Keynote Presentation

Proximal soil spectroscopy

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Abstract
Proximal soil sensing provides soil scientists with effective techniques to learn more about soils. They allow rapid and inexpensive collection of precise, quantitative, high-resolution data, which can be used to better understand soil spatial and temporal variability. In this paper I will review the use of soil spectroscopy for measuring key soil properties and the potential applicability of the techniques for proximal soil sensing.

Keywords: proximal soil sensing, soil spectroscopy, visible–near infrared spectroscopy

Soil spectroscopy

Diffuse reflectance spectroscopy has been used in soil science research since the 1950s and 1960s (e.g. Brooks, 1952). However, it is only in around the past 20 years, most likely coinciding with the establishment of chemometrics and multivariate statistical techniques in analytical chemistry, that its usefulness and importance in soil science has been realized. Interest in using reflectance spectroscopy to measure soil properties is widespread, because the techniques are rapid, relatively inexpensive, require minimal sample preparation, are non-destructive, require no hazardous chemicals and several soil properties can be measured from a single scan.

Visible light has energies between 2.1 eV and 1.65 eV, frequency in the range 4×10^{14}–7×10^{14} Hz, and wavelengths of 7×10^{-7}–4×10^{-7} m. Absorptions of visible radiation occur under high energies due to the excitation of outer electrons. Absorption of energy by an atom or molecule involves the promotion of electrons from their ground state to an excited state. Absorptions in organic molecules are restricted to certain functional groups (chromophores) that contain valance electrons of low excitation energy. Many inorganic species, such as iron oxides in soil, show charge transfer absorptions (also called charge transfer complexes). For a complex to demonstrate charge transfer behavior, one of its components must be able to donate electrons and another must be able to accept them. Thus, absorptions involve transfer of an electron from the donor to an orbital associated with the acceptor. A soil spectrum in the visible range is shown in Figure 1a.

The near infrared (NIR) portion of the EM spectrum has a frequency range of 1.2×10^{14}–4×10^{14} Hz, with wavelengths of 7×10^{-7}–2.5×10^{-6} m, while the mid infrared (mid–IR) has a frequency range of 3×10^{12}–1.2×10^{14} Hz and wavelengths of 2.5×10^{-6}–2.5×10^{-5} m. Energies in the NIR range between 1.65 eV and 124 meV, while those in the mid–IR range from 124 meV to 12.4 meV.

There is a vast amount of literature on the use of vis–NIR and mid–IR for soil analysis (e.g. Stenberg et al., 2010) and, increasingly, on the use of these techniques for PSS (e.g. Ben-Dor et al., 2008; Christy, 2008; Reeves et al., 2010; Viscarra Rossel et al., 2009). Infrared radiation does not have enough energy to induce electronic transitions as with ultraviolet and visible radiation. Their absorptions are restricted to compounds with smaller energy differences in the possible vibrational states. For a molecule to absorb infrared energy, the vibrations within a molecule must cause a net charge in the dipole moment of the molecule. The alternating electrical field of the radiation interacts with fluctuations in the dipole moment of the molecule. If

the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of the molecular vibration. The positions of the molecules are not fixed and are subject to different stretching or bending vibrations.

The mid-IR contains more information on soil mineral and organic composition than the vis–NIR, and its multivariate calibrations are generally more robust. The reason is that the fundamental molecular vibrations of soil components occur in the mid-IR, while only their overtones and combinations are detected in the NIR (Stenberg et al., 2010). Hence soil NIR spectra display fewer and much broader absorption features compared to mid-IR spectra (Figure 1b and 1c, respectively).
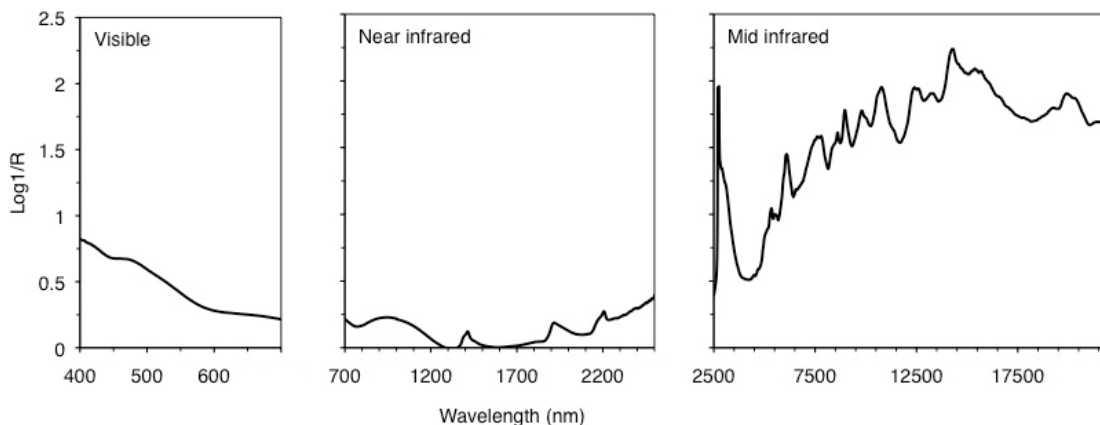

Figure 1. Typical soil spectrum in the (a) visible, (b) near infrared (NIR) and (c) mid infrared (mid-IR) portions of the EM spectrum.

The adaptation of vis–NIR spectrometers for PSS has been ongoing for the past two decades, with the first field prototype mobile systems developed by Shonk et al. (1991) and Sudduth and Hummel (1993). Since then, other prototype mobile systems have been developed by Shibusawa et al. (2001), Mouazen et al. (2005) and Christy (2008), who described a commercially available mobile vis–NIR system. Alternatively, static PSS of vis–NIR reflectance has been implemented using portable instruments (Ben-Dor et al., 2008; Kusumo et al., 2011; Viscarra Rossel et al., 2009). There are fewer reports of portable, mid–IR systems for proximal soil sensing (Jahn and Upadhyaya, 2010; Reeves et al., 2010).

Soil water and texture
Soil water content has been measured using vis–NIR (Sudduth and Hummel, 1993; Whitting et al., 2004) and mid-IR spectroscopy (Janik et al., 2007). Although soil water content as measured by these sensors is useful, measurements of plant-available water capacity (PAWC) are more important for agriculture. Plant-available water capacity is determined in the field by measuring differences between volumetric water content at the drained upper and lower limits after complete extraction of water by the plants. Measurements of bulk density are needed to convert water content measurements to a volumetric basis.

Soil texture (clay, silt and sand content) has been measured using vis–NIR and mid-IR spectroscopy (Viscarra Rossel et al. 2009). However, measurements of silt are often less accurate than for clay. Sand content has also been measured with mid-IR spectroscopy, where strong fundamental vibrations of silicon–oxygen bonds exist. There is no response to sand in the vis–NIR spectrum as quartz is insensitive in this region, although sand may affect soil albedo.

Nutrients, elements, pH and CEC
Nutrients are generally not well predicted by spectroscopic techniques because the measurements are mostly indirect. Nitrate–nitrogen, which has been measured using mid-IR spectroscopy (Jahn et al., 2006). There are reports in the literature that suggest good predictions of soil P using vis–NIR spectroscopy (e.g. Bogrekci and Lee, 2005). Janik et al. (1998) also reported good results for phosphorus sorption using mid-IR spectroscopy but not for available phosphorus. Potassium has been measured using vis–NIR and mid-IR spectroscopy, but their accuracy is generally low. Other major nutrients such as calcium and magnesium, however, appear to correlate well with both vis–NIR and mid-IR spectra (Viscarra Rossel and McBratney, 2008). Heavy metal contamination in soils can be measured using vis–NIR and mid-IR spectroscopy (Bray et al., 2009).

As a measure of acidity, the level of soil pH is important in many processes, including availability of plant nutrients and efficacy of herbicides. Soil pH, buffering capacity and lime requirement can be inferred using vis–NIR and mid-IR spectroscopy, the latter producing more accurate results (Viscarra Rossel and McBratney, 2008). Cation exchange capacity (CEC) determines the nutrient supply in soils, with cation nutrients in higher CEC soils generally more available to plants. Cation exchange capacity increases with increasing pH, clay and organic matter in the soil. It also varies with the type of clay, with smectites having the highest CEC, followed by illites and kaolinites. Cation exchange capacity can be inferred using vis–NIR and mid-IR spectra (Sudduth and Hummel, 1993; Viscarra Rossel et al., 2006).

Carbon
Carbon plays a key role in improving soil physical properties, increasing CEC and water-holding capacity, and improving soil structure. Soil carbon is thus considered important in assessing soil quality (Andrews et al., 2004). Furthermore, the ability of soils to sequester carbon is of increasing interest as a potential way to mitigate greenhouse gases in the atmosphere. Soil carbon can be measured using charge-coupled devices (Viscarra Rossel et al., 2008), vis–NIR and mid-IR (Viscarra Rossel and McBratney, 2006a). Carbon fractions can also be measured using vis–NIR (Cozzolino and Moron, 2006) but measurements are more accurate using mid-IR spectroscopy.

Soil mineralogy
Mineralogy strongly affects the physico-chemical processes occurring in soils. In particular, the mineralogy of soil clays relates to soil fertility through CEC effects and also to soil water dynamics by virtue of the shrink–swell nature of the various clays. Clay mineralogy can be measured using vis–NIR spectroscopy (Viscarra Rossel et al., 2006, 2009) and mid-IR spectroscopy (Nguyen et al., 1991). Iron oxides have also been measured using vis–NIR spectroscopy (Viscarra Rossel et al., 2010).

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