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The presence of ash as an interference factor in the estimation of the maximum temperature reached in burned soils using near-infrared spectroscopy (NIR)

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Abstract

The aim of this work was to assess the effect of the presence of ash on maximum temperature reached (MTR) estimation using near infrared reflectance (NIR) spectroscopy. The degree of combustion (ash produced by heating to 100, 300, 500 and 700 °C), the type (ash from *Pinus halepensis* and *Rosmarinus officinalis*), and different quantities of ash (0–20% in 2% interval) were evaluated in a soil heated at seven different temperatures (100 °C–700 °C). Results showed that the estimation of MTR on samples with ash, using partial least squares (PLS) models constructed with samples without ash, could be erroneous. Both, ash quantity and degree of combustion affected the estimation of MTR. However, using discriminant analysis, a good classification of samples (>97% correctly classified) according to the heating temperature classes (unheated, 100, 200, 300, 400, 500, 600 and 700 °C) was obtained despite the presence of ash.

Keywords: NIR; Wildfire; Ash; Mediterranean soil; Temperatures; Fire severity; Fire intensity

1. Introduction

Fire can affect the physical, chemical, mineralogical and biological properties of soil (Certini, 2005). The effects on soil properties depend on fire severity, which consists of the maximum temperature reached and the duration of fire, and provides a quantitative measurement related to fire impact and biomass consumption (Chuvieco et al., 2006). Depending on the properties considered, the effect of heating is more or less pronounced depending on the temperature reached. It has been reported that the threshold temperature for biological disruptions in soils is lower than that for changes in mineralogical properties (Neary et al., 1999; Ketterings et al., 2000; Pietikaïnen et al., 2000; Guerrero et al., 2005). Other important soil properties that depend on temperature reached are water repellency (DeBano et al., 1976, 1998; Doerr et al., 2006), aggregation–disruption of soil particles, enzyme denaturation, changes in the microbial structure community, nutrient volatilization–mineralization processes, and seed mortality and dormancy disruption (Raison, 1979; Bradstock et al., 1992; Saa et al., 1993; Neary et al., 1999; Pietikaïnen et al., 2000; Certini, 2005; Shakesby and Doerr, 2006). Thus, fire severity is a critical variable in fire effects assessment, and therefore new techniques are needed to map burn severity. In this sense, Guerrero et al. (2007) developed successful models relating Near Infrared Reflectance (NIR) spectra with the maximum temperature reached (MTR) in burned soils.

NIR is a fast method that offers the possibility of working with large numbers of samples, for example the characterization of the spatial pattern of soil temperatures in wildfires (Gimeno-García et al., 2004). NIR spectroscopy has been widely used to predict several soils properties (Chang et al., 2001; Cozzolino and Morón, 2003; Viscarra Rossel et al., 2006). Organic molecules

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absorb NIR radiation due to overtone and combination bands primarily of C–H, N–H, S–H, O–H and C=O groups. Therefore, NIR spectra contain information about the organic composition of the soil. They are of considerable complexity due to overlapped bands, and cannot be directly interpreted, so that sophisticated statistical techniques, called chemometrics (Martens and Næs, 1989; Burns and Ciurczak, 2001), are needed to discern the response of soil attributes from spectral characteristics.

The models constructed by Guerrero et al. (2007) opened new perspectives on studies of wildfire effects on soils, because generally the MTR data were not available with sufficient accuracy and precision. However, the presence of ash in the soils were not included in the models designed by Guerrero et al. (2007), and could probably interfere in estimations. Therefore, the first objective of this paper was to study the effect of the presence of ash on model prediction. Moreover, a second objective was to study the ability of discriminant analysis to classify heated soils according to MTR despite the presence of ash.

2. Materials and methods

2.1. Soil used

Fifty soils samples (0–5 cm depth) of ~1 kg were collected from la Torre de les Maçanes (30SYH2474) in the southeastern Spain. The most common species at the forest site were *Pinus halepensis Mill*., *Quercus coccifera* L., *Rosmarinus officinalis* L., *Cistus albidus* L., *Pistacia Lentiscus* L., *Globularia alypum* L., *Thymus* spp., *Ulex parviflorus Pourr*. and *Brachypodium retusum (Pers.) P. Beav*. Soil samples were air-dried for two weeks, sieved (<2 mm) and thoroughly mixed to obtain a homogeneous sample. The organic matter content, analysed by dichromate oxidation of organic carbon (Walkley and Black, 1934) was 6.47%, the pH (1:2.5 w/v, distilled water) 7.63 and the carbonate content 69%, determined using the Bernard calcimeter. The percentage of sand, silt and clay was 41, 48, and 11%, respectively. The soil was classified according to Soil Survey Staff (1999) as a Typic Xerorthent.

2.2. Ash source

Needles from *P. halepensis* and leaves from *R. officinalis* were collected from the same site as the soil. *P. halepensis* needles were oven dried at 60 °C for a week, ground and heated in a muffle furnace separately at 100, 300, 500 and 700 °C for 20 min, leading to ash with different degrees of combustion, identified in Fig. 1 as Ph-ash-100 °C, Ph-ash-300 °C, Ph-ash-500 °C and Ph-ash-700 °C, respectively. The same procedure was followed with leaves of *R. officinalis*, leading to ash samples identified in Fig. 1 as Ro-ash-100 °C, Ro-ash-300 °C, Ro-ash-500 °C and Ro-ash-700 °C respectively.

2.3. Sample procedures, MTR data and NIR spectra

2.3.1. Samples preparation: heating and ash addition

The soil sample was split in two similar aliquots (Fig. 1). The samples from the first aliquot were heated at 70, 160, 250, 340, 430, 520, 610 and 700 °C for 10, 20, 30, 40, 50 and 60-minute periods. Moreover, in the set of samples heated for 10 min, more temperatures were used (from 70 to 700 °C in 30 °C increments) to increase the temperature gradient set. The soil heating procedure is described in Section 2.3.2. In each of these samples, the MTR was registered (see Section 2.3.2), and after cooling, the NIR spectrum was obtained (see Section 2.3.4).

Soil samples from the second aliquot were heated at 100, 200, 300, 400, 500, 600 and 700 °C for 30 min. The MTR were also registered. After cooling, at each temperature, the heated soil was split in 24 samples, and the NIR spectrum was obtained (see Section 2.3.4). Then, these heated samples were mixed with ash (using triplicates) following a factorial (2×4) arrangement, representing two different types of ash (by plant species: *P. halepensis* and *R. officinalis*) and four degrees of ash combustion (100, 300, 500 and 700 °C). The samples of the eight categories established (2×4) were mixed successively with ash at 0, 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20% (using triplicates). NIR spectra were determined after mixing. Thus, 1848 mixtures were obtained and 1848 NIR spectra were measured, representing 7 soil temperatures, 2 types of ash, 4 degrees of ash combustion and 11 quantities of ash (per triplicate).

2.3.2. Soil heating procedure and measurement of MTR

Approximately 120 g of air-dried sieved soil were placed in a ceramic cup and placed in a muffle furnace (Nabertherm, P320, Bremen, Germany) that was preheated to the desired temperature. Each sample was heated separately. At the time of heating a sample, a thermocouple (k-type, NiCr–Ni; Testo SA, Barcelona, Spain) was inserted inside the soil (2-cm depth). The thermocouple temperature was recorded every minute. In each sample, the MTR was registered during the heating.

2.3.3. Soil–ash mixtures procedure

The heated soil samples from the second aliquot were put in individual glass vials (2×5 cm, ~4 g of soil). In each vial, ash was added and mixed by shaking, to obtain a homogeneous mixture. After this, the NIR spectrum was recorded. Ash was added successively in the same vial ranging from 0 to 20% in 2% intervals. The NIR spectrum was measured after the addition. These measurements were performed in triplicate.

2.3.4. NIR spectra measurement

After cooling, all samples were transferred to glass vials (see details in Section 2.3.3) and scanned on reflectance mode from 12,000 to 3800 cm^{-1} (approximately equivalent to 830–2630 nm). For these measurements, a Fourier-Transform near-infrared (FT-NIR) spectrophotometer (MPA; Bruker Optik GmbH, Germany), equipped with a quartz beamsplitter, PbS detector and an integrating macrosample sphere was used. This allowed the scanning of large areas of the samples. In each of the reflectance measurements, 64 scans were averaged. Samples were measured in duplicate, increasing the surface of soil sample scanned. After this, they were averaged again. The resolution used for spectral analysis was 8 cm^{-1}. Background corrections were made before each sample scan. Each spectrum was composed of more than 2000 values of absorbance