not be specifically identified, but known bands for water, hydroxyl and clay mineral-dependent absorption near 1400, 1900 and 2200 nm were involved in the improved clay calibrations and bands near 1700, 2000, 2300 and 2350 nm in the improved SOC calibrations. The SOC predictions were most inaccurate for soils with a high sand content. For these samples the average prediction error was more than twice as high as those for less sandy samples. Rewetting eliminated this bias, largely explaining the positive effects of rewetting.

1. Introduction

The interest in using diffuse reflectance spectroscopy in the visible (Vis) and near infrared (NIR) region for soil mapping purposes is steadily increasing. Applications of interest differ, but include estimation of the carbon pool to monitor carbon sequestration (Huang et al., 2007), precision agriculture (Wetterlind et al., 2008), land resource inventory and surveillance (Shepherd and Walsh, 2007), etc. Simplicity, rapidity and low cost are reported to be favourable features of Vis-NIR spectroscopy. The most frequently studied soil properties are probably soil organic carbon (SOC) and clay content, but calibration performance is reported to be very variable (Viscarra Rossel et al., 2006; Stenberg and Viscarra Rossel, in press). There are many conceivable reasons for this. The distribution of the dependent variable, the general composition of the soil and the origin of soils in the datasets studied are often mentioned. Differences in laboratory practices such as sample pretreatment, sample presentation and instrumentation could also be a factor.

Although soil organic matter (SOM) in all its complexity would, theoretically, be spectrally active over more or less the entire NIR region (Ben-Dor and Banin, 1995), it is often reported that SOM signals are weak (e.g., Viscarra Rossel and McBratney, 1998). This implies that the high variability of the mineral fraction, which is typically much greater, could mask spectral absorption by organic matter, especially as spectral features of minerals and organic matter may coincide (Stenberg and Viscarra Rossel, in press). Most minerals have unique spectral features that dominate a soil spectrum (Clark et al., 1990). The mineral composition varies geographically, but also with soil texture. The clay fraction is dominated by clay minerals such as smectites, kaolinites, illites, vermiculites, etc., while the sand fraction is dominated by resistant minerals such as quarts and feldspars. Therefore, if mineralogy and texture differ substantially

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doi:10.1016/j.geoderma.2010.04.008

between samples, the weaker features of organic matter would be more difficult to separate out in a calibration. There is also a possibility that certain mineral compositions could interfere more with organic matter than others. In a large set of samples gathered to represent Swedish agricultural land, it was found that the prediction power for SOM of all soils was very poor, but that it was substantially improved by excluding the least clayey soils (Stenberg et al., 2002).

Water and hydroxyls (OH) have strong influences in the Vis-NIR region. Overtones of OH stretching absorb near 1400 nm and combinations of H–O–H bending and OH stretching absorb at 1900 nm (Clark, 1999). There are also weaker bands all over the Vis-NIR range. Water is apparent in all soils, even when dried. Its absorption pattern changes when adapting to physical and chemical matrix variations. Aquaphotomics, a relatively new term in NIR spectroscopy (Tsenkova, 2007), is the study of how the water peaks in the near infrared spectrum change under the influence of other molecules in samples and systems. For example, water peak frequencies can contribute to protein calibrations by means of hydrogen bonding interactions. It can be assumed that a similar process can be responsible for phenomena observed in the measurement of moist or wet soil. It is also well known that the bands near 1400 and 1900 nm can be attributed to free water, as well as water contained in the lattice of various clay minerals or adsorbed to particle surfaces. Depending on the mechanisms and minerals involved, absorption bands may shift and be sharp or broad (Clark et al., 1990).

It has frequently been shown that Vis-NIR relates better to organic matter than NIR alone. For example, Islam et al. (2003) obtained considerably better results for Australian soils by including the visible region (350–700 nm) in the calibration. Similar observations have been reported for Norwegian soils (Fystro, 2002). It has been suggested that the brightness of the sample is an important feature in the visible region for prediction quality of organic C content (Udelhoven et al., 2003). However, the converse has been reported for US land resource areas (Chang et al., 2001) and south-eastern Australia (Dunn et al., 2002). Although the general observation is that darker soil contains more organic matter, many other soil properties, such as texture, structure, moisture and mineralogy, are also influential in this respect (Clark, 1999; Hummel et al., 2001), implying that darkness would only be a useful feature within a limited geological variation.

The purpose of this study was to test the effect of sample pretreatment, such as standardisation of dryness and sample presentation, and rewetting on the calibration performance of Vis-NIR and NIR spectra for SOC and clay content. The benchmark was a defined volume of sieved, air-dried and stored soil prepared to avoid particle size stratification. This was assumed to represent a fairly normal procedure for laboratory NIR analysis. In relation to this, further standardisation steps regarding moisture were tested. Soils were subjected to additional drying directly before analysis with the reflectance probe and samples remoistened in a high humidity chamber. The effect of particle size stratification due to shaking was also tested, as this can easily occur if care is not taken to avoid it. In addition, the influence on spectra and calibration performance of rewetting by adding volumetrically defined amounts of water was evaluated.

2. Materials and methods

2.1. Soil sampling, analysis and selection

For the experiments, 400 soil samples representative of Swedish agricultural land were selected (see below) from a soil library of approximately 3000 Swedish topsoil samples taken between 1988 and 1995. In the original sampling performed for a national monitoring project (Eriksson et al., 1997) random sampling within small geographical areas evenly distributed over Swedish agricultural soil was performed to reach a density of approximately 1 sample per 900 ha. Each sample comprised 6–20 soil cores from 0 to 20 cm taken from an area of 10–20 m^2 each. These samples were dried at 25–30 °C, crushed and passed through a 2 mm screen (Eriksson et al., 1997). Organic carbon was analysed on finely ground soil using a LECO CNS 700 elemental analyser (LECO, St. Joseph, MI). All soils with a pH exceeding 6.7 were corrected for carbonate by treatment with 2 M HCl and reanalysed for carbon. Soil clay content was analysed by the sedimentation/pipette method according to Gee and Bauder (1986). Clay was defined as particles <2 µm.

Soil classes were not specifically analysed for this original dataset, but mineral agricultural soils in Sweden are dominated by young weakly developed Eutric and Dystric Cambisols (European Commission, 2005). The dominant clay mineral is illite, but in some soils almost as much vermiculite can occur and in southern Sweden a significant amount of smectite can be present (Eriksson et al., 2005).

Soil material in the original dataset not used for chemical analyses was stored in plastic jars. During sub-selection in 2007 for the present study, soils exceeding 7% SOC were excluded, as the frequency of soils with higher SOC decreased drastically and soils high in both SOC and clay were lacking. The clay content of the remaining 2600 soils was plotted against SOC content and 400 evenly distributed samples were selected. In this way, any interdependence between clay and SOC was avoided ($r=0.06$) and the selection was fairly well distributed over both the clay and SOC range, although the strong bias towards low SOC and clay content in the original dataset could not be completely avoided.

2.2. Vis-NIR analysis and pretreatments

Vis-NIR spectra were collected using a FieldSpec Pro FR scanning instrument (Analytical Spectral Devices Inc., Boulder, CO, USA, www.asdi.com). The spectral range covered both the visible and the near infrared regions, 350–2500 nm, sampled at 1.4–2 nm intervals with a spectral resolution of 3–10 nm. A wavelength interval of 1 nm was interpolated to the instrument output file. Thus, spectra consisted of 1 data point every nm. The instrument was equipped with a bare optic fibre connected to a self constructed probe with a 20 W Al-coated halogen tungsten light source placed 7 cm over the sample, resulting in a field of view of ~7.5 cm^2. Each soil sample spectrum comprised 100 averaged spectra collected from one Petri dish placed on a rotating sample stage. The total sample area analysed was about 50 cm^2. The total time a sample was allowed to remain under the light source was standardised to 12–18 s to avoid heating of the sample but still ensure that all 100 spectra were properly collected.

Before scanning, each sample was thoroughly mixed and 40 cm^3 soil were measured with a baker and carefully transferred into a 10 cm Petri dish. First, *shaking* of the sample in the Petri dish was performed by rapidly moving the dish in circles over the table to produce an even surface. This is a rapid method and would be preferable from a rationality perspective, but may result in interfering particle size stratification of samples. Thereafter the sample was remixed and flattened by exerting a little pressure on the surface, without changing the total volume significantly, using a cardboard disc slightly smaller than the Petri dish. This produced an even and smooth soil surface for the spectroscopic measurements, while care was taken to avoid particle size stratification. This pretreatment was considered the standard procedure and is hereafter referred to as *flat-dry*. All other pretreatments were performed in sequence on the same sample.

Additional drying of the flat-dry samples was performed at 35 °C for 12 h, which is a common temperature used in labs for producing air dry soil before analyses (Pretreatment: 35 °C). The spectra of these samples were measured 30 min after they were exposed to room temperature (22 °C). Remoistening, as a potential standard procedure, of flat-dry samples was performed in a climate chamber for 12 h